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Chemistry and Technology of Explosives
VOLUME 4

by
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PERGAMON PRESS
OXFORD · NEW YORK · TORONTO · SYDNEY · PARIS · FRANKFURT
PREFACE

Since 1964-67 when the previous three volumes of *Chemistry and Technology of Explosives* appeared, considerable progress has been made in the field of the science of explosives—the science in a broader sense which includes not only the theoretical knowledge of explosives but also their manufacture, problems of safety in the manufacturing processes and handling.

As in the previous three volumes the author limited his text to *chemistry* and technology of explosives. The problems of the theory of detonation and analytical ones are not discussed here and are only touched as much as it was needed to understand the properties of explosives. Thus in the 'Introduction' chapter a description is given of the relationship between the chemical structure and the parameters of the explosive properties, as this refers to the structural problems of organic substances possessing such properties.

However, the author wishes to point out that he is not giving the full review of the existing progress for some particular reasons—a general philosophy for Peace in the World and some personal reason as a former POW. He is completely against the use of explosives for military purposes and has dedicated his book to peaceful applications.

The author wishes to quote from the book by S. Fordham, *High Explosives and Propellants* (Pergamon Press): "The explosives technologist, who has usually seen and perhaps even experienced the effects of explosives is the last to want war or for his products to be used for warlike purposes. It is no accident that Nobel who founded the modern explosives industry also founded the Peace Prize associated with his name."

Once more the author would like to repeat what he said in the preface to his book in 1964-67: "...more explosives have been used in peace than in war. Modern civilization and modern progress would be impossible without explosives." Nevertheless, following this line of thought no mention is made in this book on shells, projectiles, fuses etc., or other parts of military weapons. However it is still difficult to distinguish between military and peaceful application of military weapons. Here are a few examples:

Gas burning from a newly drilled oil pit in Karlin in northern Poland in 1981 was successfully extinguished with howitzer shells; the danger of an avalanche of snow can be prevented by firing special guns with shells filled...
with high explosives; firing rockets with explosives loaded with silver iodide is in use for promoting rain (Vol. III, p. 324). Silver iodide dispersed in higher layers of atmosphere by anti-aircraft rounds is in use in the U.S.S.R., according to "TWA Ambassador" (p. 37, May 1981).

A conscientious attempt has been made to cover the available literature on the subject, however not every paper and report has been mentioned as it was considered to be of greater value to couple a reasonably comprehensive coverage with a critical assessment of the available information and not to describe every paper. The excellent Encyclopedia of Explosives and related items produced by (the late) B. T. Fedoroff, O. E. Sheffield and S. M. Kaye should be consulted for the whole literature on explosives.

Also excellent reviews have appeared in Volumes of Annual Reviews of Applied Chemistry, issued by Society of Chemical Industry, London, between 1950 and 1975, written by J. Taylor, E. Whitworth, W. E. Batty, I. Dunstan and a number of authors from I.C.I. Ltd.

The author apologises to the authors for any important work overlooked in the present volume.

It is the pleasant duty of the author to thank all the colleagues who responded to his request for information. I am most grateful to them. They were from:

(1) Federal Republic of Germany: Dr A. Homburg (Köln), Dr R. Meyer (Essen), Dipl. Ing. H. Plinek (Bad Homburg), Dr H. Schubert and Dr Fred Volk (Pfingstal).

(2) France: Ingénieur A. Delpeuch (Sevran), Ingénieur Général P. Tavernier (Paris).

(3) Holland: Professor Th. J. de Boer (Amsterdam).

(4) India: Dr A. K. Chatterjee (Hyderabad) and Dr S. P. Panda (Poona).

(5) Japan: Mr K. Yamamoto (Asa), Professor T. Yoshida (Tokyo).

(6) Italy: Dr E. Camera (Udine).

(7) Sweden: Dr Jan Hanson (Sundbyberg), Dr G. A. Wetterholm (Göteborg).

(8) Switzerland: Mr Guido Bianzzi, Dr G. S. Biasutti and Dr A. Fauci (Vevey).

(9) U.K.: Mr A. Brewin, M.A. (ERDE, Watlink Abbey).

(10) U.S.A.: Professor J. F. Bunnett (Santa Cruz, Cal.), Mr C. L. Coon (Livermore, Cal.), Professor J. A. Concling (Chestertown, Md.), Professor H. Feuer (Lafayette, Ind.), Dr Mortimer J. Kamlet (Silver Spring, Md.), Professor Nathan Kornblum (Lafayette, Ind.), Dr A. T. Nielsen (China Lake, Cal.), Professor G. A. Olah (Los Angeles, Cal.), Professor Glen A. Russell (Ames, Iowa), Dr R. W. Van Dolah (Pittsburgh, Pa.).

(11) U.S.S.R. (Moscow): particularly to the late Professors K. K. Andreev and S. S. Novikov, Professors V. I. Pepekin and V. V. Sevostyanova and Dr G. T. Afanasyev, Dr G. N. Bezpalov, Professor V. K. Bobolov, Profes-

sors L. V. Dubnov and A. P. Glazkova, Dr B. N. Kondrikov, Professor V. V. Perekulin (Leningrad).

(12) Poland: the late Professor W. Cybulski/Mikołaj/, Dr T. Krasięcko, Dr R. Kuboszek, Dr K. Lewarińska, Dr T. Mrzwiński, Dr M. Parulski, Dr W. Sas, Professor M. Witanowski and Mr M. Ziółko – all from Warsaw, and the Directors of the Institute of Organic Industry, Warsaw: Prof. S. Fulde, Dr W. Moszczyński and Mrs J. Zofeński for their assistance.

My thanks are due to Dr R. Kuboszek for his help in the proof reading and preparing the subjects index.


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1. American Chemical Society,
2. Department of Defence, Dover, N.J., U.S.A.,
3. John Wiley and Sons, Inc., New York,
4. Plenum Press, New York,
5. Verlag Chemie, Weinheim, FRG.

Finally my thanks are due to Mr I. Robert Maxwell, M.C., Chairman of Pergamon Press Ltd, Oxford, Mr Alan J. Steel, Publishing Director, Dr Colin J. Drayton, Senior Managing Editor and Mr Peter A. Henn, Senior Publishing Manager of Pergamon Press, and Mrs Eileen Morrell for tidying up my ‘foreign’ English.
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INTRODUCTION
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NOVEL INFORMATION ON EXPLOSIVE PROPERTIES

It has been shown that some non-explosive organic and inorganic substances can explode when subjected to the action of very high pressure. This was recorded for the first time by Bridgman [1]. Teller [2] tried to find an explanation in terms of the activation energy which should be lowered with increased pressure.

More recently Malmrud and Claesson [3] examined the behaviour of a number of compounds at a pressure of 35,000 kg/cm². They found that some acids, such as oxalic acid hydrate malonic, tartaric and citric acid, and other common substances such as aspirin, sucrose, polystyrene and calcium chloride, exploded when high pressure was released. A number of substances (e.g. succinic, glutaric, adipic, maleic, fumaric, phthalic acids) did not show this behaviour. According to the authors they did not explode because they required higher pressure.

The explanation given by Malmrud and Claesson is similar to that given by Bridgman. They believe that over a critical pressure, which depends on the coefficient of friction, plastic flow stress and disc thickness, the sample becomes mechanically unstable when pressure is released and is violently expelled.

Polystyrene was simultaneously carbonized which was probably caused by an increased temperature due to heating by friction.

The author of the present book is inclined to rationalize that under very high pressure considerable deformation of the crystal-net can occur and the atoms are approaching distances which produce their repulsion.

The problem arises as to whether explosives can be brought to explosion by high static pressure. So far the only published paper [4] indicated that nitromethane, perdeuteronitromethane and a few dinitroalkanes cannot explode at static pressure up to 50 kbar.

It is known that acetylenic bond possesses endothermic characteristics (Vol. III, p. 227) and it is interesting to point out that a number of acetylenic compounds were found in nature as early as 1889 [5] and 1892 [6]. Currently important are the works of E. R. H. Jones [7] and Bohlmann [8] who isolated and established the structure of numerous naturally occurring polyacetylenes and confirmed their structure by synthesis. Most of the polyacetylenes possess explosive properties.
INTRODUCTION

With the advent of the development of the hydrodynamic theory of detonation, based on the concepts of Chapman [17] and Jouguet [18], it was possible to calculate the velocity of detonation. The pioneering work was done by A. Schmidt [19] and his method was improved by a number of authors. Critical reviews of the methods have been described in a number of monographs: Cook [20], Zeldovich and Kompaneets [21], Andreev and Belyaev [22], Johansson and Persson [23], Fickett and Davis [24].

The problems connected with the hydrodynamic theory of detonation are outside the scope of this book and only papers dealing with the correlation between the structure of explosives and their power will be given here. Originally the papers were directed to correlate the oxygen balance (OB) with the "explosive power". This was initiated by Lothrop and Hendrick (Vol. I, p. 2) and met with a well-founded criticism (A. Schmidt, Vol. I, p. 2). The criticism was based on the fact that oxygen in nitro groups has a different thermochemical function than that of carboxylic and hydroxyl groups. The discussion aroused much interest in the attempt to introduce a differentiation of oxygen atoms.

The first of the kind were papers by Martin and Yalloo [25a, b]. They proposed a 'corrected OB' calculated as follows:

\[ \text{OB} = \Omega = (z - 2x - y/2)100/n \pm 100 \text{ w/n}, \]  

(2)

where: \( x, y, z \) are the respective numbers of atoms of carbon, hydrogen and oxygen in the molecule,

\( n \) – the number of atoms in the molecule,
\( w \) – summation of O atoms according to their linkages, thus:
\( w = O \) for oxygen atoms in \( \text{NO}_2 \) groups in \( C \)-nitro, \( O \)-nitro and \( N \)-nitro compounds,
\( w = 1 \) for oxygen \( \text{C} - \text{O} - \text{N} \) in \( O \)-nitro compounds,
\( w = 1.8 \) for oxygen \( \text{C} = \text{O} \) in carboxylic groups,
\( w = 2.2 \) for oxygen in phenols and alcohols. \( \pm \) is taken: + if the first term is +, and – if the first term is –.

The rate of detonation \( D \) was calculated from semiempirical equation (3) [25a].

\[ D_{\text{calc}} = 2509 + 13.25 \Omega + 3793 \rho + 12.81 \rho \Omega \]  

(3)

where: \( \rho \) is the density of the explosive (g/cm\(^3\)).

In another equation they introduced the value \( \text{H cal/g} \) of the heat of formation [25b].

The work of Martin and Yalloo was met with criticism. Thus Price [26] concluded that OB cannot determine the heat of explosion or detonation and the rate of detonation cannot be a linear function of OB. Roth [27] pointed out that the correlation between Martin and Yalloo's 'corrected OB' is successful only for a restricted group of similar explosives. The correlation breaks down for
explosives with a positive OB. He concluded that "OB is a concept that can provide useful qualitative information. It should not be used for quantitative correlation except for chemically similar explosives."

A number of authors: Głowacki [28], Mustafa and Zabran [29] and Pagowski [30] tried to extend the method of Martin and Yallop. In particular Pagowski's work merits attention. He attempted to correct equation (2) of Martin and Yallop suggesting the 'effective oxygen balance' B:

\[ B = \left(z - 2x - \frac{Y}{2} \right) \pm 100/n. \] (4)

\( P \) is the correction accounting for energy gains or losses from the actual chemical structure of the compound while taking into account different oxygen atoms: those which are already bonded with carbon (C=O, C–O–N) and those (NO₂) which are free to develop the exothermic reaction of oxidation.

For the rate of detonation Pagowski gave a semi-empirical equation (5):

\[ D = 8600 + 32.7 B \] (5)

\( \rho = 1.6. \)

According to Pagowski the calculated values of \( D \) fit well to experiments Table 1.

<table>
<thead>
<tr>
<th>Explosive</th>
<th>( D_{\text{exp}} )</th>
<th>( D_{\text{calc}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>6980</td>
<td>6345</td>
</tr>
<tr>
<td>Tetryl</td>
<td>7450</td>
<td>7505</td>
</tr>
<tr>
<td>1 DNA (III, 18)</td>
<td>7920</td>
<td>7900</td>
</tr>
<tr>
<td>Cyclonite (RDX)</td>
<td>8200</td>
<td>8185</td>
</tr>
<tr>
<td>PETN</td>
<td>7820</td>
<td>7850</td>
</tr>
</tbody>
</table>

Later a remarkable semi-empirical method of calculating the detonation pressure and velocity was given by Kamlet and co-workers [31].

Kamlet and Jacobs [31a] have shown that the detonation pressure and velocity of \( C-H-N-O \) explosives can be calculated at their initial densities above \( 1 \text{g/cm}^3 \) while using the following simple empirical equations:

\[ P = 15.58 \varphi \rho^2 \] (6)

\[ D = 1.029 \varphi (1 + 1.30 \rho_0)^2 \] (7)

\[ \varphi = \frac{N\Delta H}{Q^2}, \] (8)

where:

\( P \) is the pressure in kbar,

\( D \) the detonation velocity in m/s,

\( N \) the number of moles of gaseous detonation products per gram of the explosive,

\( M \) the average weight of these gases in g/mol,

\( Q \) the chemical energy of the detonation reaction (enthalpy \( \Delta H \)/g).

\( \rho = \) the initial density.

A few examples of the calculation of the velocity of detonation [25d] which give an average error of \( 1\% \) only, are given in Table 2.

<table>
<thead>
<tr>
<th>Explosive</th>
<th>( D_{\text{exp}} )</th>
<th>( D_{\text{calc}} )</th>
<th>% deviation</th>
<th>( D_{\text{calc}} - D_{\text{exp}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>6950</td>
<td>6959</td>
<td>-0.1</td>
<td>+0.1</td>
</tr>
<tr>
<td>Picric acid</td>
<td>6480</td>
<td>6395</td>
<td>-1.4</td>
<td>+1.4</td>
</tr>
<tr>
<td>Ammonium picrate</td>
<td>6070</td>
<td>6000</td>
<td>-1.2</td>
<td>+1.2</td>
</tr>
<tr>
<td>Tetryl</td>
<td>7560</td>
<td>7681</td>
<td>+1.6</td>
<td>-1.6</td>
</tr>
<tr>
<td>RDX (Cyclonite)</td>
<td>7750</td>
<td>7789</td>
<td>+0.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>PETN</td>
<td>8500</td>
<td>8671</td>
<td>+2.0</td>
<td>+2.0</td>
</tr>
</tbody>
</table>

A few examples of the calculation of Chapman-Jouguet pressure are given below — Table 3 [31c]. The Kamlet method is very useful for the rapid calculation of most important constants characterizing high explosives.

<table>
<thead>
<tr>
<th>Explosive</th>
<th>( C_{\text{a}}H_{\text{b}}O_{\text{c}}N_{\text{d}} )</th>
<th>( \Delta H_f )</th>
<th>( Q_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>28.9 b + 470 (c - b/2) + \Delta H_f</td>
<td>28.9 b + 470 (c - b/2) + \Delta H_f</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 3. Calculation of pressure developed by detonation

<table>
<thead>
<tr>
<th>Explosive</th>
<th>$P_{\text{exp}}$ kbar</th>
<th>$P_{\text{calc}}$</th>
<th>% deviation ($P_{\text{calc}} - P_{\text{exp}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>1.62</td>
<td>212</td>
<td>197.8</td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td>123</td>
<td>123.4</td>
</tr>
<tr>
<td></td>
<td>1.14</td>
<td>94</td>
<td>97.9</td>
</tr>
<tr>
<td>RDX</td>
<td>1.80</td>
<td>347</td>
<td>342.5</td>
</tr>
<tr>
<td></td>
<td>1.63</td>
<td>283.7</td>
<td>280.8</td>
</tr>
<tr>
<td></td>
<td>1.40</td>
<td>213</td>
<td>207.1</td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>152</td>
<td>152.2</td>
</tr>
<tr>
<td>HMX</td>
<td>1.90</td>
<td>393</td>
<td>380.9</td>
</tr>
<tr>
<td>PFTN</td>
<td>1.77</td>
<td>350</td>
<td>332.1</td>
</tr>
<tr>
<td></td>
<td>1.67</td>
<td>300</td>
<td>295.7</td>
</tr>
<tr>
<td>Tetryl</td>
<td>1.70</td>
<td>263</td>
<td>252.8</td>
</tr>
</tbody>
</table>

where:

$Q_{\text{max}}$ is the maximum possible heat of detonation in kcal/kg,
MW is the molecular weight of the compound.

The heat of detonation at the density $\rho$ g/cm$^3$ is $Q_\rho$, and equation (10) makes it possible to calculate:

$$Q_\rho = Q_{\text{max}} \left[ 1 - (0.528 - 0.165\rho)(1.4 - \alpha) \right] \quad (10)$$

where $\alpha$ is 'oxygen coefficient' calculated from equation (11):

$$\alpha = \frac{c}{2a + 2b/2} \quad (11)$$

When $\alpha \geq 1.4$, $Q_\rho = Q_{\text{max}}$.

Another more complicated formula was worked out for explosives with a high content of hydrogen and low value of $\alpha$, for example $\alpha < 0.4$.
The calculated figure for some common explosives are given in Table 4.
The average deviation is 2.3% and at $\rho > 1.0$ it is 1.8%.

In another paper Pepekin, Kuznetsov and Lebedev [13] worked out more complicated equations which made it possible to calculate the rate of detonation of explosives with a bulk formula $C_a H_b O_c N_d F_e$ at a given density $\rho_f$ g/cm$^3$.
The following are equations given by these authors:

$$K_{BB} = \frac{0.135 \frac{a}{a+b} + 21 \frac{b}{a+b} + 0.4 (c+d+e)}{\text{MW}} \quad (12)$$

and

$$n = K_{BB} \rho_f^{1/4} \quad (13)$$

where:

$K_{BB}$ – the coefficient of the composition of the compound,
$n$ – the number of molecules in the products of the detonation,
$\rho_f$ – the density of the explosive.

The rate of detonation $D$ m/s can be calculated from formula (14)

$$D^2 = 8.0 (Q + R) \quad (14)$$

where $Q$ is the heat of detonation in kcal/kg calculated from formula (10),

$$R = \left( \frac{N}{n_f} \right)^5 \rho_f^2 \quad (15)$$

where $n_f$ is the number of molecules in the products of detonation.

Pressure is calculated from equation (16):

$$P = \rho_f D^2 (x_1 - 1)x_1 \quad (16)$$

where $x_1$ is the experimental degree of compression in the front of the detonation wave where density is $\rho_f$.

$$x_1 = \frac{\rho}{\rho_f} \quad (16)$$

The calculated and experimental data for $D$ and $P$ are collected in Table 5. Mean deviation is ca. 1.4%.
TABLE 5. Calculated and experimental data for D and ρ

<table>
<thead>
<tr>
<th>Compound</th>
<th>ρ₁</th>
<th>Q</th>
<th>k_BB</th>
<th>x₁</th>
<th>D_calc</th>
<th>D_exp</th>
<th>P_calc</th>
<th>P_exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>1.64</td>
<td>1010</td>
<td>0.0202</td>
<td>1.38</td>
<td>6900</td>
<td>6940</td>
<td>215</td>
<td>220</td>
</tr>
<tr>
<td>Picric acid</td>
<td>1.80</td>
<td>1173</td>
<td>0.0207</td>
<td>1.37</td>
<td>7600</td>
<td>7760</td>
<td>297</td>
<td></td>
</tr>
<tr>
<td>Tetryl</td>
<td>1.70</td>
<td>1150</td>
<td>0.0215</td>
<td>1.37</td>
<td>7480</td>
<td>7560</td>
<td>257</td>
<td>263</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>1.70</td>
<td>820</td>
<td>0.0298</td>
<td>1.31</td>
<td>8140</td>
<td>8200</td>
<td>266</td>
<td></td>
</tr>
<tr>
<td>Cyclonite (RDX)</td>
<td>1.80</td>
<td>1300</td>
<td>0.0260</td>
<td>1.34</td>
<td>8740</td>
<td>8800</td>
<td>349</td>
<td>347</td>
</tr>
<tr>
<td>Octogen (HMX)</td>
<td>1.90</td>
<td>1320</td>
<td>0.0260</td>
<td>1.33</td>
<td>9100</td>
<td>9150</td>
<td>390</td>
<td>393</td>
</tr>
<tr>
<td>PETN</td>
<td>1.77</td>
<td>1375</td>
<td>0.0243</td>
<td>1.36</td>
<td>8500</td>
<td>8370</td>
<td>338</td>
<td>350</td>
</tr>
<tr>
<td>TACOT</td>
<td>1.85</td>
<td>1044</td>
<td>0.0201</td>
<td>1.37</td>
<td>7310</td>
<td>7250</td>
<td>267</td>
<td>263</td>
</tr>
</tbody>
</table>

Recently Bernard [34] worked out a different formula for the rate of detonation based on his kinetic theory of detonation [35]. His equation for the correlation of the rate of detonation and the density ρ₁ in the shock wave front is as follows:

\[ D_{\text{max}} = \rho_1 \frac{k T_0}{h} \frac{k T_0}{h} d. \] (17)

\( D_{\text{max}} \) is the experimental rate of detonation at an infinite diameter and maximum density ρ_max.
\( k \) the Boltzmann constant,
\( h \) the Planck constant,
\( T_0 \) the initial temperature of the explosive,
\( d \) the mean molecular diameter.

Bernard applied his equation to a number of nitrate esters at room temperature.

Some of his results are shown in Table 6.

TABLE 6. Density in front of the shock wave and experimental rate of detonation

<table>
<thead>
<tr>
<th>Substance</th>
<th>D_{\text{max}}</th>
<th>ρ_max</th>
<th>ρ₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroglycerine</td>
<td>7700</td>
<td>1.6</td>
<td>2.57</td>
</tr>
<tr>
<td>Ethylene glycol dinitrate</td>
<td>8000</td>
<td>1.49</td>
<td>2.79</td>
</tr>
<tr>
<td>PETN</td>
<td>8600</td>
<td>1.37</td>
<td>2.94</td>
</tr>
<tr>
<td>Hexanitrate of dipentaerythritol</td>
<td>7450</td>
<td>1.63</td>
<td>1.93</td>
</tr>
<tr>
<td>Methyl nitrate</td>
<td>8260</td>
<td>1.73</td>
<td>2.43</td>
</tr>
<tr>
<td>Methyl nitrate</td>
<td>8000</td>
<td>1.20</td>
<td>2.61</td>
</tr>
</tbody>
</table>

A plot of \( \log D_{\text{max}} \) against \( \log \rho_1 \) gives a straight line.

Bernard and co-workers [51] extended his calculations to the rate of detonation of C-nitro, O-nitro and N-nitro compounds by using two equations:

\[ D_{\text{max}} = \rho_1 \frac{k T_0}{h} \left( \frac{6 M}{\pi N \rho_{\text{max}}} \right)^{\frac{1}{3}} \] (17a)

and

\[ D^2 = C_0 (M/n) \] (17b)

where:
\( h \) is the Planck constant,
\( M \) denotes the mean molecular mass of the products,
\( N \) Avogadro number,
\( C_0 \) concentration of molecules on the surface of the explosive,
\( n \) number of the nitro groups in the molecule,
\( a \) exponent varying from 1.5 to 2.

A characteristic feature of the calculation by Bernard is that he does not use the enthalpy of detonation but considers that the density \( \rho_1 \) in the shock front, that is, the compression by the shock wave is decisive for the rate of detonation. The groups 'explosophores', such as NO₂, N₃ are particularly strongly compressed. Thus \( \rho_1/\rho_{\text{max}} \) for dinitrobenzene is 1.40 and for picric acid is 1.88. For azides it is approaching 1.7.

Two more papers should be mentioned: that by Aizenshtadt [52] and one recently given by Rothstein and Petersen [53]. The latter authors like Bernard [34, 51] point out that a simple empirical linear relationship exists between the detonation velocity at theoretical maximum density and a factor \( F \) which solely depends upon chemical composition and structure.

Thus:

\[ D' = D_o + (\rho_{TM} - \rho_o) \times 3.0, \] (18)

where
\( D' \) is calculated rate of detonation,
\( D_o \) experimental rate of detonation,
\( \rho_{TM} \) theoretical maximum density,
\( \rho_o \) experimental density.

Factor \( F \) can be calculated:

\[ F = 100 \times \left[ \frac{n(O) + n(N)}{2n(O)} + \frac{n(H)}{3} + \frac{n(\theta)}{1.75} + \frac{n(D)}{4} - \frac{n(\varphi)}{5} \right] - G \] (19)

where \( G = 0.4 \) for liquid and \( G = 0 \) for solid explosives. \( A = 1 \) if the compound is aromatic, otherwise \( A = 0 \) and \( MW = \) molecular weight.
The other expressions:

\[ n(O) = \text{number of oxygen atoms}, \]
\[ n(N) = \text{number of nitrogen atoms}, \]
\[ n(H) = \text{number of hydrogen atoms}, \]
\[ n(B) = \text{number of oxygen atoms in excess of those already available to form} \]
\[ \text{CO}_2 \text{ and } \text{H}_2\text{O}, \]
\[ n(C) = \text{number of oxygen atoms double bonded to carbon as in } \text{C}=\text{O}, \]
\[ n(D) = \text{number of oxygen atoms singly bonded directly to carbon in } \]
\[ \text{C}-\text{O}-\text{R linkage where } \text{R} = \text{H, NH}_4 \text{ or C}, \]
\[ n(E) = \text{number of nitrate groups either as nitrate-esters or nitrate salts.} \]

The relation between \( D' \) and \( F \) can be expressed by the linear equation

\[ D' = \frac{F - 0.26}{0.55}. \quad (20) \]

The deviations between the calculated and experimental values in 95% of explosives is of the order of 5%. Some of the results are given in Table 7.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( TM )</th>
<th>( D ) (calc)</th>
<th>( F )</th>
<th>( D_0 ) (exp)</th>
<th>Deviation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>1.65</td>
<td>6960</td>
<td>3.93</td>
<td>6670</td>
<td>-4</td>
</tr>
<tr>
<td>TNB</td>
<td>1.64</td>
<td>7270</td>
<td>4.26</td>
<td>7270</td>
<td>0</td>
</tr>
<tr>
<td>Picric acid</td>
<td>1.76</td>
<td>7500</td>
<td>4.31</td>
<td>7360</td>
<td>-2</td>
</tr>
<tr>
<td>HNB</td>
<td>2.0</td>
<td>9500</td>
<td>5.27</td>
<td>9110</td>
<td>-4</td>
</tr>
<tr>
<td>Tetryl</td>
<td>1.73</td>
<td>7910</td>
<td>4.54</td>
<td>7780</td>
<td>-2</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>1.72</td>
<td>8160</td>
<td>4.81</td>
<td>8270</td>
<td>+1</td>
</tr>
<tr>
<td>EDNA</td>
<td>1.71</td>
<td>8230</td>
<td>4.83</td>
<td>8310</td>
<td>+1</td>
</tr>
<tr>
<td>Cyclonite (RDX)</td>
<td>1.83</td>
<td>8850</td>
<td>5.18</td>
<td>8950</td>
<td>+1</td>
</tr>
<tr>
<td>Octogen (HMX)</td>
<td>1.90</td>
<td>9140</td>
<td>5.24</td>
<td>9050</td>
<td>-1</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>1.60</td>
<td>7700</td>
<td>4.35</td>
<td>7440</td>
<td>-3</td>
</tr>
<tr>
<td>DGDN</td>
<td>1.38</td>
<td>6760</td>
<td>3.97</td>
<td>6750</td>
<td>0</td>
</tr>
<tr>
<td>PETN</td>
<td>1.77</td>
<td>8290</td>
<td>4.71</td>
<td>8090</td>
<td>-2</td>
</tr>
<tr>
<td>DIN ( )</td>
<td>1.67</td>
<td>8000</td>
<td>4.63</td>
<td>7950</td>
<td>-1</td>
</tr>
<tr>
<td>TACOT</td>
<td>1.85</td>
<td>7250</td>
<td>4.14</td>
<td>7050</td>
<td>-3</td>
</tr>
</tbody>
</table>

It appears that the calculation of important parameters of detonation is still in progress and further improvements with two basic methods:

1. taking into account the enthalpy of detonation,
2. taking into consideration the kinetic theory of detonation.

The problems are tackled in a few monographs: the earlier ones: [54-60] and more recent by Fickett and Davis [24] and Mader [61].

INTRODUCTION

A more detailed discussion of the problems of the theory of high explosives are outside the scope of the present book.

SENSITIVITY OF EXPLOSIVES TO IMPACT

The experimental finding of Wöhler and Wenzelberg (Vol. I, p. 3) gives a general estimation of the sensitivity of nitroaromatic explosives to impact as a function of the character and number of substituents to the benzene ring. On the other hand T. Urbasinski [36] expressed the view in 1933 that the sensitivity of solid explosives to impact is a complicated function of a few factors, among which the most important are:

(a) sensitivity to high temperature,
(b) sensitivity to friction.

This was based on two observed factors:

1. similarity of the curves of the sensitivity of mixtures of explosives to impact and sensitivity to temperature,
2. the shape of the curves of sensitivity of solid mixtures to impact indicates that the sensitivity of mixtures is greater than that of the components due to the friction of particles of two different solid substances.

In turn, the friction can obviously generate a high temperature (Bowden and Tabor [37]).

The related curves are given in Vol. III, pp. 250, 251, 262 and reproduced now in Fig. 1. Both curves (\( T \)-sensitivity to elevated temperature, \( M \)-sensitivity to impact) are clearly composed of two parts: I and II. Curve \( T \) was established by determining the temperature of ignition of the samples of 5 g in test tubes placed in wood alloy at 150° C by increasing the temperature of the alloy at the rate of 10° C/min. The sensitivity to impact is expressed in ordinates as the work in kg/cm² produces 50% of explosion. The sensitivity to impact is manifest by a shape where fraction 1 of the curve \( M \) indicates the increase of the sensitivity of compound \( A \) by adding a less sensitive compound \( B \). This is rationalized in terms of the friction between two foreign solid particles.

The sensitivity of mixtures to impact through friction is particularly noticeable in examples of mixtures of TNT with hard crystals of ammonium nitrate (Fig. 70, Vol. III, p. 262).

Papers have been published on the increase of sensitivity to impact by adding gritty compound, Ubbelohde et al. [38] and recently Scullion and McCormack [39].

Bowden and Yoffe [40] have developed the well known concept of 'hot spots' and that the initiation of explosion stems from 'hot spots' created by thermal factors and crystal hardness and shape. Small bubbles of air included in
liquid explosives (e.g. nitroglycerine) also increase the sensitivity to impact through the adiabatic compression of air and a rapid increase in temperature. See also Lovey [41].

Kamlet [42, 43] also agrees with the thermal character of the sensitivity to impact. He developed an ingenious method of calculating the sensitivity of explosives to impact. For similar explosives he found a linear relationship between logarithmic 50\% impact heights and values of oxygen balance \( \text{OB}_{100} \). The latter value is calculated for C-H-N-O explosives from the equation:

\[
\text{OB}_{100} = \frac{100(2n_O - n_H - 2n_C - 2n_{COO})}{MW}
\]  

(21)

where \( n_O, n_H, n_C \) represent the number of atoms of the respective elements in the molecule and \( n_{COO} \) is the number of carboxylic groups.

Fifty per cent impact heights on a logarithmic scale give a straight line.

A few figures are given (Table 8) for typical nitroaromatic compounds [42] and nitramines [43].

Cherville and associates [44] have examined a number of explosives in a mass spectrophotograph. Particularly important and reproducible were results at 77K. The formation of \( \text{NO}_2 \) was readily established in the spectrophotographs. The authors introduced a concept of the radiochemical yield \( G_{\text{NO}_2} \) of the formation of \( \text{NO}_2 \). A considerable difference exists between the values of \( G_{\text{NO}_2} \) of nitramines and nitroaromatics. They correlated the values of \( G_{\text{NO}_2} \) with those of the sensitivity of explosives to impact, friction and high temperature (temperature of initiation \( t_f \) at the rate of heating 5°C/min): Table 9.

A very important contribution to the knowledge of the sensitivity of explosives to impact has been given by Delpeuch and Cherville [45]. They came to the conclusion that the basic criterion of sensitivity of explosives lies in the distribution of electrons in their ground state and the comparison with that in the excited state. With the advent of quantum mechanical methods, and particularly that of I.N.D.O. [46] they were able to calculate the distribution of electrons in explosives, thus introducing a new and original criterion of sensitivity of explosives. For quantitative estimation they introduced a parameter \( \Delta\text{C}^{\text{a}}/\text{I} \),
where
\[ \Delta C^\circ \] is the dissymmetry of the distribution of electrons in the ground state,
\[ l \] the length of the bond \( \text{C} - \text{NO}_2, \text{N} - \text{NO}_2 \) or \( \text{O} - \text{NO}_2 \).

The following are a few figures thus calculated (Table 10). Higher sensitivity of explosives is manifested by a higher \( \Delta C^\circ/l \). The data for excited state \( \Delta C^\circ/l \) were calculated with the method C.N.D.O.-S/C.I. [47].

**TABLE 10. Sensitivity of explosives to impact**

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Bond*</th>
<th>( C^\circ )</th>
<th>( C^\circ/l )</th>
<th>( C^\circ/l^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNB</td>
<td>C(1)–NO₂</td>
<td>0.539</td>
<td>0.363</td>
<td>0.308</td>
</tr>
<tr>
<td>TNB</td>
<td>C(5)–NO₂</td>
<td>0.575</td>
<td>0.391</td>
<td>0.303</td>
</tr>
<tr>
<td>RDX</td>
<td>N(1)–NO₂</td>
<td>1.044</td>
<td>0.764</td>
<td>0.343</td>
</tr>
<tr>
<td>HMX (δ)</td>
<td>N(1)–NO₂</td>
<td>0.937</td>
<td>0.673</td>
<td>0.345</td>
</tr>
<tr>
<td>EDNA</td>
<td>N–NO₂</td>
<td>0.880</td>
<td>0.676</td>
<td>0.499</td>
</tr>
<tr>
<td>Tetryl</td>
<td>N–NO₂</td>
<td>0.841</td>
<td>0.624</td>
<td>0.478</td>
</tr>
<tr>
<td>PETN</td>
<td>O–NO₂</td>
<td>0.878</td>
<td>0.645</td>
<td>0.417</td>
</tr>
</tbody>
</table>

* The numbers in brackets indicate the position of atoms of C and N in the molecule as given in their formulae based on crystallographic analysis (Vol. I, 181; II, 372, 385).

The relative change \( \delta \) from \( \Delta C^\circ \) to \( \Delta C^\circ/l \) can be expressed by equation (22)

\[
\delta = \frac{100 (\Delta C^\circ/l - \Delta C^\circ)}{\Delta C^\circ} \tag{22}
\]

Delpuech and Chererville [45b] suggest using values of \( \Delta C^\circ/l \) and \( \delta \) as data indicating the tendency of explosives to decompose under impact. This would be particularly advisable with new explosives which although their structure is known, possess unknown properties.

While examining the shape of the curve of the sensitivity to impact of TNT at different temperatures (Vol. I, p. 320, Fig. 74), T. Urbanski [48] advanced an hypothesis that the increase of sensitivity is due to the increase of entropy (S) and therefore decrease of free energy \( G = H - TS \). A critical change is at the melting point of TNT – ca. 80°C which is well known, is manifested by a rapid increase of entropy (Fig. 2). Crucual [79] drew attention to the electric phenomena which accompany the shock and friction produced by the impact. Charging with static electricity is an important factor influencing the explosion according to this author.

Attention is drawn to two monographs dealing with the initiation of explosives by impact: solid explosives by Afanasev and Bobolev [49] and liquid by Dubovik and Bobolev [50]. The authors based their views on the considerable work carried out by Khariton, Andreev, Belyaev, Kholevo, Sukhikh, Avanesov, Bolkovitomin, Baum and their own experiments. The authors agree with the thermal nature of the sensitivity of explosives to impact. However most of the problems raised by the authors of the monographs are outside the scope of the present book.

**Sensitivity** of high explosives (HE) to initiation by an initiating explosive ('gap sensitivity', 'initiability') is less defined than the sensitivity to impact and cannot be expressed in absolute units. The sensitivity of HE to initiation is usually determined:

1. by the amount of the initiating explosive in the detonator (this method is also used to determine the 'initiating strength' of primary explosives),
2. by transmitting the detonation from one charge to another through air or other medium (water or a sheet of metal or a polymer) of different thickness,
3. by determining the critical diameter, that is the minimum diameter which is able to transmit the detonation.

It is well known that the HE can be arranged in the sense of decreasing sensitivity to detonation: O-nitro, N-nitro and C-nitro compounds.
Cachia and Whitbread [63] described a 'gap' test of different explosives and determined the minimum gap thickness that inhibits detonation.

Recently Ahrens [64] reviewed the problem of determination of the sensitivity of explosives to initiation.

Sensitivity to friction is also less defined than the sensitivity to impact and can be expressed only by figures comparative to a standard. By decreasing sensitivity the explosives can be arranged as follows [65]:

initiating explosives (with exclusion of azides),
O-nitro compounds,
N-nitro compounds and metal azides,
C-nitro compounds.

The sensitivity of explosives to heating, naked flame, impact and friction is decisive in the international rules for railway traffic 'RID' (Règlement International Concernant le Transport des Marchandises Dangereuses) [65]. Analogous rules 'ADR' are concerned with international motor traffic [66].

Important reviews have appeared on the sensitivity and initiation of explosives [67, 68].

**Action of Ultrasonic Waves and Laser Pulse**

Early work on the action of ultrasonic waves on explosives indicated that such sensitive substances as nitrogen tetroxide could explode [73, 74] but that silver fulminate could not be brought to detonation [74].

Some experiments by Wolflke [69] have shown that high intensity waves were required to bring mercury fulminate to detonation. Negative results were obtained by Renaud [75] who pointed out that the positive results of Marinesco [74] were due to the mechanical action of pushing crystals by the oscillator. This query was recently solved by Leiber [76] who stated that the detonation of nitroglycerine by ultrasonic waves can occur provided that the explosive contains bubbles and the nature of the effect is mainly thermal bringing the temperature to 300–500°C through the adiabatic pressure of the order of 33 bar.

Mizushima and Nishiyama [77] examined the action of laser and found that compressed explosives can be brought to decomposition by a giant laser pulse. Loose explosives cannot detonate. They examined initiating explosives, PETN, RDX, TNT and Tetryl.

**Action of Irradiation**

Numerous publications particularly in recent years have been dedicated to the sensitivity of explosives to various forms of irradiation.

Bowden and Yoffe [70] reviewed the literature and their own work on the decomposition of initiating explosives by irradiation with electrons, neutrons, fission products, α-particles, X-rays and γ-rays.

Recently two abundant reviews appeared in the Encyclopedia of Explosives edited by Kaye and Herman [71, 72].

Thus Avrami [71] reviewed radiation effects on explosives, propellants and pyrotechnics. Here are some of the main conclusions taken from the work of Avrami and numerous authors: initiating explosives are decomposed under irradiation with α-particles, neutrons, γ-radiation, electron irradiation and underground testing. Among the reviewed papers Avrami reported his own work on the influence of Co60 gamma radiation on the detonation velocity of explosives: they all show a fall in velocity after irradiation. Cyclonite (EDX) appears to be particularly sensitive; less sensitive are PETN and HMX. Aromatic compounds such as TNT and Tetryl seem to be still less sensitive.

A good stability is shown by heat resistant explosives: TACOT, DATB (Diaminotrinitro-) and TATB (Triaminobenzotribenzenes) (Chapter VII).

Helf [72] described the technique of radiation gauging in energetic materials.

A remarkable paper has been published by Cheriville and co-workers [80]. They examined the behaviour of a few secondary explosives to the irradiation from Co60 and introduced the value GNO2 the quantity of NO2 by irradiation. They found the values of GNO2 being correlated to the ability of explosives to detonate. The following are the figures for GNO2:

<table>
<thead>
<tr>
<th>Explosive</th>
<th>GNO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETN</td>
<td>3.80</td>
</tr>
<tr>
<td>Hexogene, Cyclonite (RDX)</td>
<td>0.90</td>
</tr>
<tr>
<td>Octogene (HMX)</td>
<td>0.80</td>
</tr>
<tr>
<td>Tetryl</td>
<td>0.006</td>
</tr>
<tr>
<td>Picric acid</td>
<td>0.001</td>
</tr>
<tr>
<td>TNT</td>
<td>0.001</td>
</tr>
<tr>
<td>Nitroguanidine</td>
<td>0</td>
</tr>
</tbody>
</table>

**Influence of High Temperature**

The behaviour (including the decomposition) of explosives at high temperature is one of their important characteristics. With the advent of DSC (differential scanning calorimeter) high precision can be reached of the examination of endo- and exothermic changes in substances with the increase of temperature. This was reviewed by Collins and Haws [81]. The pioneering work on DSC by Tucholski in 1932–33 [82] should be recalled (see also Vol. I, p. 525).

Two Soviet monographs appeared [63, 64] both dedicated to thermal decomposition and burning of explosives, and a review by Maycock [85].

**INCREASING THE STRENGTH OF EXPLOSIVES BY ADDING METALS**

A popular method of increasing the strength of explosives is by adding aluminium and less frequently calcium silicate, ferro-silicon, silicon (Vol. III, p. 266).
The following figures illustrate the action of aluminium on the calorific value of RDX (Cyclonite) given by Belave [86]:

<table>
<thead>
<tr>
<th>RDX + Al</th>
<th>0% Al cal. val.</th>
<th>1200 kcal/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5%</td>
<td>1380</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1420</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1520</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1690</td>
</tr>
<tr>
<td></td>
<td>22%</td>
<td>1890</td>
</tr>
</tbody>
</table>

Recently the addition of Boron or its compounds with hydrogen, for example, ‘ortho-borane’ (C₂H₃B₁₀) was investigated by Pepek, Makov and Apin [87]. They examined mixtures of PETN and Cyclonite with boron or ortho-borane. The calorific value of Cyclonite–Boron reached a maximum with 1890 kcal/kg with ca. 16.5% B, PETN with ca. 22% reached a value of ca. 2050 kcal/kg.

REFERENCES

36. T. URBANSK, Przemysłow Chem. 22, 521 (1933); Atti del X Congresso de IUPAC, Roma 1933, Mém. de l’Arts, France 20, 237 (1946).
CHAPTER 1

NITRATION AND NITRATING AGENTS

(Vol. I, p. 4)

A considerable number of papers were dedicated to the problem of nitration in the years following the publication of Vol. I.

Among nitrating agents the most important still remain nitric acid–sulphuric acid mixtures, but some other very efficient nitrating agents related to nitric acid have been found and are in use, mainly on a laboratory scale.

NITRIC ACID (Vol. I, p. 6)

Considerable attention is currently being paid to nitric acid (and nitrogen dioxide) because of their wide use, not only for nitration, but also as oxidizing agents in rocket propellant systems. A review has recently been published by Addison [1].

Pure nitric acid free of nitrogen dioxide, so called white fuming nitric acid (WFNA), is in use as an oxidizer and for nitration of some compounds (e.g. hexamethylene tetramine [hexamine], Vol. III, p. 87).

However WFNA is relatively unstable and with time develops a certain amount of dinitrogen tetroxide. More stable for rocket propulsion is red fuming nitric acid (RFNA) which contains ca. 14 wt% N₂O₅. It is formed from WFNA or from nitric acid with added N₂O₅. RFNA is the equilibrium product formed from both extremes of the concentration range:

\[
\begin{align*}
HNO_3 & \rightleftharpoons HNO_3 + N_2O_4 + H_2O \\
WFNA & \quad 84.5\% \quad 14\% \quad 1.5\% \\
& \text{(in excess, subject to evaporation).}
\end{align*}
\]

RFNA is more reactive than WFNA, N₂O₅ being a sui generis catalyst of the oxidation reactions. Subsequently RFNA is more recommended in rocket fuel than WFNA, but should be avoided in most nitration reactions. Dinitrogen tetroxide (usually given in analytical data as NO₂) is present in spent acids contain-
ing nitric and sulphuric acids and is formed in the course of nitration as a result of the oxidation of the nitrated substances. The content of NO₂ in the spent acid can be as high as 5%. Commercial 'fuming nitric acid' ('anhydrous nitric acid') usually contains less than 1% NO₂ and is used for the nitration of hexamime.

Pure nitric acid (WFNA) can be obtained by distillation of nitric acid from a mixture of concentrated nitric acid (d 1.50 at 25°C) and concentrated sulphuric acid, under reduced pressure at room temperature. A white crystalline solid results with the following properties [1]:

m.p. 41.6°C  
b.p. +82.6°C  
d 1.549 at 0°C  
viscosity 10.92 cP at 0°C  
dielectric constant 50 ± 10 at 14°C  
surface tension 43.5 dy/cm at 0°C  
specific conductivity 3.77 × 10⁻² ohm⁻¹ cm⁻¹.

The latter two figures are high due to hydrogen bonding (Vol. I, p. 7, Fig. 1). The data in Fig. 1a (Vol. I, p. 7) should be slightly altered on the basis of more recent measurements by micro-wave spectroscopy [2, 3]. They are now given in Fig. 3.

![FIG. 3. Structure of the molecule of nitric acid (2, 3).](image)

It is well known that nitric acid forms an azeotropic solution with water. It contains 68.5 wt% HNO₃ and boils at 122°C under standard atmospheric pressure.

Cryoscopic measurements (Vol. I, pp. 15–16) have shown that only a little over 3% of pure nitric acid is dissociated at −40°C according to the equation:

\[
2\text{HNO}_3 \rightleftharpoons \text{H}_2\text{NO}_3^+ + \text{NO}_3^- + \text{H}_2\text{O} \]

\[1.2 \quad 1.7 \quad 0.5 \text{ wt%}.

Water is in the form of the nitric acid hydrate.

A few more spectroscopic data for nitric acid should be added to those previously given (Vol. I, p. 22). Vitse [31d] has found bands in nitric acid: 1680, 1300 and 930 cm⁻¹ assigned to NO₂ and band 3200 cm⁻¹ to OH stretching vibrations.

It is now generally accepted that the nitronium ion NO₂⁺ is the main nitrating agent. Although most industrial nitration is carried out by nitric acid–sulphuric acid mixtures, some compounds can be nitrated with nitric acid alone (production of tetryl, Vol. III, p. 42). Some products, such as PETN (Vol. II, p. 185) are usually obtained by nitration with nitric acid alone and Cyclonite (if made by nitration) is produced exclusively with nitric acid free of N₂O₅ (Vol. III, p. 87).

Although the nitronium ion is the nitrating agent, there are known examples when nitration can occur in media in which the concentration of NO₂⁺ is too small to be detected spectroscopically (Vol. I, pp. 25, 48). This was pointed out by Buntun and Halevi [4] who succeeded in nitrating aromatic compounds with 40–60% aqueous nitric acid. Buntun and co-workers [5, 6] showed that the nitronium ion was an intermediate in both oxygen-exchange and aromatic nitration in the sense of reactions:

\[
2\text{HNO}_3 \rightleftharpoons \text{H}_2\text{NO}_3^+ + \text{NO}_3^- + \text{H}_2\text{O} \]  \[2\text{HNO}_3 \rightleftharpoons \text{H}_2\text{NO}_3^+ + \text{NO}_3^- + \text{H}_2\text{O} \]

Hydrated nitronium ion (nitracium ion) H₂NO₃⁺ is a source of the nitrating agent NO₃⁻.

It was reported [7] that nitration of 1,5-dinitro-naphthalene can occur with 70% nitric acid to yield trinitro-naphthalenes.

The problem of nitration with aqueous nitric acid was reviewed by Hanson and associates [8]. They confirmed the idea of nitracium ion being a nitrating agent and pointed out that attention should be paid to the presence of nitrous acid in the system, as nitration with dilute nitric acid can proceed through the nitrosation by nitrous acid formed as the result of oxidation–reduction. T. Urbasński and Kutekiewicz [9] (Vol. I, p. 85) found that 8-hydroxyquinoline can be nitrated by boiling with 0.5% nitric acid to yield 5,7-dinitro-8-hydroxyquinoline. It was also found that 8-hydroxy-5-nitroquinoline yielded the same dinitro derivative.

As far as the mononitration of phenol and the formation of 8-hydroxy-5-nitroquinoline can be explained in terms of the conventional mechanism of
nitration followed by the oxidation of nitroso to the nitro group (p. 23), this
mechanism could not explain the formation 5,7-dinitro-8-hydroxyquinoline
from mononitro compound. The mononitrophenols cannot be nitrated with
nitric acid and subsequently the formation of the second nitro group cannot
occur through nitrosation. Nevertheless, the reaction of formation of the dinitro
compound from the mononitro product is preceded by the oxidation and evolu-
tion of NO₂. This would apparently suggest that nitrosation (as shown above)
is not possible with 8-hydroxy-5-nitroquinoline.

Also Ross and co-workers [87] pointed out that the accepted scheme of
nitration of phenol in 56.2% sulphuric acid through nitrosation prior to nitra-
tion, is inconsistent with the results and expressed the view that another route
should exist.

The author of the present book suggests the solution of the problem of
nitration of phenols with dilute nitric acid in a two-fold way:

(1) Through oxidation (which always accompanies nitration and particularly
the nitration of phenols) NO₂ is evolved and the well known reaction occurs:

\[ 2 \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2 \]  \hspace{1cm} (5a)

(2) The dilute nitric acid originally present in the solution and also formed
in reaction (5a) can given rise to NO₂⁻ in a readily oxidizable medium
according to scheme (5b) rationalized by the author [112]:

\[ \text{NO}_2^- \rightarrow \text{NO}_2^+ + \text{O}^- \]  \hspace{1cm} (5b)

Reaction (5b) can take place in readily oxidizable mediums such as phenols
and aromatic amines.

NITRIC AND SULPHURIC ACID

Mixtures of nitric and sulphuric acids contain nitronium sulphates which have
been described by Ingold and associates, Woolf and Emeléus (Vol. I, p. 19). Revallier
and co-workers [10] have found by Raman spectroscopy and vapour pressure
measurements, that compounds made by acting with SO₃ on nitric acid are
salts of nitronium ion (NO₂⁺) and sulphate anions. Vitse [11] established the
structure of the compound N₂O₅ · ASO₃ as nitronium ion salt by X-ray crystallo-
graphy. The salts of pyrosulphuric acid (Vol. I, p. 12) can be present only in a
mixture of nitric acid with oleum or SO₃. They are described in the paragraph
on nitronium salts (p. 27). The presence of NO₂⁻ in various solutions was dis-

The basicity of nitric acid in the sense of the dissociation NO₂OH ⇌ NO₂⁺ +
OH⁻ in concentrated sulphuric acid was recently studied by Marziano et al.

[12]: the ionization ratio NO₂⁺/HNO₃ of nitric and 80–96% sulphuric acids has
been evaluated by Raman and ultraviolet spectroscopy. The function pKₐ of
nitric acid as a base was calculated pKₐ ≈ -15.2.

As far as the activity of the nitrating mixture (Vol. I, p. 29) is concerned, a
novel approach to the problem was recently developed by Marziano and associ-
ates [13]. In a series of papers on thermodynamic analysis of nitric acid with
sulphuric or perchloric acid these authors introduced a new function of the
activity coefficient MC:

\[ M_C = \log \frac{f_B f_H^+}{f_{BH}^+} \]

where \( f_B \) is the activity coefficient of the nitrated substance, \( f_H^+ \) activity
coefficient of the proton H⁺.

Effects of Adding Salts on Nitration in Sulphuric Acid

A few authors have examined the effect of adding salts on the rate of nitrat-
ion in sulphuric acid.

Thus Surfield and Wyatt [14] studied the nitration of benzenesulphonlic acid
in sulphuric acid and found that the addition of hydrogen sulphates of various
metals increases the nitration rate. The most marked effect occurred with cal-
cium and barium hydrogen sulphates. An explanation of the effect was sought
in terms of the Brønsted salt-effect theory. It was suggested that the main
influence of ionic solutes is in the activity coefficient of the nitrated substance
(\( f_B \)) since the activity coefficients of the other two species, the nitronium ion
(\( f_{NO_2}^- \)) and the similarly charged transition complex (\( f_{NO_2}^+ \)) as a ratio in the
Brønsted equation and would be approximately equally affected by changes in the
ionic environment. The view was expressed that reactions involving only ionic
species would exhibit small salt effects.

Bonner and Brown [15] expressed the view that the increase in reaction rate
due to added salts is similar to the increase initially resulting from the addition
of water to anhydrous sulphuric acid, attaining the maximum at ca. 90% acid.
They supported it by examining the rates of nitration of trimethylphenyl-
ammonium ion and 1-chloro-4-nitrobenzene. When ammonium sulphate was
added, the rate increased more than 10% their value in the anhydrous acid. On
the nitration of cellulose with nitric acid in the presence of inorganic salts (see

Nitric Acid and Trifluoromethane Sulphonic Acid

A very interesting nitrating mixture has been reported by Coon, Blucher and
Hill [16]. It was composed of nitric acid and trifluoromethane sulphonic acid:
Nitration and Nitrating Agents

Mentioned with nitric acid and acetic anhydride with a small quantity of sulphuric acid at 35°C on ethoxyvinylphosphate. The ester was hydrolysed to yield a nitromethane derivative:

\[(\text{RO})_2\text{PO(CH)}_2\text{H} = \text{HOC}_2\text{H}_2\text{C} = \text{CH}_2\text{COO}^\text{N^+}\text{H}_2\text{O}_2\]  
\[(\text{RO})_2\text{PO(O)CH} = \text{HOC}_2\text{H}_2\text{C} = \text{CH}_2\text{CO}^\text{N^+}\text{H}_2\text{O}_2\]  
\[(\text{N})\text{O}^\text{H}_2\text{O}_2\]  
\[
(\text{RO})_2\text{P(OH)CH} = \text{N} = \text{O}^\text{H}_2\text{O}_2\]  
\[
(\text{RO})_2\text{P(OH)CH} = \text{N} = \text{O}^\text{H}_2\text{O}_2\]  

Literature on the practical use of nitric acid–acetic anhydride includes also some warnings on explosion hazards associated with the use of mixtures of fuming (97%) nitric acid with acetic anhydride. Thus Brown and Watt [25] demonstrated that mixtures of nitric acid with acetic anhydride containing more than 50% by weight of nitric acid can undergo a spontaneous explosion.

Dingle and Pryde [26] extended this warning also to mixtures containing less than 50% nitric acid. Particularly dangerous is the addition of small quantities of water or some mineral acids to such a mixture. A mixture containing 6% nitric acid in acetic anhydride with 1.7% concentrated hydrochloric acid was found to self-heat at 20°C and to fume-off vigorously at 60°C with gas evolution.

Nitric Acid with Cerium Ammonium Nitrate or Tallium Nitrate

Considerable interest has been shown recently in the use of cerium (IV) salts as oxidizing agents. Cerium (IV) ammonium nitrate can also be a nitrating agent [125]. It can also act in the presence of acetic acid [119]. In the presence of nitric acid [120] it can form nitrate esters from the methyl group, viz.:

\[-\text{CH}_3\text{O}^\text{N^+}\text{H}_2\text{O}_2\]  

(see Chapter X).

Tallium (III) nitrate can also be used as a nitrating agent [119].

Nitronium Cation (NO$_2^+$) and Its Salts

Crystalline nitronium salts were first obtained as early as 1871 by Weber [27] (see also Vol. I, p. 12). He gave the composition N$_2$O$_5$, 4SO$_3$, 3H$_2$O and N$_2$O$_5$, 4SO$_3$, 4H$_2$O. Several similar salts have been obtained by a number of authors [10, 28–30]. The most important contribution to the knowledge of stoichiometry of N$_2$O$_5$, SO$_3$ and N$_2$O$_5$, SO$_3$, H$_2$O complex-salts has been made by Vitse [31].

All these salts possess ionic structure comprising cation NO$_2^+$ bonded in various proportions to HSO$_4^-$, HS$_2$O$_7^-$, S$_2$O$_7^{2-}$ etc.
Some of the salts possess a great stability if protected from moisture. Thus Werner compound \( \text{N}_2\text{O}_4 \cdot \text{HSO}_3 \) \( \cdot \text{H}_2\text{O} \) has the structure \( \text{NO}_2^+ \text{HSO}_4^- \) and m.p. 105.6°C [10a]. The compound \( 8\text{N}_2\text{O}_4 \cdot 2\text{SO}_3 \cdot 7\text{H}_2\text{O} \) with the structure \( (\text{NO}_2^+)_4 \text{S}_2\text{O}_7^{2-} (\text{HSO}_3^-)_4 (\text{H}_2\text{SO}_4^-)_{10} \) has m.p. 119.8°C. Its crystal structure was determined by X-ray analysis [11] as already mentioned (p. 28).

Other salts of nitronium ion and sulphuric acid have been previously described (Vol. I, p. 19). Ingold and co-workers (Vol. I, p. 19) obtained crystalline nitronium perchlorate which was relatively stable, but decomposed on storage and was not further investigated.

R. J. Thomas, Anzilotti and Hennion [32] reported that boron trifluoride could play the same part as sulphuric acid in the nitration of aromatics. Olah and co-workers [33, 40] prepared and successfully applied a number of stable salts of nitronium ion in a relatively simple way:

\[
\text{NO}_2^+ X \text{ where } X = \text{BF}_4, \text{AsF}_6, \text{PF}_6
\]

and

\[
(\text{NO}_2^+) Y \text{ when } Y = \text{SiF}_6^{2-}.
\]

Particularly important is nitronium tetrafluoroborate obtained by adding anhydrous HF to nitric acid in a solvent such as nitromethane or methylene chloride and then saturating the solution with boron trifluoride (8):

\[
\text{HNO}_3 + \text{H}^+ + 2\text{BF}_3 \rightarrow \text{NO}_2^+ \text{BF}_4^- + \text{BF}_3 + \text{H}_2\text{O}.
\]  

An almost quantitative yield of stable nitronium salts \( \text{NO}_2^+ \text{BF}_4^- \) can be obtained in that way [34] and it is now commercially available [35]. It is a colourless, crystalline very stable compound which decomposes above 170°C into \( \text{NO}_2 \) and \( \text{BF}_3 \) without subliming. It is a very strong nitrating agent [36].

Among other compounds nitric acid–boron trifluoride \( \text{HNO}_3 \cdot 2\text{BF}_3 \) complex (m.p. 53°C) obtained by Revalleri and associates [37] proved by Raman spectroscopy to possess the structure of nitronium salt \( \text{NO}_2^+ (\text{BF}_3)_2 \text{OH}^- \) [38].

Nitronium ion is able to form nitroxonium and pyridinium ions with ethers and pyridine or collidine respectively by acting on ethers and pyridine or collidine respectively with nitronium tetrafluoroborate [39, 40d]:

\[
\text{NO}_2^+ Y^- + R/X/R \rightarrow \left[ \begin{array}{c}
\text{NO}_2 \\
\text{R} \\
\text{R} \\
\text{Y}^- \\
\end{array} \right]
\]

\( Y = \text{PF}_6, \text{BF}_4 \)

\( X = \text{O, S, } R = \text{Alkyl, H} \)

The nitroxonium and nitropyridinium (or nitrocollidinium) ions are efficient nitrating agents. They also can form \( \text{O}-\text{nitro compounds} \). Nitronium hexafluorophosphate (\( \text{NO}_2^+ \text{PF}_6^- \)) is also a strong nitrating agent according to Olah and Lin [40b]. It can nitrate alkanes at 25°C to a small yield of nitro compounds (2–5% for ethane to butane). Nitronium tetrafuoroborate in fluorosulphuric acid (\( \text{F}_2\text{SO}_4 \)) possesses strong nitrating properties. It can nitrate \( m\)-dinitrobenzene to \( \text{sym-} m\text{-dinitrobenzene} \) with a yield of 66% [40c].

Among the salts of nitronium ions a very active nitrating agent is nitronium trifluoroethyl sulphate (\( \text{NO}_2^+ \text{CF}_3\text{SO}_4^- \)) as already mentioned [16].

Nagakura and Tanaka [41] explained a great reactivity of \( \text{NO}_2^+ \) by calculating its lowest vacant orbital and the highest occupied orbital of benzene. The figures are \(-11.0\) and \(-9.24\) eV respectively. Other electrophilic reagents, such as \( \text{Br}^+ \) and \( \text{Cl}^+ \) are less reactive. They gave values of \(-11.8\) and \(-13.0\) eV respectively.

Nitronium salts are usually applied in an apotic solvent [35]. Such is tetramethylene sulphone (‘Sulfolan’) used by Olah [40]. However, Giaccio and Marcus [42] suggested acetic acid as a solvent. This, however, reacts with nitronium tetrafluoroborate on standing at room temperature to yield acetyl nitrilot:

\[
\text{CH}_3\text{COOH} + \text{NO}_2^+ \text{BF}_4^- \rightarrow \text{CH}_3\text{C(O)O}_2^- + \text{BF}_3 + \text{H}_2\text{O}.
\]  

The nitrating action of acetyl nitrilot differs from that of nitronium tetrafluoroborate [40]. Also the stability of acetyl nitrilot is not satisfactory.

**Dinitrogen Pentoxide (\( \text{N}_2\text{O}_5 \)) (Vol. I, p. 105)**

Dinitrogen pentoxide (nitric anhydride) can be a source of the nitronium ion. As previously mentioned Titov suggested (Vol. I, p. 106) that dinitrogen pentoxide undergoes a heterolytic dissociation:

\[
\text{N}_2\text{O}_5 \rightarrow \text{NO}_2^+ + \text{NO}_3^-.
\]  

The infra-red bands of the ionic form at liquid nitrogen temperature have been examined by Tanash and Decius [43] and substantiated by Hisatsune and co-workers [44] who also examined Raman spectra. They found a temperature dependence of the structure of solid \( \text{N}_2\text{O}_5 \) which changed the covalent structure \( \text{O}_2\text{N}—\text{O}—\text{NO}_2 \) into ionic at temperatures from \(-175^\circ\) to \(-80^\circ\) C.
The covalent structure is characterized by a bent of the central N—O—N group. Dinitrogen pentoxide readily forms nitronium salts. As mentioned, Weber [27] and other authors [28–31] obtained a number of sulphates of NO₄⁺. Bachman and Dever [45] prepared a complex with BF₃ which most likely possesses the structure NO₄⁺BF₃ONO₇⁻. Kuhn and Olah [33] obtained nitronium tetrafluoroborate by adding anhydrous HF as a solvent to N₂O₅ and BF₃:

\[ N₂O₅ + HF + BF₃ \rightarrow NO₄⁺BF₄⁻ + HNO₂. \] (13)

T. Urbanski used N₂O₅ in vapour phase or in a solution in nitric acid to nitrate cellulose (Vol. II, p. 348) and starch (Vol. II, p. 430).

N₂O₅ was successfully used by Schöllkopf and associates [46] to nitrate aliphatic diazo compounds to obtain eventually nitrodiazo methane [46b] and dinitrodiazo methane [46c]. As the first step esters of diazoacetic acid were nitrated with half a mole of N₂O₅ in carbon tetrachloride at −20 to 30°C:

\[ 2N₂ = CH₂COOR + N₂O₅ \xrightarrow{CCl₄} N₂ \xrightarrow{COOR + O₂NCH₂COOR} NO₂ \]

(14)

\[ (R = C₃H₇ or \text{ter}-C₄H₉) \]

Nitro diazo ester (I) is relatively acid-stable, but the COOR group can be cleaved off by acting with trifluoroacetic acid in ether to obtain nitro diazo methane (II). O₂N=CHNO₂ m.p. 55°C. It is a substance which is sensitive to impact and explodes on heating.

Nitro diazo methane was nitrated [46c] with N₂O₅ in dichloromethane at −30°C to yield dinitro diazo methane (III) and a nitromethyl nitrate ester (IV):

\[ 2CH₂NO₂ + N₂O₅ \rightarrow N₂ \xrightarrow{NO₂} N₂ \xrightarrow{CH₂} NO₂ \]

(15)

III is an explosive substance with m.p. 65°C (with decomposition).

N₂O₅ possesses marked oxidizing properties [47]: a small yield of CO₂ was formed by acting with N₂O₅ on CO. Baryshnikova and Titov [123] have found an interesting reaction of N₂O₅ on aromatic compounds which consists in both nitration and oxidation. Thus chlorobenzene was transformed into chloronitrophenols.

**Dinitrogen Tetroxide and Nitrogen Dioxide (Vol. I, p. 90)**

The increasing importance of dinitrogen tetroxide brought to light a number of new facts on the properties of the substance.

Some physical constants are [1]:

- freezing point −11.2°C
- b.p. 21.15°C
- density 1.470–1.515 g/cm³ between +10°C and −10°C
- viscosity 0.468–0.599 cP between +10°C and −10°C
- dielectric constant 2.42
- surface tension 26.5 dyne/cm at 20°C
- specific conductivity 10⁻¹² ohm⁻¹ cm⁻¹.

An extensive review of the properties of dinitrogen tetroxide has been given by Riebsomer [47]. The addition of N₂O₅ to olefins was reviewed by Shechter [48] and free radical reactions of NO₂ by Sosnovsky [48a].

The N—N bond in dinitrogen tetroxide can readily be split above room temperature. The case of breaking N—N bond is due to low enthalpy: ΔH of N—N in N₂O₅ is 14.6 kcal/mol and similarly in N₂O₃ is 10.2 kcal/mol. [49].

The N—N bond is mainly σ in nature, not of pure π character according to Green and Linnett [50]. This was based on a calculation by LCAO MO method and was contradictory to earlier views. The bond N—N seems to be of an unusual kind, not fully understood, as the two NO₂ units do not rotate with respect to each other in spite of the length of the bond.

The views of Green and Linnett were subjected to criticism by R. D. Brown and Harcourt [113]. The latter pointed out that Green and Linnett had overlooked the significant effect of o-electron delocalization upon N—N and N—C bonds. Brown and Harcourt proposed a new electronic structure with α + π model.

A review recently appeared [126] on the spectrum of NO₂ in gas phase. The spectrum is rich and complex and was examined by modern techniques. The study is outside the scope of the present book.

N₂O₅ is miscible with many organic liquids and is a solvent of many solid organic substances.

Ammonium nitrate is insoluble in N₂O₅ but alkylammonium nitrates dissolve readily [1].

Nitrogen dioxide at high temperature (ca. 620°C) was subjected to homolytic dissociation into nitric oxide and oxygen atom. The same occurred upon irradiation with 313 and 316 nm light [51, 52].
The heterolytic dissociation can be represented in two ways:
\[
\begin{align*}
\text{N}_2\text{O}_4 & \rightleftharpoons \text{NO}_2^+ + \text{NO}_2^- \\
\text{N}_2\text{O}_4 & \rightleftharpoons \text{NO}^+ + \text{NO}_3^-
\end{align*}
\] (16) (17)
and there is also an irreversible heterolytic oxygen exchange:
\[
\text{NO}_2^+ + \text{NO}_3^- \rightarrow \text{NO}^+ + \text{NO}_2^-. \tag{18}
\]

However, the species \(\text{NO}_2^+\) and \(\text{NO}_3^-\) have not been identified as free ions in liquid \(\text{N}_2\text{O}_4\). They exist as the ion pair \([\text{NO}_2^+ \cdot \text{NO}_3^-]\). In the presence of an electron-pair acceptor, complexes are formed which contain the nitrogen ion. This happens in the presence of Lewis acid halides used for the first time (\(\text{AlCl}_3\)) by Schaarhschmid (Vol. I. p. 103). Boron trifluoride reacts with \(\text{N}_2\text{O}_4\) to form \(\text{N}_2\text{O}_4\cdot\text{BF}_3\) \([53, 54]\) and \(\text{N}_2\text{O}_4\cdot2\text{BF}_3\). Their structures were suggested as being \(\text{NO}_2^+\cdot\text{BF}_3\cdot\text{NO}_3^-\) and \(\text{NO}_2^+\cdot[\text{N}\cdot\text{O}\cdot\text{BF}_3\cdot\text{O}_2^-]\), respectively. These complexes possess only a moderate nitrating ability, a fact which casts some doubt on whether they possess the structure with nitrionium ion. It is known that \(\text{N}_2\text{O}_4\) in nitric acid is almost fully ionized into \(\text{NO}_3^-\) and \(\text{NO}_3^+\). In view of the absence of \(\text{NO}_2^+\) the complex \(\text{N}_2\text{O}_4\cdot\text{BF}_3\) may have the structure of a nitrionium salt \(\text{NO}_2^+\cdot\text{BF}_3\cdot\text{NO}_3^-\).

Indeed it shows an ability to nitrosate and to diazotize \([53]\) and spectroscopic examination \([56]\) showed only a relatively weak band at 1400 cm\(^{-1}\) and a strong one at ca. 2340 cm\(^{-1}\).

It is suggested \([40]\) that an equilibrium exists between nitrionium and nitrionium forms of the complex \(\text{N}_2\text{O}_4\cdot\text{BF}_3\) i.e.
\[
\text{NO}_2^+\cdot\text{BF}_3\cdot\text{NO}_3^- \rightleftharpoons \text{NO}^+\cdot[\text{BF}_3\cdot\text{NO}_3^-] \tag{19}
\]

A solution \(\text{N}_2\text{O}_4 + \text{HF}\) should be considered as a potential nitrating agent \([57]\).

Dinitrogen tetroxide can give additional complexes with compounds possessing an ether bond. They were examined by Shechter et al. and described in his review paper \([48]\).

Here are the most important of the compounds:

1. \(2(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{N}_2\text{O}_4\) m.p. -74.8°C
2. \(2(\text{C}_3\text{H}_6\text{O}) \cdot \text{N}_2\text{O}_4\) m.p. -56.8°C (Tetrahydrodropyren)
3. \(\text{C}_4\text{H}_9\text{O} \cdot \text{N}_2\text{O}_4\) m.p. -20.5°C
4. \(2\text{C}_4\text{H}_9\text{O} \cdot \text{N}_2\text{O}_4\) m.p. (indefinite) (Tetrahydrodropyran)
5. \(\text{O}(\text{CH}_3\text{CH}_2)_2\text{O} \cdot \text{N}_2\text{O}_4\) m.p. +45.2°C

Davies and C. B. Thomas \([58]\) reported an interesting instance of nitrination of arylithium (III) aromatic complexes with nitrogen dioxide at room temperature. Gallium (III) fluoroacetate was used as the agent metallating an aromatic ring which can react with \(\text{NO}_2\):

\[
\text{Alk C}_3\text{H}_5\text{THOCOCF}_3\cdot\text{H}_2 \text{NO}_2^+ \rightarrow \text{Alk C}_3\text{H}_5\text{NO}_2
\] (20)

A remarkable feature of the reaction is the high proportion of \(p\)-nitro products. More details are given in the chapter on the nitration of toluene.

Dinitrogen tetroxide in vapour phase can be used as an energetic nitrating agent (Vol. I, pp. 92–105). The nitrination of aromatics can be facilitated by irradiation with ultraviolet light. The claim of Gorislovets (Vol. I, p. 105) was substantiated by Bunbury \([59]\).

As far as nitration with liquid \(\text{N}_2\text{O}_4\) is concerned, attention should be paid to the danger of keeping solutions of alkanes with \(\text{N}_2\text{O}_4\).

T. Urbanski and Palczewski \([60]\) reported a spontaneous explosion when a solution of \(\text{N}_2\text{O}_4\) in \(n\)-alkanes was kept for a few days at room temperature. This was most likely a consequence of the formation of branched reaction chains through free radicals.

In addition to the use of dinitrogen tetroxide as an oxidizer in rocket propellant systems, and as a potential nitrating agent is also used as a cooling liquid in nuclear energy reactors under the name of ‘Nitrin’ \([61]\).

Dinitrogen Tetroxide – Nitric Acid

The two liquids: \(\text{HNO}_3\) and \(\text{N}_2\text{O}_4\) are not miscible in all proportions. At room temperature (20°C) an immiscibility region extends between ca. 54 and 92 wt% of \(\text{N}_2\text{O}_4\). The critical solution temperature is 60.9°C at a composition 68.2 wt% \(\text{N}_2\text{O}_4\). The phase diagram is shown in Fig. 4 \([62, 63]\).

A solid compound \((\text{HNO}_3)_2\cdot\text{N}_2\text{O}_4\) exists, it contains 42.2% \(\text{N}_2\text{O}_4\). It gives an eutectic m.p. -65°C at 25.6% \(\text{N}_2\text{O}_4\) \([64]\). The compound gives maximum values of density and viscosity \([65]\). Spectroscopic examination shows \([1]\) that the species present in \(\text{HNO}_3-\text{N}_2\text{O}_4\) mixtures are as follows:

\[
\text{NO}^+, \text{NO}_2^+, \text{NO}_3^-, \text{H}_2\text{O}, \text{HNO}_3, \text{NO}_2, \text{N}_2\text{O}_4.
\]

The mixtures \(\text{HNO}_3-\text{N}_2\text{O}_4\) are highly corrosive and attack metals (steel, aluminium or chromium, nickel). Corrosion can be inhibited by the addition of fluorine compounds, notably HF or \(\text{PF}_5\) \([1]\). The addition of 0.7 wt% of HF reduces the corrosion by a factor over 100 and the mixture of 44% \(\text{N}_2\text{O}_4\) and 56% \(\text{HNO}_3\) with 0.7–1.0% HF termed ‘standard HDA’ is in current use as a rocket oxidant fuel.

When HF is added to the nitric acid–dinitrogen tetroxide mixture, the following are reactions:
NITRATION AND NITRATING AGENTS

FRIEDEL-CRAFTS NITRATING AGENTS (Vol. I, p. 103)

The use of Friedel-Crafts catalysts in nitrating systems was originally suggested by Schaarschmidt (Vol. I, p. 103) and Topchiev (Vol. I, p. 46). Currently it is related to the concept of 'Supercoids' [66, 67]. The term 'supercoid' refers to acid systems which show acidity stronger than 100% sulphuric acid function $H_a$ [68] lower than $-10.60$. A superacid is usually formed by Lewis Acid and a mineral acid.

As already pointed out $N_2O_4$ can form complexes such as $BF_3$ with Friedel-Crafts catalyst.

Most mixtures of Friedel-Crafts catalysts are non-homogeneous. However, Olah [37] has found that a homogeneous system can be obtained with TiCl$_4$, BF$_3$, PF$_5$ and AsF$_5$ while using tetramethylene sulphone 'Sulfolan' as a solvent. Nitronium fluoride or chloride can then be formed, e.g.

$$2N_2O_4 + TiCl_4 \rightarrow NO_2Cl + 2NOCI + TiO_2.$$

(23)

Olah [33, 40] drew attention to a number of nitrating agents, such as nitronium halides (usually referred to as nitryl halides): $NO_2X$ ($X = F, Cl, Br$). Nitronium chloride and fluoride were reported as nitrating agents in Vol. I, pp. 58, 107; Vol. II, p. 355 and Vol. I, p. 109 respectively. Nitronium chloride is usually prepared by reacting nitric acid with chlorosulphonic acid [69]. Nitronium bromide is unstable and was not isolated [33, 40]. According to Aynsale, Heatherington and Robinson (Vol. I, p. 109) nitronium fluoride is a more powerful nitrating agent than nitronium chloride. Infra red and Raman spectra of nitronium fluoride were examined [70].

Nitronium halides should be regarded as acyl halides and are able to take part in Friedel-Crafts acylation, which in this case is nitration, according to scheme:

$$ArH + NO_2X \rightarrow Ar NO_2 + HX.$$

(24)

In the presence of aluminium halides nitronium halides react forming complex nitronium salts [33, 40]:

$$NO_2X + AlX_3 \rightleftharpoons NO_2^+ AlX_4^-.$$

(25)

Solid Superacid Catalysts

Olah [40c] has drawn attention to the fact that the first solid acid catalyst was suggested by Kameo, Nishimura and Manabe [71]. They used polystyrenesulphonic acid with nitric acid, but the system was unstable, as the catalyst was degraded by the strong acid. Olah and associates [72] developed a nitrating agent from $n$-butyl nitrate and acetone cyanohydrine nitrate by adding a per-
fluorinated resin sulphonic acid (nafion - H). It provides an exceptionally clean way of preparing nitrating aromatic compounds. Nitro compounds can be isolated by a simple filtration of the catalyst, without the need of any aqueous basic washing or workup. All by-products are removed during the reaction, as they are volatile. By way of azeotropic removal of water, the nitrilation can be brought to a very high yield.

ALKYL NITRATES AND BORON TRIFLUORIDE

Alkyl nitrates in sulphuric acid have already been used as nitrating agents (Vol. 1, p. 122). Poly(phosphoric) acid [73] and Lewis acid halides [74-76] were also used with alkyl nitrates. Olah and Lin [77] nitrated a number of aromatic compounds with methyl nitrate and BF₃ in nitromethane solution. Only mononitrination took place.

Spectroscopic examination of the nitrating solutions (infra red and Raman spectroscopy) did not show the presence of a detectable concentration of NO₃⁻ ion. This does not exclude the possibility of nitrating aromatics (as has already been discussed pp. 23-24). Either the system NO₂⁺ BF₄⁻ or a polarized complex CH₃ONO₂ → BF₃ is the nitrating agent.

Narang and M. J. Thompson [78] suggested using acetonecyanhydrine nitrate (ACN) CH₃CNONO₂ and BF₃ as a nitrating agent. Olah and co-workers [124] reported recently that aromatic compounds can be nitrated with silver nitrate in acetonitrile solution in the presence of boron trifluoride at 25°C. With p-xylene the yield is up to 91% of mononitro compound. (See also Vol. 1, p. 46).

NITRIC ACID AND MERCURY SALTS (Vol. 1, p. 110)

Among different metal salts catalysing the nitrilation of aromatic systems, mercury salts occupy an exceptional position (perhaps tellium would also play a certain part, see p. 27).

A review on mercuric salts in nitrilation was given by Titov and Laptev [79]. Japanese authors: Tsutsumi and Iwata [80], Osawa and co-workers [81] have found that mercuric oxide and mercuric nitrate were catalysts of nitrilation with nitric acid. Komoto and co-workers [82] found that mercuric acetate catalysed nitrilation of toluene with nitric and acetic acid at 80°C.

Stock and T. L. Wright [83] came to the conclusion that nitrilation occurred in three steps:

1. mercurilation,
2. nitrosodemercuration by the nitrosonium ion (NO⁺) which exists in the nitrating mixture and is more energetic than the nitronium ion (NO₂⁺) which does not produce the demercuration and only deprotonation,
3. oxidation of the nitroso to nitro compound.

NITRATION AND NITRATING AGENTS

This can be depicted by a scheme established for toluene:

\[
\begin{align*}
\text{CH}_3\text{C}_6\text{H}_4 + \text{Hg(OAc)}_2 & \rightarrow \text{CH}_3\text{C}_6\text{H}_4 \text{Hg(OAc)} + \text{HOAc} \\
& \text{NO}^+ \text{ (demercuration)} \\
\text{CH}_3\text{C}_6\text{H}_4 \text{NO + H}_2\text{OAc}^+ & \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{NO}_2 + \text{HNO}_2.
\end{align*}
\]

Inorganic Nitrate Salts and Trifluoroacetic Acid (Vol. 1, p. 46)

Nitric acid salts in the presence of other acids have been previously described (Vol. 1, p. 46). It was recently reported by Crivello [125] that metal nitrates in trifluoroacetic anhydride (TFAA) can nitrilate aromatic compounds at room temperature in very good yields. Thus ammonium nitrate with TFAA nitrated benzene to nitrobenzene with a yield of 95%.

NITROUS ACID (Vol. 1, p. 116)

Dinitrogen trioxide (nitrous anhydride) was found to have m.p. -100.7°C [84]. Its structure \(\text{N}_2\text{O}_3\) was confirmed by Anderson and Mason [84] through \(\text{N}_2\text{O}_3\) NMR examination.

Nitrilation with nitrous acid can proceed in three ways:

1. through the addition to double bonds (Schechtler [48]),
2. through the nitrosation which is the first step of the reaction followed by the oxidation of the nitroso product,
3. through the formation of nitric acid from the nitrogen dioxide built from nitrous acid:

\[
\begin{align*}
\text{HONO} & \rightarrow \text{N}_2\text{O}_3 \\
& \rightarrow \text{NO} + \text{NO}_2 \rightarrow \text{2NO}_2.
\end{align*}
\]

The known reaction of \(\text{NO}_2\) with water yields equimolar proportions of \(\text{HNO}_3\) and \(\text{HNO}_2\). The latter can again furnish \(\text{NO}_2\) according to (29) and finally \(\text{NO}_2^+\) according to (5a) and (5b).

Nitrous salts in strong acids are subjected to dissociation with the formation of nitrosonium ion \(\text{NO}_2^+\):

\[
\text{HONO} + \text{H}_2\text{O}^+ \rightarrow \text{NO}_2^+ + \text{2H}_2\text{O}.
\]

The nitrosonium ion can be subjected to oxidation with the release of \(\text{NO}_2\) and further formation of \(\text{HNO}_3\) and \(\text{HNO}_2\).

The presence of nitrosonium ion has been spectroscopically established by Singer and Vamplew [85] in aqueous (58%) perchloric acid. It showed strong
bands 260 and 420 nm, and molecular HONO gave weak maxima of 340 and 390 nm. The equilibrium constant of the reaction (30) was determined by Turney and Wright [86].

It was stated by T. Urbański and Kutkiewicz [9] that 8-hydroxyquinoline could be nitrated by boiling with a dilute (ca. 0.3%) solution of NaN₃ in 10% hydrochloric acid to yield 5,7-dinitro-8-hydroxyquinoline. If the reaction passes through the nitrosation it cannot give a dinitro product, as the nitrosation can introduce only one nitroso group. Still more convincing is the fact the 8-hydroxy-5-nitroquinoline when heated to ca. 90°C with ca. 0.4% solution of sodium nitrite in 10% hydrochloric acid produced 5,7-dinitro-8-hydroxyquinoline with 60% yield. It is known that a mononitrophenol (and thus the 8-hydroxy-5-nitroquinoline) cannot be nitrated. Subsequently the formation of the dinitro compound is the result of nitric acid formed from NO₂ and yielding NO₂⁺ according to the scheme rationalized already – reactions (5a) and (5b) (p. 24).

The view that the nitration of phenol is inconsistent with the commonly accepted prior nitrosation scheme was also expressed by Ross and co-workers [87].

A few more examples of nitration by nitrous acid should be mentioned: the nitration of m-fluoro-N,N-dimethylaniline [88], nitration of phenothiazine-3 [89] and phenothiazine-5-oxide [90]. They also should be rationalized by formulae (5a) and (5b).

Recently Olah and associates [91], [40c] obtained S- and N-nitrito onium ion salts (31) and (32), and found them to be electrophilic nitrating agents:

\[
\begin{align*}
\text{NO}^+ & \rightarrow \begin{array}{c}
\text{ONO}^+ \\
\text{CH}_3 \quad \text{CH}_3
\end{array} \quad (31) \\
\text{NO}^+ & \rightarrow \begin{array}{c}
\text{ONO}^+ \\
\text{NO}_2
\end{array} \quad (32)
\end{align*}
\]

The addition of N₂O₃ to a double bond C= C was given in Vol. I, p. 96. Recently Hauff, Traillon and Perrot [92] described the addition of nitrosous anhydride to α, β-unsaturated ketones of the chalcone type to yield pseudonitroso-compounds, which were reduced with LiAlH₄ to a number of amines.

NITROSYL CHLORIDE

Nitrosyl chloride, NOCl (b.p. −5.5°C, m.p. −64.5°C) is the acid chloride of nitrous acid. As is known, it is evolved from 'aqua regia' together with chlorine and can be formed from NO and chlorine in the presence of charcoal as a catalyst at 40–50°C.

Nitrosyl chloride can be added to a double bond to yield dichlorides, dichlorominitro compounds and also chloronitro compounds of the type Cl–C–C–NO₂ through the secondary reaction of oxidation [114–117].

NITRATE ESTERS IN ALKALINE MEDIUM (Vol. I, p. 122)

The nitration of active methylene compounds by the action of nitrate esters under basic conditions is a general and convenient method for introducing a nitro group in α-position to the activated group. The pioneering work of Thiele [93] and Wislicenus [94] should be added to the previously (Vol. I) mentioned papers. Also the work of Wieland and associates [95] should be mentioned as producing the dipotassium salt of dinitro cyclic ketones, according to equation (33):

\[
\begin{align*}
\text{C}_2\text{H}_5\text{ONO}_2 + \text{C}_7\text{H}_5\text{OK} & \rightarrow \text{C}_7\text{H}_5\text{C}^\text{NO}_2 \quad 2\text{K}^+ \quad (33)
\end{align*}
\]

The authors claimed 75% yield, but Feuer and co-workers [96] obtained only 10% yield with the formation of tarry by-products. They also carried out a ring opening reaction which is already known [97]

\[
\begin{align*}
\left[\text{O}_3\text{N}^+\text{C}^\text{NO}_2\text{C}\text{NO}_2\right]^2^- + \text{Br}_2 & \rightarrow \text{O}_3\text{N}^+\left(\text{C}_7\text{H}_5\right)\text{Br} \quad (34)
\end{align*}
\]

Kornblum [98] reviewed earlier papers on the nitration of ketones and nitrites.

Feuer [99] carried out a considerable amount of work on nitration with nitrate esters and introduced a number of improvements. The basic features of his method consist in:

(a) using a stronger base than potassium ethoxide,
(b) using an aprotic solvent.

Thus he reacted on compounds with an active methylene group with a basic
reagent such as sodium or potassium amide and liquid ammonia as a solvent. He summarized his earlier work in a review paper [99].

A few examples should be mentioned here. Feuer and co-workers [100] nitrated cycloheptanone, hexanone and heptanone with an excess of amyl nitrate (3–3.5 eqv.) in the presence of potassium amide (3–3.5 eqv.) in liquid ammonia at −35°C obtained dinitro-dipotassium salts of the type as in equation (33) with yields of 94, 94.5 and 85% respectively. With 2 eqv. of alkyl nitrate and 1 eqv. of KNH₂ mononitration occurred with a simultaneous ring opening to α-nitrocyclohexyl ester [100, 101]:

\[
\text{CH}_3\text{COOH} \xrightarrow{\text{KNO}_2, \text{CH}_3\text{COOH}} \text{CH}_3\text{CO}_2\text{H} + \text{NO}_2\text{CH}_2\text{C}=(\text{CH}_2)_n=\text{C}O+\text{H}_2\text{O}
\]

(35)

In the case of cyclooctanone the yields were: 60% mononitropotassium salt and 21% nitroester.

While experimenting with esters of the homologues of acetic acid RCH₂COO, C₂H₅, with the same nitrating agent Feuer and Monier [102] obtained not only the nitro product RCH₂COOC₂H₅ but also nitroalkanes of the type RCH₂NO₂ sometimes with a high yield (48% when R = C₆H₅). If R = O₂NC₆H₅, the nitration does not take place due to the high acidity of the nitrated compound.

An interesting application of the method of nitration of active methylene group is the nitration of methyl group in α- and γ-picolines [103], for example:

\[
\text{N}_2\text{H}_4, \text{H}_2\text{O} \xrightarrow{\text{NO}_2\text{CH}_2\text{COOH}} \text{C}_6\text{H}_5\text{CH}_2\text{COOH} \xrightarrow{\text{NO}_2} \text{C}_6\text{H}_5\text{CH}_2\text{NO}_2
\]

(92%) (58%)

(36)

This should be rationalized (according to the author of the present book) in terms of the reactivity of tautomeric forms of α- and γ-picolines:

\[
\text{N} \begin{array}{c} \text{H} \\ \text{H} \end{array} \begin{array}{c} \text{N} \\ \text{H} \end{array} \text{H} \text{CH}_2 + \text{O}_2\text{N}^- \xrightarrow{\text{CH}_2\text{C}=(\text{CH}_2)_n=\text{C}O} \text{O}_2\text{N}^- \text{CH}_2\text{NO}_2 + \text{FC(NO}_2)_2^- \]

(37)

Sitzman, Kaplan and Angers [109] used fluorotrintrimethane [110] to nitrate the methyl group in 2,4,6-trinitrotoluene. The reaction was carried out in ca. 14% aqueous NaOH at 0–5°C followed by quenching with hydrochloric acid.

\[
\text{O}_2\text{N}^- \text{CH}_2\text{NO}_2 + \text{FC(NO}_2)_2^- \rightarrow \text{O}_2\text{N}^- \text{CH}_2\text{NO}_2 + \text{FC(NO}_2)_2^- \]

(38)

Also Feuer and Friedman [104] in a similar way obtained phenylnitromethane derivatives with a yield of 40–55% by experimenting with amyl nitrate and KNH₂ in liquid ammonia at −33°C on α- and β-substituted toluene R₅C₆H₄CH₃, on condition that the substituent is an electron attracting group, for example R = CN, SO₂C₆H₅ etc.

The same method of nitration was used to nitrate compounds with active CH groups: arylidene [105] and aldimesines [106] i.e. compounds of the structure RCH = N—NH C₆H₅ and RN = CH₂CH₃ R respectively. Nitro compounds RC = N NH C₆H₅ (yield 91%) RN = CH₂CH₃ R (yield 40–70%) respectively were obtained.

Feuer and co-workers [107] obtained nitroalkylphosphonate esters.

R CH P (O) (OR)₂ from the alkyl esters R CH₂P(O)(OR)₂ by using a modification of his method while potassium amide in liquid ammonia proved to be unsuitable to nitrate. More energetic agents, such as butyllithium in THF or Lidiisopropylamine in THF were applied at −60°C and gave a yield of 27–41%.

Recently, Petrov and co-workers also [121, 122] published a number of papers on the nitration of active methylene groups with nitrate esters.

ALIPHATIC NITRO COMPOUNDS

Tetranitromethane (TNM) continued being used as a nitrating agent. An extensive review of the properties of TNM including nitration was given by Perekalin and Al'tukhov [118]. The property of TNM as a nitrating agent is based on the fact that one of the four nitro groups of this compound can readily be split off. The properties of TNM are described in Chapter VIII.

Penczek, Jagur-Grodzinski and Szwarz [108] described the mechanism of the nitration of 1,1-diphenylethylene with tetranitromethane. As the first step an undefined charge-transfer complex (CT) is formed which dissociates into ions reacting to yield 1,1-diphenyl-2-nitroethyleno:

\[
\text{(C H}_5)_2\text{C} \rightarrow \text{CH}_2 + \text{C(NO}_2)\text{H} \rightarrow \text{(CT)} \rightarrow \text{(C H}_5)_2\text{C}^+ \text{CH}_2\text{NO}_2 + \text{(NO}_2)_2\text{C}^- \rightarrow \text{(C H}_5)_2\text{C} \rightarrow \text{CH}_2\text{NO}_2 + \text{(NO}_2)_2\text{CH} \]

(37)

Saitzman, Kaplan and Angers [109] used fluorotrintrimethane [110] to nitrate the methyl group in 2,4,6-trinitrotoluene. The reaction was carried out in ca. 14% aqueous NaOH at 0–5°C followed by quenching with hydrochloric acid.
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NITRATION AND NITRATING AGENTS

CHAPTER 2
NITRATION OF AROMATIC SYSTEMS

A considerable number of excellent monographs and review papers have been published on the nitration of aromatic systems and all references can be found therein [1–8]. Only main outlines will be given here.

It is now generally accepted that the nitration of aromatics proceeds stepwise. A stepwise process of substitution (known now as electrophilic substitution) was first suggested in 1901 by Lapworth [9] then by Pfeiffer and Wizinger [10], Melander (Vol. I, p. 38) but only later the idea was rationalized by a number of authors almost simultaneously due to the advent of spectroscopy and improvements of preparatory methods of new reagents.

A reference should be made to the paper by Nagakura and Tanaka [11] on the calculated reactivity of the nitronium ion NO$_2^+$ and aromatic hydrocarbons. They suggested the formation:

1. of an aromatic cation which is a $\pi$ complex,
2. Wheland transition state with the formation of a $\sigma$ complex.

This can be depicted at present by scheme (1):

```
H
H
\longrightarrow
\begin{array}{c}
\text{H} \\
\text{NO}_2^+
\end{array}
\longrightarrow
\begin{array}{c}
\text{H} \\
\text{NO}_2
\end{array}
\longrightarrow
\begin{array}{c}
\text{H} \\
\text{NO}_2
\end{array}
\longrightarrow
\begin{array}{c}
\text{NO}_2
\end{array}
```

A simplified energy diagram is presented in Fig. 5 based on that of Olah and associates [12, 13]. In a similar way R. D. Brown [14] considered that an electrophilic substitution begins by the formation of unstable charge–transfer complexes. R. Taylor [15] observed anomalously high and solvent dependent $\sigma/\pi$ ratios for the nitration of biphenyl and rationalized it that a $\pi$-complex between NO$_2^+$ and biphenyl is formed initially and rearranges to a more stable $\sigma$-complex at the ortho position of one of the aromatic rings of biphenyl. The final exper-

![Energy diagram](image)

FIG. 5. Simplified energy diagram of the nitration of aromatics with nitronium ion.

...mental proof for stable Wheland $\sigma$-complexes being formed as intermediates of the nitration was given by Olah and co-workers [12] when they isolated benzaltrifluoride-nitronium boron tetrafluoride

![Molecule](image)

by acting on benzaltrifluoride (C$_6$H$_5$CF$_3$) with nitronium fluoride (NO$_2$F) and boron trifluoride at $-120^\circ$ to $-100^\circ$C, a yellow coloured complex stable up to $-50^\circ$C resulted. Olah and associates [13] pointed out that the Wheland structure is not a transition state (as $\sigma$ complexes) but a relatively stable intermediate.

Recently Fujiwara and co-workers [16] found that the nitration of $N,N$-dimethyl-$p$-toluidine in 70–77% sulphuric acid proceeds by a formation of the $\sigma$ complex through the ipso-attack (on ipso-nitration see p. 50) and after that the ion is rearranged to the nitro compound (2):
NITRATION OF AROMATIC SYSTEMS

where $k_o$ and $k_m$ are the rate constants of one of the o- and m-positions respectively and $k_p$ the rate constant of the p-position. If the rate constant of one of the positions of benzene is $k_b$, the total rate constant of benzene $k_B$ is equal to $6k_b$. From this can be written:

$$\frac{k_T}{k_B} = \frac{(2k_o + 2k_m + k_p)}{6k_b} = 24.$$  (4)

The fraction of each isomer, for example the rate at the ortho position relative to the total rate of the substituted benzene can be calculated:

$$\text{fraction of o-product} = \frac{2k_o}{(2k_o + 2k_m + k_p)} = \frac{13.56}{24} = 0.565.$$  (5)

From equations (4) and (5) the rate of nitration can be calculated of a single position in toluene to that of in benzene:

$$2k_o + 2k_m + k_p = 144 \, k_b$$  (6a)

and

$$2k_o + 2k_m + k_p = \frac{2k_o}{0.565}.$$  (6b)

hence:

$$144 \, k_b = \frac{2k_o}{0.565}$$  (6c)

and

$$\frac{k_o}{k_b} = 41.$$  (6d)

The value $k_o/k_b$ is called partial rate factor in ortho substitutions and expressed now by symbol $f_o$ or $o_f$. Similarly the partial rate factors for the other positions in toluene can be calculated:

for meta positions $f_m$ or $m_f = k_m/k_b = 2.5$,

for para position $f_p$ or $p_f = k_p/k_b = 58$.

Bird and Ingold [20] have given the following comparative figures for the nitration of toluene and chlorobenzene with nitric acid in nitromethane at 25°C – Table 11.

For partial rate factors of different hydrocarbons and under different nitration conditions see [4].

The figures of the rate constants $k$ for the reactions of $m$- and $p$-substituted benzene derivatives have been taken for Hammett equation [21]:

\[ \text{INFLUENCE OF SUBSTITUENTS ON NITRATION} \]

Very important from both theoretical and practical points of view were experiments on the influence of substituents on the rate and the yield of nitration. For that purpose the method of competitive nitration was used. It was originally developed by Wibaut [17] to study the rate of nitration with nitric acid–acetic anhydride of toluene, chlorobenzene and bromobenzene in relation to benzene. The experiments established a higher rate of nitration of toluene and a lower rate of chloro- and bromobenzene:

$$C_6H_5CH_3 > C_6H_5Cl > C_6H_5H > C_6H_5Br.$$  

Thus it was stated that the methyl group activates the aromatic ring, whereas chloride and bromine deactivate it.

The method of competitive nitration was extensively used by Ingold and co-workers [18] and by a number of other authors. Very spectacular are the results of the relative rates of nitration of benzene and toluene obtained by Cohn and co-workers [19]. The nitration was carried out with nitric acid in nitromethane. They gave relative reactivities of each position of toluene:

\[ \text{Thus the relative rate of the substitution of toluene is 24.0 (benzene being postulated as 1.0).} \]

The following is an example of the calculation of 'partial rate factors'. The rate constant of the substitution of toluene $k_T$ is: $k_T = 2k_o + 2k_m + k_p$. 

\[ \text{Thus the relative rate of the substitution of toluene is 24.0 (benzene being postulated as 1.0).} \]
TABLE 11. Isomer distribution and partial rate factors of the nitration of toluene and chlorobenzene

<table>
<thead>
<tr>
<th></th>
<th>Relative rates $k/k_B$</th>
<th>% Isomer distribution</th>
<th>Partial rate factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\alpha$</td>
<td>$m$</td>
</tr>
<tr>
<td>Toluene</td>
<td>21</td>
<td>61.7</td>
<td>1.9</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.031</td>
<td>29.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>

$$\log k/k_B = \rho \sigma$$  \hspace{1cm} (9)

where:

$\rho$ is the measure of the sensitivity of the substance to ring substitution; $\rho = 1$ in benzoic acid,

$\sigma$ is characteristic to the substituent.

For nitration $\rho = -6.0$

A plot of $\log k/k_B$ against $\sigma$ was given by Stock [22] and reproduced here – Fig. 6.

A particular instance of nitration is $ipso$-nitration.

**IPSO-NITRATION**

The aromatic electrophilic substitution is usually represented by replacing a hydrogen atom with an electrophilic agent. However, it was recently shown that the electrophilic attack is not restricted to aromatic carbon bonded with hydrogen. This is the case in $ipso$-nitration where the attack occurs at a substituted aromatic ring carbon. The $ipso$-reaction was placed in focus by Perrin and Skinner [23] in 1971 and two excellent review papers appeared on the subject by Myhre [24] and by Hahn and associates [25].

A general trend of $ipso$-nitration can be depicted by scheme (10):

$$Ar - R + NO_3^+ OH^- \rightarrow ArNO_2^- + OH^-$$  \hspace{1cm} (10)

*Ipso* ion (Nitrosoenium ion)

The reaction is characterized by its reversibility. The *ipso* ion is able to further react and can be used as a valuable intermediate. By using the rate data existing in the literature [26] Myhre [24] calculated the partial rate factors of the nitration of toluene as shown in formula 1. Fischer and Wright [27] found that the nitration of toluene at low temperature with acetic acid–acetic an-
hydride–nitric acid solution in ipso position is more than twice faster than in meta position:

Thus, surprisingly enough, position I is more reactive than meta.

While reacting p-halogenotoluenes (I) with nitric acid–acetic anhydride at -40°C Fischer and co-workers [28] obtained two isomers: ortho II and para III of nitrocyclohexadienyl acetates. In the instance of X = F, the overall yield was 100% and the ratio o/p = 25/75.

On warming to -20°C both isomers were converted to 4-methyl-4-nitrocyclohexa-2,5-dienone (IV). Barnes and associates [29] reported that they prepared several 4-alkyl-4-nitrocyclohexa-2,5-dienones in good yield up to 85% by low temperature -40°C to 0°C nitration of the appropriate 4-alkylphenylacetates with 90% nitric acid or acetyl nitrate in acetic anhydride.

Nitration of a number of 4-substituted toluenes with a formation of ipso-compounds, their transformation and Hammett equation for ipso-nitration was also described [30].

The transformation of ipso-products leading to different compounds was summarized by Galley and Hahn [31]. The nitroareniunm ion cyclohexadienyl cation (V) derived from ipso attack can undergo the reactions:

1. dealklylation [32],
2. nitro group migration, followed by deprotonation [33, 34],
3. nucleophilic trapping which may be followed by HNO₂ elimination [35] (12).

The formation of acetoxy compounds VII which was originally thought to be a result of electrophilic substitution [36] has been shown to occur as an addition–elimination reaction through the ipso-attack [37]. The formation of cyclohexadienyl derivatives of type VI provide a rational explanation of some non-conventional aromatic substitutions [38].

Recently Myhre and co-workers [39, 40] described the nitration of a number of 4-alkylphenol acetates to yield 4-alkyl-4-cyclohexadienones. Reduction of these dienes with sodium borohydride gave 4-alkyl-nitrocyclohexadienols which can be converted to nitrophenols. Here an interesting intramolecular migration of a hydroxyl group was recorded [39]:

The influence of the temperature of nitration of 4-alkyl-phenol acetates was examined by the same authors [40] and simultaneously and independently by Schofield and associates [41]. The latter examined the thermal migration of the nitro group:
An interesting reaction of the nitrination of 1,2-dimethyl-4-nitrobenzene in a mixture of nitric acid with trifluoroacetic anhydride was reported by Fischer and Iyer [42]. 4,5-Dimethyl-2,4-dinitrocyclohexa-2,5-dienyl acetate was originally formed. It reacted with nucleophiles, such as $\text{NO}_2^-$ to yield eventually 1,2-dimethyl-4,5-dinitrobenzene:

(15)

One of the possible practical applications of nitro cyclohexadienyl acetate is coupling it with some aromatics to obtain diphenyl derivatives [43]:

(16)

NITRATION OF AROMATIC SYSTEMS

An interesting $\text{ipso}$-nitrination of nitrofurane derivative was reported [44]. gem-Nitro compound is formed and $\text{NO}_2$ is converted to $O = C = O$.

Some recent investigations of the nitration of heterocyclic aromatic systems, such as derivatives of pyrrol should be mentioned, as they seem to support the idea of the additional mechanism of $\text{NO}_2^+$ in the sense of $\text{ipso}$-reaction. Thus, Sonnet [45] described the reaction:

(17)

He explains it in terms of the formation of intermediate $\text{ipso}$-addition product II which is transformed into III through the migration of iodine atom (17).

The loss of the proton from III yielded eventually IV.

AROMATIC RADICAL CATION

Dynamic nuclear polarization of aromatics in the course of nitration was suggested [92] and recently Ridd and Sandal [93] gave evidence of it on the nitrination of $N,N$-dimethylaniline in sulphuric acid and stated a strong polarization of $13N$ nuclei rationalized in terms of the formation of the radical pair $[\text{ArH}^+\text{NO}_2^-]$ from the preformed radicals $\text{ArH}^+$ and $\text{NO}_2^-$.

REVERSIBILITY OF AROMATIC NITRATION

It is generally accepted that the C-nitration of the aromatic system is an irreversible process. The problem has already been discussed in Vol. I, p. 41 and the conclusion was that the C-nitration group can migrate if this meets with steric hindrance, for example, the nitro group in ortho position to adjacent group or groups. It was also substantiated by T. Urbaniński and Ostrowski (Vol. I, p. 41) but the conclusion was that the mobility of the nitro group cannot be regarded as the proof of the reversibility of the C-nitration.

However, the problem was recently revived. It was recalled that Frisch, Silverman and Bogart [46] pointed out the lability of $\alpha$-nitro group in 4-amino-3-nitroveratrole. This compound in acid condition can be transformed into 4-
NITRATION OF AROMATIC SYSTEMS

Another example of the migration of a nitro group through an ipso-nitro form was described by Myhre [33], Hahn and co-workers [34].

NITRATION UNDER THE INFLUENCE OF GAMMA RADIATION
(Vol. I, p. 126)

Several papers appeared after the pioneer work of Minc and co-workers (Vol. I, p. 126). Papers by Chernova and co-workers [53] and Sugimoto and co-workers [54] have shown that even dilute nitric acid (0.1–1.7 N) can nitrate aromatic compounds when subjected to gamma radiation from Co$^{60}$. Benzene yielded nitrobenzene and p-nitrophenol as the result of free radical reactions.

Nitric acid is decomposed by radical mechanism according to equation [55]:

\[ \text{HNO}_3 \rightarrow \text{HNO}_2^+ \rightarrow \cdot \text{OH} + \cdot \text{NO}_2^- \]

As a result of the formation of free radicals OH and NO$_2^-$ the following are reactions which can be rationalized through the diagrams (21) [54]:

\[ C_6H_6 \rightarrow C_6H_5 \cdot \text{NO}_2^- \rightarrow C_6H_5\text{NO}_2 \]

\[ C_6H_5 \cdot \text{OH} \rightarrow [C_6H_5\text{OH}] \cdot \text{OH} \rightarrow C_6H_5\text{OH} + H_2O \]

\[ C_6H_5\text{OH} \cdot \text{NO}_2^- \rightarrow C_6H_5\text{OH} + \text{NO}_3^- + \cdot \text{OH} \]

The yield of these reactions was found to be $G = 0.47–0.96$. $G$ value is the number of molecules produced by the radiation energy of 100 eV. The yield is small when $G < 1$.

Falecki, Minc and T. Urbański [56] examined the action of liquid N$_2$O$_4$ at room temperature on n-hexane when subjected to irradiation with Co$^{60}$, and obtained 1% yield of 1-nitrohexane along with a considerable amount of carboxylic acids and some nitrate esters.

Lee, Chung and Albright [57] examined the nitration of propane with nitric acid vapours at 425–430°C when propane to nitric acid ratios were 6:1 and 10:1. Gamma irradiation with 195,000 rontgens per hour from Co$^{60}$ source of propane gas did not significantly increase the yield of the nitration, except when oxygen was added to the reactants. Also the irradiation of liquid propane prior to the reaction increased the yield by 10–15% relative percentages. The products distribution (nitromethane, nitroethane, 1-nitropropane and 2-nitropropane) was unaffected by radiation.

A number of papers were dedicated to the nitration of aromatics by gamma
radiation of the aromatics present in aqueous solutions of sodium nitrate [58–61]. Brosziewicz [59] found that sodium nitrate in the presence of oxygen yielded α-nitrophenol from benzene (yield $G = 41$). Chernova and Orekhova [58] obtained nitrobenzene (yield $G = 0.2$) when irradiation was carried out in an atmosphere of nitrogen.

Nowak [62] examined the influence of radiation on the system dodecane – 30% TBP tributyl phosphate – nitric acid used as extractants of burned up nuclear fuel and found that nitro compounds were formed even at low concentrations of nitric acid. Nitroso and carbonyl compounds were also formed.

INDIRECT METHODS OF INTRODUCING A NITRO GROUP

Substitution of Sulphonic Group (Vol. I, p. 126)

In addition to the work of Marqueyrol, Carré and Lorticette (Vol. I, p. 500), and Pascal (Vol. I, p. 501), two more papers should be mentioned: by King [63], Olsen and Goldstein [64]. King pointed out the importance of the presence of phenol-2,4-disulphonic acid and $p$-phenolsulphonic acid in the sulphonated phenol, whereas Olsen and Goldstein suggested that the nitration of sulphonated phenol involves, in the first stage, the introduction of nitro groups into the aromatic ring. In the light of more recent investigations by T. Urbanśki and Leśnikiak [65a], it was found that two processes run simultaneously:

1. Introduction of a nitro group into phenol – sulphonic acid,
2. Substitution of the sulphonic group.

This was established by the chromatopolarographic method of Kemula [65b].

Also it was rationalized [65] that by reacting nitric acid on $o$- and $p$-phenolsulphonic acid coloured quinoid intermediate additions products are transformed into nitrophenol:

\[
\begin{align*}
\text{HO-SO}_2\text{H} + \text{HONO}_2 & \rightarrow \text{HO-SO}_2\text{NO}_2 + \text{H}_2\text{SO}_4 \\
\text{HO-SO}_2\text{H} + \text{HONO}_2 & \rightarrow \text{NO}_2 + \text{HO-SO}_2\text{H}
\end{align*}
\]

NITRATION OF AROMATIC SYSTEMS

Substitution of Diazo Group

The well known reaction of Sandmeyer [66a] was suggested by Waters [66b] in terms of free radical intermediates generated by electron transfer. Russell [66c] rationalized the reaction with a stable nitroaromatic anion where copper metal serves as the electron donor and cuprous ion as the electron acceptor (23):

\[
\begin{align*}
\text{ArN}_2^- + \text{Cu}^+ & \rightarrow \text{Cu}^{2+} + [\text{ArN}_2^+] \\
\text{ArN}_2^- + \text{NO}_2^- & \rightarrow \text{ArNO}_2^-
\end{align*}
\]

Substitution of Halogen (Vol. I, p. 127)

The reaction of Kornblum (Vol. I, p. 127) became a much more convenient method of making longer chain nitroalkanes.

In halogen derivatives of benzene, halogen can be replaced by the nitro group under the action of nitric acid. The first paper on the subject by Zinke [67] should be mentioned.

Substitution of $t$-Butyl Group

The nitration of 2,4,6-tri$-t$-butyl nitro benzene leads to several unexpected products as shown by Myhr and Beng [68] (24):

\[
\begin{align*}
\text{NO}_2 + \text{CH}_3\text{CH}=\text{CH}-\text{NO}_2 + \text{NO}_2 & \rightarrow \text{NO}_2^+ + \text{CH}_3\text{CH}=\text{CH}-\text{NO}_2^- \\
\text{CH}_3\text{CH}=\text{CH}-\text{NO}_2^- + \text{NO}_2 & \rightarrow \text{CH}_3\text{CH}=\text{CH}-\text{NO}_2 + \text{H}_2\text{O}
\end{align*}
\]

In addition to the replacement of $t$-butyl by the nitro group a transformation of $t$-butyl into the methyl group was established. This is rationalized in terms of the reactions:

\[
\begin{align*}
\text{NO}_2 + \text{CH}_3\text{CH}=\text{CH}-\text{NO}_2 + \text{NO}_2 & \rightarrow \text{NO}_2^+ + \text{CH}_3\text{CH}=\text{CH}-\text{NO}_2^- \\
\text{CH}_3\text{CH}=\text{CH}-\text{NO}_2^- + \text{NO}_2 & \rightarrow \text{CH}_3\text{CH}=\text{CH}-\text{NO}_2 + \text{H}_2\text{O}
\end{align*}
\]
INTRODUCING THE NITRO GROUP BY OXIDATION (Vol. I, p. 131)

Oxidation of Primary Amino Group

Oxidation of primary amino group in aromatic compounds by peroxytrifluoroacetic acid has been reported by Clarke and Steele [69]. The yield was 90%.

A much spectacular achievement was recently obtained by Nielsen and co-workers [70]. By oxidizing the primary amino group attached to a benzene ring bearing a number of nitro groups, polynitrobenzenes were obtained. Thus, by oxidizing 2,3,4,6-tetranitroaniline and pentaazotriamine they obtained penta-nitro- and hexanitrobenzene respectively. They used peroxy disulphuric acid (98% hydrogen peroxide in sulphuric acid or oleum at 25°C) as an oxidizing agent.

Further use of this oxidant to produce a number of polynitro aromatics was reported by Nielsen and co-workers [71] in their remarkable paper. The authors also reviewed work on the other oxidants used to pass from HN₃ to NO₂: Caro acid, peracetic, permaleic, m-chloroperbenzoic and perbenzoic acids. They pointed out that the power of the oxidant is proportional to the acid strength of deoxy peracid. Peracetic and m-chloroperbenzoic acids are suitable for the oxidation of aliphatic primary amines, whereas peracetic, peroxytrifluoroacetic and peroxymaleic acids are best for the oxidation of ring substituted amines. Potassium persulphate in sulphuric acid was also used successfully [71].

Oxidation of Oximes

Ifland and co-workers [72] described an original method of forming nitro derivatives of alicyclic compounds by the oxidation of oximes:

\[ \text{C=NOH} \rightarrow \text{H}_2\text{O}_2 + \text{HNO}_3 \rightarrow \text{NO}_2 \rightarrow \text{NO}_2^- + \text{H}^+ \] (26)

The first step was the bromination of the oxime with bromocuccionimidio to yield a bromonitroso compound on which the oxidation of hydrogen peroxide with nitric acid was transformed into bromonitro compound. The latter by acting with sodium borohydride furnished a secondary nitro compound with a yield of 33–80%. The method was particularly suitable for the formation of nitro derivatives of nitro cycloalkanes. The method is unsuitable for aromatic ketoximes and aldoximes. However, Barnes and Patterson [73] extended the method to aldoximes by using ozone as an oxidizing agent on gem-chloro-

NITRATION OF AROMATIC SYSTEMS

Nitroso compounds. The removal of chlorine was accomplished by palladium. Plotowska, Sas and Winiarski [74] used the Adams catalyst for the removal of chlorine.

Emmons and Paganò [75] succeeded in oxidizing oximes of alicyclic ketones with trifluoro peracetic acid to yield nitrocyclopentan and nitrocyclohexane with the yield of 60–62%. Oximes of steroids were oxidized with nitric acid–hydrogen peroxide to yield gem-dinitro derivative which under hydrogenation on platinum gave nitrostereoids with the nitro group in positions 3, 4, 6, 7 and 17 [76].

DIFFUSION CONTROL IN NITRATION

The importance of diffusion in chemical kinetics was pointed out by Eyring in 1936 [77], and subjected to a wide description by Glassstone, Laidler and Eyring [78]. The applicability of the principles of the diffusion control in various reactions and the nitration among them was recently reviewed by Ridd [79].

For reaction in solution the analysis of diffusion control is usually based on the concept of a molecular encounter. When two solute molecules come together in a solution they are effectively held within a cage of solvent molecules and make a number of collisions with each other within this cage. Such a set of repeated collisions is termed an encounter. The lifetime of each encounter is very short, 10⁻¹⁰ to 10⁻⁸ sec.

While considering the influence of the encounter rate on chemical reactivity a microscopic and macroscopic diffusion control should be mentioned. In microscopic diffusion control, the reactants exist together in a homogeneous solution and the reaction occurs on every encounter.

The term macroscopic diffusion control describes processes in which the rate of the reaction is determined by the rate of mixing of the reactant solutions.

According to Ridd [79] the clearest evidence for microscopic diffusion control in nitration comes from the kinetic studies of Coombs, Moodie and Schofield [80] with low concentration of nitric acid in 68.3% sulphuric acid as a solvent. In this medium the concentration of nitronium ions is proportional to the concentration of molecular nitric acid according to equation (27):

\[ \text{HNO}_3 + \text{H}^+ \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}. \] (27)

Since the concentration of nitronium ion is very small the rate of the nitration is determined by equation (28):

\[ \text{Rate} = k \cdot [\text{ArH}] \cdot [\text{HNO}_3]. \] (28)

Relative rate coefficients from (28) are listed in Table 12. The most interesting feature of the results according to Ridd [79] is the limiting reaction rate of
TABLE 12. Relative rates of nitrilation at 25°C by nitric acid in various media

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Sulphuric acid 68.3%</th>
<th>Perchloric acid 61.85%</th>
<th>Sulfolan 7.5%aq</th>
<th>Acetic acid 8–19%aq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Toluene</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
<td>1*</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>17</td>
<td>19</td>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>38</td>
<td>100</td>
<td>136</td>
<td></td>
</tr>
<tr>
<td>p-Xylene</td>
<td>38</td>
<td>85</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>Mesitylene</td>
<td>38</td>
<td>78</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>Anisole</td>
<td>13†</td>
<td>31</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>24</td>
<td>31</td>
<td>15.5</td>
<td>ca. 66</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>16</td>
<td>15.5</td>
<td>33</td>
<td>ca. 66</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>28</td>
<td>27</td>
<td>33</td>
<td>ca. 150</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>28</td>
<td>27</td>
<td>33</td>
<td>ca. 150</td>
</tr>
<tr>
<td>n-Naphthalon</td>
<td>28</td>
<td>27</td>
<td>33</td>
<td>ca. 150</td>
</tr>
<tr>
<td>Thiophene</td>
<td>52</td>
<td>ca. 150</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Postulated; † According to Barnett et al. [81].

the compounds being about forty times the reactivity of benzene. This limit is quite inconsistent with the predictions of the additivity principle. From the additivity principle and the partial rate factors for the nitrilation of toluene the reactivities of m-xylene and mesitylene would be expected to exceed that of benzene by factors of 400 and 16,000 respectively [80].

Thus the limiting reaction rate does not arise from the rate of formation of the electrophile NO$_2^+$ and from a general breakdown in the additivity principle. The authors [80] suggest that the limit arises from the rate-determining formation of an encounter pair ArH NO$_2^+$ between the nitronium ion and the aromatic substrate according to scheme (29):

\[
\text{NO}_2^+ + \text{ArH} \rightarrow \text{ArHNO}_2^+ \rightarrow \text{Ar}^+ + \text{NO}_2 \rightarrow \text{Product} \quad (29)
\]

A number of Swiss authors described their experiments on mass diffusion and the influence of mixing on nitrilation: Ott and Rys [82], Pfister, Rys and Zollerger [83].

Schofield and co-workers [94] determined the half life of the nitronium ion on nitrilation of benzene in the presence of phosphoric acid of the concentration 90.3 to 97.9%. The values were found to be 2 to 33 (increasing with the concentration of H$_3$PO$_4$). On the basis of these data they concluded that nitrilation with NO$_2^+$ is diffusion controlled at H$_3$PO$_4$ over 95%.

**NITRATION OF AROMATIC SYSTEMS**

Ridd [6] examined the influence of positively charged substituent on the yield of para and meta product of nitrilation. He found that $\text{–NH}_3$ deactivated the position meta much more strongly than para. Modro and Ridd [95] rationalized the influence of a positively charged substituent on the reaction of nitrilation of compounds taking into consideration the distance $r$ between two positive charges in the Wheland intermediate:

![Diagram](image)

Thus when $n = 0$ the partial rate factor $f_m$ was $0.9 \times 10^{-7}$. When $n = 2$ and 3 the values for $f_m$ were 0.13 and 0.47 and the yield of meta derivative was 19 and 5% respectively.

**SIDE REACTIONS** (Vol. I, pp. 75, 437)

Nitrating medium, that is, nitric acid or mixtures of nitric acid with sulphuric acid or other agents promoting the formation of nitronium cation, is obviously a strongly oxidizing medium, hence a number of side reactions—mainly oxidation reactions—take place during nitrilation. This was described in Vol. I (pp. 75, 437) and more recently reviewed in a number of excellent papers [84–86].

It is generally accepted that nitric dioxide and nitrous acid are catalysts of oxidation reactions. Thus Ross and Kirshen [84] came to the conclusion that the NO$_2$ evolved in the equilibrium

\[
2 \text{HNO}_3 \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2 \text{NO}_2. \quad (30)
\]

is the active oxidizer. This was based on their study of the action of nitric acid/sulphuric acid on dinitrotoluenes. The oxygen evolved in (30) is the oxidizing agent.

A striking fact was reported by Longstaff and Singer [87]. They found that formic acid cannot be oxidized by pure nitric acid alone or in mixtures with other mineral acids at 25°C, but oxidation took place in the presence of nitrous acid or NO$_2^+$ ion. Halahan and co-workers [88] studied the oxidation of several
dinitrotoluenes in the course of their nitrination and found that the relative rates of oxidation were in direct inverse relationship to their rates of nitrination.

Hanson and co-workers [85] pointed out that nitro compounds with phenolic function are the main by-products of nitrination of aromatic hydrocarbons. A number of papers by Dodak and co-workers [89] were dedicated to the formation of phenols in the course of nitrination of hydrocarbons. However, the idea of phenols being formed through the action of NO$_2^-$ ion does not seem to be feasible on the experimental grounds that the addition of urea to the nitrating mixture does not prevent the formation of phenols and the addition of sodium nitrite does not forestall the formation of nitrophenols [85]. Hanson rationalized the mechanism of formation of nitrophenols by an ipso-attack of NO$_2^-$ on hydrocarbon (31):

Phenols on nitrination can yield derivatives of p-benzoquinone, for example [90].

Gaseous products which accompany the nitration are CO and CO$_2$. Toluene on nitrination to trinitro derivative forms tetrinitromethane (the mechanism of its formation is given in the chapter dedicated to the production of trinitrotoluene). Chlorobenzene and other chlorinated aromatic hydrocarbons yield chloropiridin.

In papers dedicated to side reactions to nitrination, no attention has been paid to the formation of ammonia in the course of the reaction. It is formed from hydrogen cyanide produced by drastic decomposition of nitro compounds. This was discussed in detail in Vol. 1, pp. 76–77. The mechanism of the formation of HCN from C-nitro compounds also explains the fact that these nitro compounds yield ammonia in Kjeldahl analysis, where the substance is subjected to the action of oleum at high temperature.

A very important oxidation by-product of the nitrination of toluene to trinitrotoluene is so called 'white compounds'. It was found in the course of continuous methods of nitrination of toluene.

Its structure is dicarboxy-tetranitroaoxybenzene as shown by Joshi and Patwardhan [91]. The formation and proof of the structure will be given in the chapter on formation of trinitrotoluene.

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NITRATION OF AROMATIC SYSTEMS

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CHAPTER 3
STRUCTURES AND PHYSICO-CHEMICAL PROPERTIES OF NITRO COMPOUNDS

A few excellent reviews appeared recently on the structure of the nitro group and the spectroscopy of nitro compounds [1-5] including mass spectroscopy of nitro derivatives of arenes and heterocycles reviewed by Khmelinskii and Terentiev [145] and particularly on the C-NO₂ bond [3]. Thus only some problems related to the nitro group will be given here.

The geometry of the nitro group and electron density is depicted in the diagrammatic presentation of the molecule of nitrobenzene [3]:

FIG. 7. Geometry and electron density in nitrobenzene (according to Wigniere [3]).

Four $p_x$ electrons of oxygen and nitrogen are present in the nitro group. They are used for π bonding and belong to the three $p_x$ atomic orbitals $AO$ - one from nitrogen and one from each oxygen atom. These $AO$ combine three nitro molecular orbitals $MO$ one of which is bonding π₁, Fig. 8a, one antibonding π*₁, Fig. 8b and one non-bonding π₃, Fig. 8c.

The diagram also includes the lone-pair orbitals: two and $sp$ hybrid orbitals of the two oxygen atoms slightly split in the NO₂ group because of the interaction between the two atoms.

FIG. 8. The three atomic orbitals of the nitro group: (a) bonding, (b) antibonding, (c) non bonding (according to Jaffe and Orchin [11]).

ELECTRONIC SPECTRA OF THE NITRO GROUP

The nitro group is a chromophore. In the visible and ultraviolet absorption spectra bands π (bonding) → π* (anti-bonding) and π (non-bonding) → π* occur most frequently in conjugated molecules including aromatics [1-7].

The energy level - diagram is given in Fig. 9.

The classical example of the spectrum of a nitro compound is that of nitromethane. It consists of two broad bands; a high intensity band at $\lambda_{max} = 210$ nm (log ε = 4.2) and a weak band at $\lambda_{max} = 270$ nm (log ε = 1.3) which probably arise from π₁ → π₃ and π₂ → π₅ transitions respectively. Theoretically a third band $n$ → π* from the transition n₃ → π₅ is also present at a very low wavelength in the 'vacuum' ultraviolet and is of low intensity. Ultraviolet-spectra of nitroalkanes including polynitro compounds were described in detail by Skolztskii [6] and reviewed by Novikov et al. in their monograph [7].

Attention should be drawn to the fact that polynitro aliphatic compounds such as 1,1-dinitroalkanes and trinitromethane exhibit a cloud in aqueous solutions. This is attributed to the presence of the anion [8].

Nitroalkanes (nitroolefins) are marked by the conjugation of double bonds with those of the nitro group. They show a high intensity absorption band due to π → π* transition within the range 220-250 nm. The n → π* band is strongly overlapped there by the intense red shifted π → π* absorption band. The spectra of nitroalkenes are reviewed by Perekalin and Sopova [9] and Novikov and associates [7].

The following are data in ethanol [4] which illustrate the effect of lengthening the conjugated system in aliphatic unsaturated compounds Table (13). Kochany and Piotrowska [10] examined the ultraviolet-spectra of a number of nitroalkenes. Their π → π* were observed between 360 and 420 nm. The ultraviolet absorption spectra of nitroethylene, nitropropane and nitro methane have been taken and interpreted with the Pariser-Parr-Pople self-consistent field - MO calculation. The absorption bands π → π* are in good agreement with calculated values [11].
The nitro group in aromatic systems causes strong bathochromic shifts of all the aromatic absorption bands when the nitro group is attached immediately to the aromatic ring. This is the consequence of the fact that the nitro group is strongly electron attracting. Figure 10 shows the spectra of toluene, phenylnitromethane and nitrobenzene.

![Figure 10: Electronic spectra of phenylnitromethane and nitrobenzene](image)

When the nitro group is not directly attached to an aromatic ring as in phenylnitromethane then the \( \pi \rightarrow \pi^* \) bands are only weakly affected by the nitro group and they do not differ appreciably from that of toluene [2].

The band around 260 nm has been assigned by Nagakura and co-workers [12] as being produced in ca. 6% by the internal charge-transfer structure.

Extensive study of numerous para-substituted \( \beta \)-nitrovinyl- and \( \beta \)-nitropropenylbenzenes were carried out by Skulski and co-workers [13]. Both groups are weaker electron attracting than the nitro group.

The nitro group attached to an aromatic ring takes part, as a rule, in the conjugation of double bonds of the aromatic ring. However, a considerable devi-
An example of the steric influence on the ultraviolet-spectrum of the nitro group in non-aromatic systems was given by T. Urbas, Piotrowska, and Kiedzielski [18]. Absorption bands of the nitro group ($\pi \rightarrow \pi^*$) in 5-nitro-1,3-dioxane were found to be 279 and 283 nm respectively. This was confirmed by Eiel [19].

A few more papers should be mentioned as regards electronic spectra of aromatic nitro compounds: nitrobenzene, dinitrobenzene and trinitrobenzene [20] and the work of Barth [21] who subjected mono-, di- and tri-nitrobenzenes and toluenes to detailed spectrophotometric ultraviolet-visible studies and developed a quantitative analysis of TNT in the presence of cyclonite, octogone and waxes.

Theoretical calculation of $\sigma + \pi$ electronic structure of nitrobenzene and nitrotoluenes were carried out by LCAO method and gave a good agreement with electronic spectra and dipole moments [22]. Later the CNDO and $ab$ initio calculation for nitro-, dinitro- and trinitrobenzenes gave a very good agreement with spectral features and dipole moments [23].

**SOLVENT EFFECT**

A very prominent effect is of solvent upon the $\pi \rightarrow \pi^*$ aromatic band in aromatic nitro compounds. When given spectra of organic compounds, thought should be given to the solvent used. This is particularly important in the ultraviolet region. Schubert and Robins [24] give some figures for nitrobenzene in some common solvents – Table 16.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{max}$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>267.5</td>
</tr>
<tr>
<td>95% Ethanol</td>
<td>259.7</td>
</tr>
<tr>
<td>t-Butanol</td>
<td>257.7</td>
</tr>
<tr>
<td>t-Butyl chloride</td>
<td>257.1</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>250.1</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>261.0</td>
</tr>
<tr>
<td>Nitrobenzene in gas phase</td>
<td>239.0</td>
</tr>
</tbody>
</table>

Solvatochromic shifts in the ultraviolet-visible absorption spectra of $p$-nitrophenol and $p$-nitroaniline have been taken as measures of relative solvent affinities [25].

It should be borne in mind that the acidity and basicity of the examined compounds and the use of some solvents can influence the ionic dissociation (the equilibrium acid-base) in a more appreciable way and produce the change of $\lambda_{max}$ and the intensity, in electronic spectra.
INFRA-RED AND RAMAN SPECTROSCOPY

Numerous published papers have dealt with infra-red and Raman spectroscopy of nitro compounds. A general description is given in the monograph by Bellamy [26] and more recent reviews by Rao [27] and for non-aromatic nitro compounds by Novikov and co-authors [7].

The following are fundamental frequencies for nitromethane, the simplest nitro compound: Table 17.

<table>
<thead>
<tr>
<th>Vibrational class</th>
<th>Vibrational motion</th>
<th>Frequencies cm(^{-1})</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asymmetric</td>
<td>NO(_2) asym stretching</td>
<td>(\nu_{as}) = 1582</td>
<td>vs</td>
</tr>
<tr>
<td>Symmetric</td>
<td>NO(_2) sym stretching</td>
<td>(\nu_{s}) = 1384</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>C–N stretching</td>
<td>(\nu) = 921</td>
<td>w</td>
</tr>
<tr>
<td>Deformation</td>
<td>ONO</td>
<td>(\delta) = 647</td>
<td>m</td>
</tr>
<tr>
<td>Non-planar</td>
<td>NO(_2) bending</td>
<td>(\rho) = 559</td>
<td>w</td>
</tr>
<tr>
<td>Deformation</td>
<td>C–NO non-planar</td>
<td>(\delta) = 476</td>
<td>vv</td>
</tr>
</tbody>
</table>

Table 17: Fundamental frequencies for infra-red and Raman spectra of nitromethane according to Popov and Shlyapochnikov [28]

Popov and Shlyapochnikov [28] were able to calculate force constants in the molecule of nitromethane and Novikov [7] extended the calculation to a number of nitro compounds.

Sloven斯基 and co-workers according to [7] examined the frequencies of principal NO\(_3\) bands for primary, secondary and tertiary nitro groups (Table 18).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\nu_{as})</th>
<th>(\nu_{s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCH(_2)NO(_3)</td>
<td>1554 ± 6</td>
<td>1382 ± 6</td>
</tr>
<tr>
<td>RR'CHNO(_3)</td>
<td>1550.5 ± 2.5</td>
<td>1360 ± 3.5</td>
</tr>
<tr>
<td>RR'R''CNO(_3)</td>
<td>1538.5 ± 4.5</td>
<td>1348.5 ± 4.5</td>
</tr>
</tbody>
</table>

Table 18: Mean \(\nu\) values of frequencies of mononitro alkanes

Bellamy [26] collected information on the range of two main bands of aliphatic and aromatic nitro compounds:

- asymmetric 1650–1500 cm\(^{-1}\),
- symmetric 1350–1250 cm\(^{-1}\).

Higher nitrated alkanes, for example, di- and trinitromethane show a splitting of the bands of symmetric vibrations. Thus Levin and Legin according to [7] reported bands for dinitromethane:

\[ \text{CH}_3\text{NO}_2 \quad \delta = \text{ca.} 650\,\text{cm}^{-1} \]
\[ \text{CH}_2\text{NO}_2 \quad \delta = \text{ca.} 402\,\text{cm}^{-1} \]
\[ \text{CHNO}_2 \quad \delta = \text{ca.} 360\,\text{cm}^{-1} \]
\[ \text{CNO}_2 \quad \delta = \text{ca.} 340\,\text{cm}^{-1} \]

Buczkowski and T. Urbański [29] found the bands in 2,2-dinitropropane in both infra-red and Raman spectra: asymmetric NO\(_2\): 1588 cm\(^{-1}\), symmetric NO\(_2\): 1367, 1342 and 1258 cm\(^{-1}\).

Salts of nitro compounds show a considerable deviation from the non-ionized nitroalkanes. Novikov and co-workers [7] give the frequencies of mononitro anion as follows:

\[ \nu(C–N) = 1610–1440\,\text{cm}^{-1} \]
\[ \nu_{as}(\text{NO}_2) = 1285–1140\,\text{cm}^{-1} \]
\[ \nu_s(\text{NO}_2) < 1000\,\text{cm}^{-1} \]

Figure 11 depicts the change of frequencies when 'true' nitro compounds are transformed into their salts, according to Novikov and co-workers [7].

Conduit [14] established the influence of steric effects upon the symmetric vibrations. All dinitro derivatives of benzene and toluene which contain one nitro group strongly hindered and non-planar with the benzene ring show a splitting of the symmetric vibrations, Table 19.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\nu_{as})</th>
<th>(\nu_{s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-dinitrobenzene shows</td>
<td>1368 and 1350 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>2,3-dinitrotoluene shows</td>
<td>1364 and 1346 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>3,4-dinitrotoluene shows</td>
<td>1360 and 1346 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>2,6-dinitrotoluene shows</td>
<td>1363 and 1348 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>3,5-dinitrotoluene shows</td>
<td>1356 and 1341 cm(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

Unsymmetrically substituted trinitrotoluenes show a splitting of both bands, for example, 2,3,4-trinitrotoluene show asymmetric 1572, 1558 and symmetric vibration 1360, 1347 cm\(^{-1}\). Similar bands are given by 2,3,5-, 2,3,6- and 3,4,5-trinitrotoluenes.

The asymmetric band widths reveal a regularity. The band width of an isolated nitro group is 8–11 cm\(^{-1}\) but in the presence of some hindering groups such as CH\(_3\), C\(_2\)H\(_5\) broadens to 19 cm\(^{-1}\).

Vasányi, Holly and Fenichel [30] confirmed the finding of Conduit [14]
and added one more band of C—N stretching vibrations in nitrobenzene, nitrotoluene and nitroanisole as being 859—851 cm\(^{-1}\).

Steric influence was also referred to NO\(_2\) deformation and C—N stretching vibrations in aromatic nitro compounds by Nakamura and co-workers [31]. They examined aromatic nitro compounds containing halogen substituents in various positions. They found (as anticipated) that ortho substitution lowered NO\(_2\) bending and deformation modes owing to steric hindrance. This can be seen from Table 20.

**TABLE 20. NO\(_2\) bending and deformation vibration in substituted nitrobenzenes**

<table>
<thead>
<tr>
<th></th>
<th>NO(_2) bending cm(^{-1})</th>
<th>NO(_2) deformation cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-chloronitrobenzene</td>
<td>537</td>
<td>733</td>
</tr>
<tr>
<td>p-chloronitrobenzene</td>
<td>533</td>
<td>740</td>
</tr>
<tr>
<td>o-chloronitrobenzene</td>
<td>459</td>
<td>686</td>
</tr>
<tr>
<td>m-bromonitrobenzene</td>
<td>535</td>
<td>728</td>
</tr>
<tr>
<td>p-bromonitrobenzene</td>
<td>522</td>
<td>732</td>
</tr>
<tr>
<td>o-bromonitrobenzene</td>
<td>413</td>
<td>685</td>
</tr>
</tbody>
</table>

The C—N stretching frequencies are not much influenced by substituents and in some cases the substitution increases the frequency. Thus the C—N frequency in pentabromonitrobenzene 895 cm\(^{-1}\) is much higher than in nitrobenzene 852 cm\(^{-1}\). This is in agreement with Trotter’s conclusion [32] that the C—N bonds in nitrobenzene derivatives have no resonance interaction.

T. Urbasński and Dąbrowska [33a] examined infra-red spectra of mono-, di-, and trinitrophenols and particularly [33b] the action of solvents on hydrogen bonding between \(\alpha\)-nitro and the phenolic group. They found that polar solvents can break a hydrogen bond. This is discussed in the paragraphs on hydrogen bonds and in the description of dinitro and trinitro phenols.

The already mentioned work of Kędzierski, Piotrowska and T. Urbasński [18] on spectra of 5-nitro-1,3-oxazine revealed also the influence upon the infra-red frequency of the nitro group of its stereochemistry.

Thus the axial and equatorial NO\(_2\) groups showed the frequencies 1556–1548 cm\(^{-1}\) and 1536–1533 cm\(^{-1}\) respectively.

A very interesting attempt was made by Boisard et al. [34] to use the rapid Raman spectrometry of 10 ns to study the structure of explosives immediately preceding the decomposition produced by a shock. They obtained spectra of cyclonite after the shock and the beginning of decomposition. A displacement was observed by 11 cm\(^{-1}\) of the frequency of the bond N—NO\(_2\). This is probably due to lengthening of the bond N—N. It is expected to obtain more information in the future.

**NUCLEAR MAGNETIC RESONANCE OF NITRO COMPOUNDS**

(Vol. I, p. 179)

The application of nuclear magnetic resonance spectroscopy involves proton and nitrogen chemical shifts: \(^1\)H-NMR and \(^14\)N—NMR respectively.

**Proton Magnetic Resonance**

A number of aliphatic nitro compounds were examined by T. Urbasński, Witanowski and co-workers [35]. The nitro group, being strongly electron attracting, decreases local electron density around alkyl protons in nitroalkanes, thus shifting their resonance signals to lower magnetic fields. The effect depends on the number of nitro groups, as can be seen in the series:

\[
\begin{array}{cccc}
\text{CH}_4 & \text{CH}_3\text{NO}_2 & \text{CH}_2(\text{NO}_2)_2 & \text{CH}(\text{NO}_2)_3 \\
\delta \text{ ppm} & 0.23 & 4.28 & 6.10 & 7.52
\end{array}
\]

The negative inductive effect of the NO\(_2\) group operates significantly as far as the third carbon atom in the chain. This can be seen from \(\delta\) ppm data for 1-nitropropane to 1-nitropentane:
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{NO}_2 \\
1.05 & \quad 2.04 & \quad 4.30 \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{NO}_2 \\
1.00 & \quad 1.46 & \quad 2.03 & \quad 4.33 \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{NO}_2 \\
0.96 & \quad 1.33 & \quad 1.33 & \quad 2.03 & \quad 4.30
\end{align*}
\]

Also a difference was observed between primary and secondary nitroalkanes:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{NO}_2 & \quad 4.38 \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{NO}_2 \\
4.58
\end{align*}
\]

Proton spectra have also been used for the examination of nitroalkenes such as the isomerization of nitropropenes [36]:

\[
\begin{align*}
\text{CH}_2 = \text{CH} - \text{CH}_2 \text{NO}_2 & \quad \text{RONa} \\
\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3
\end{align*}
\]

A number of aromatic nitro compounds, derivatives of benzene, toluene, xylene, mesitylene and durene have been investigated by proton resonance spectra [37–41]. The nitro group was found to shift the aromatic proton resonance signals to low fields from that of benzene in the order \textit{ortho} > \textit{para} > \textit{meta}.

T. Urbaniński, Witanowski and associates [42] found convincing proof of the hydrogen bond between the phenolic group and the \textit{o}-nitro group through \textit{H}–NMR examination of dilute solutions of nitrophenols, 2,4-dinitrophenol and picric acid. Thus \textit{o}-nitrophenol gives \(\delta = 10.67\) ppm whereas \textit{m}– and \textit{p}-nitrophenols 8.87 and 5.14 ppm respectively.

More information on \textit{H}–NMR of nitro compounds is given by Rao in his review paper [2].

Nitrogen Magnetic Resonance

Recently less attention has been dedicated to the study of proton NMR of nitro compounds and attention has been shifted to nitrogen – \textit{\textsuperscript{14}N}–NMR.

The first systematic study of \textit{\textsuperscript{14}N}–NMR of nitroalkanes has been done by Witanowski, T. Urbaniński and Stefaniak [43]. It led to a simple spectral differentiation between nitromethane, primary, secondary and tertiary nitroalkanes.

Nitromethane was taken as a primary standard for referencing nitrogen chemical shifts.

A summary of the existing data is given in Table 21 [44–46].
The $^{14}\text{N}$ resonance spectra of aromatic nitro compounds [55] show inductive effects of substituents on the nitro group.

The nitrogen resonance spectra have been reported for the nitronium ion (NO$_2^+$) [56].

For more information and details the monographs [44–46] should be consulted.

**Electron Spin Resonance**

As is generally known, electron spin resonance reveals the presence of unpaired electrons. This is of course characteristic of free radicals and the most well known stable free radical is $\alpha, \alpha'$-diphenyl-$\beta$-picrylhydrazyl (DPPH) (I, 213). In the ESR spectrum it gives a narrow signal close to free spin value $g = 2.0036$ and is used for calibrating the magnetic field [2].

Unpaired electrons are also present in free radicals, radio-ions and in charge-transfer complexes. Among the latter a very prominent group is formed by poly-nitro compounds as acceptors and aromatic hydrocarbons mainly with condensed rings. The nature of these complexes is discussed further on p. 83. Now it should be mentioned that all CT complexes give a prominent ESR signal. More recently T. Urbański and co-workers [57] found that nitro compounds, both aliphatic and aromatic, give ESR signals if they contain a donor such as the amino group. Typical examples are nitroanilines, $m$-nitroaniline. Among aliphatic compounds 1,1-dinitropropenyl-3-dialkylamines show a strong ESR signal very likely due to the structure

\[
\begin{align*}
&\text{O}_2\text{N} \\
&\text{O}_2\text{N} \\
&\text{C} = \text{CH} \\
&\text{CH}_2 \\
&\text{+ NH(Alk)}_2
\end{align*}
\]

These compounds can be regarded as 'internal' CT complexes, or 'auto-complexes'. A number of such complexes with nitro groups were described by Freimanis et al. [141].

**Micro-wave Spectroscopy**

Micro-wave spectroscopy has been very little used for the examination of nitro compounds. Only a few data exist on the rotational constants of NO$_2$ group about the symmetry axis for nitromethane [2, 7] and some derivatives of nitromethane [7].

**Magnetic and Electric Birefringance**

Magnetic birefringence (Cotton–Mount effect) and electric birefringence (Kerr effect) of nitrobenzene, $p$-dinitrobenzene and 1,3,5-trinitrobenzene was recently examined by Battaglia and Ritchie [58] at 25°C and 633 nm.

The following were figures for $\Delta\chi$ molecular magnetic anisotropy:

- benzene $= 64$
- nitrobenzene $= 96$
- $p$-dinitrobenzene $= 151$
- 1,3,5-trinitrobenzene $= 147$

**Optical Rotatory Dispersion**

Optical rotatory dispersion and circular dichroism of compounds with a nitro group as a chromophore was described by Djerassi and co-workers [59].


Malinowski and T. Urbański [60] advanced a suggestion that a hydrogen bond can exist between the nitro and the hydroxy group in $\beta$-nitro alcohols. This was based on the experimental fact that 2-nitropropane-1,3-diol (I) formed cyclic acetals, 1,3-dioxane derivatives (II) and ketals with great difficulty, while on the contrary the triol 2-hydroxymethyl-2-nitro-propane-1,3-diol (III) forms the corresponding cyclic acetal (IV) and ketal with great ease.

These facts were rationalized in terms of the hydrogen bonds between the nitro and the hydroxy groups: Ia and IIIa

\[
\begin{align*}
\text{H} & \text{CH}_2\text{OH} & \text{RCHO} & \text{H} & \text{CH}_2\text{OH} & \text{CH}_2\text{OH} \\
\text{O} & \text{N} & \text{CH}_3 & \text{O} & \text{Alk} & \text{O} \\
\text{H} & \text{CH}_2 & \text{O} & \text{CHR} \\
\text{H} & \text{CH}_2 & \text{O} & \text{CHR} \\
\end{align*}
\]

(2a)

\[
\begin{align*}
\text{HOC}_2\text{H}_2\text{OH} & \text{RCHO} & \text{HOC}_2\text{H}_2\text{OH} & \text{CH}_2\text{OH} \\
\text{O} & \text{N} & \text{CH}_3 & \text{O} & \text{CH}_2 & \text{OH} \\
\text{HO} & \text{CH}_2 & \text{O} & \text{CHR} \\
\text{HO} & \text{CH}_2 & \text{O} & \text{CHR} \\
\end{align*}
\]

(2b)

\[
\begin{align*}
\text{H} & \text{CH}_2\text{OH} & \text{O} \\
\text{O} & \text{N} & \text{CH}_3 \\
\text{H} & \text{CH}_2 & \text{O} \\
\text{H} & \text{CH}_2 & \text{O} \\
\end{align*}
\]

Ia

\[
\begin{align*}
\text{H} & \text{CH}_2\text{OH} & \text{O} \\
\text{O} & \text{N} & \text{CH}_3 \\
\text{H} & \text{CH}_2 & \text{O} \\
\text{H} & \text{CH}_2 & \text{O} \\
\end{align*}
\]

IIIa
The presence of the intramolecular hydrogen bond between NO₂ and OH groups or NO₂ and NH groups was later confirmed by the author [61] on the basis of ultraviolet spectra of ca. 50 β-nitroalcohols, diols and β-aminomethyl-β-nitroalcohols and the comparison of their spectra with those of nitroalkanes. The conclusion of T. Urbánski was questioned by Ungnad and Kissinger [62] who admitted only a very weak hydrogen bond between β-nitroalcohol and chloroform used as a solvent. Schleyer and co-workers [63] have criticized the conclusions of Ungnad and Kissinger thus supporting the view of T. Urbánski. Also Krueger and Mettee [64] confirmed the existence of the discussed hydrogen bonding. Two earlier papers [65, 66] referred to infra-red spectra of β-aminoalcohols and the authors rationalized the results in terms of the hydrogen bond between NO₂ and OH groups.

Final proof of the existence of the hydrogen bonding between NO₂ and OH groups in β-nitroalcohols was given by further experiments of T. Urbánski and co-workers. The following methods were used in their experiments: measurement and calculation of dipole moments [67], ultraviolet, infra-red (including overtone region), NMR spectroscopy [68a, b].

A number of nitrophenols, nitronalines, nitronaphthols etc. have been examined through ultraviolet spectroscopy, the point of acid-base equilibria, solute-solvent effect and internal hydrogen bonding and partly reviewed [2, 69, 70] Lutskii and Gorokhova [71] have calculated and interpreted the electronic spectra of nitrophenols by a LCAO SCF MO method in Pariser–Parr–Pople approximation. On scrutinizing the experimental electronic spectra (both ultraviolet and visible) of nitrophenols in different solvents (cyclohexane, absolute and 20% aqueous methanol) Skulski [72] has come to the conclusion that o-nitrophenol is strongly chelated in cyclohexane solution, but not appreciably in methanolic and probably not at all in aqueous methanol. Also by measuring dipole moments in dioxane and benzene he obtained [73] valuable information on the stability of the intramolecular hydrogen bond to the action of dioxane and other active solvents. The effect was examined [74] of surfactants on the visible spectra of nitrophenols in 3% aqueous ethanol and interactions between the nitrophenols and micelles. The electron absorption spectra of dinitronalines have been discussed [75] in terms of energy and intensity of lowest energy absorptions, the intramolecular hydrogen bond extension of the π electron conjugated system etc.

T. Urbánski and Dąbrowska [33b] examined infra-red spectra of several mono-, di- and trinitrophenols and established the influence of the solvent on the hydrogen bond between the o-nitro and phenolic groups. It was found that polar solvents can break the intramolecular hydrogen bond.

Reeves and co-workers [76] correlated the change in the chemical shift of NMR spectra caused by formation of an intramolecular hydrogen bond in o-substituted phenols including o-nitrophenol, 2,4-dinitrophenol, 1-nitro-2-naphthol, 2,4-dinitro-1-naphthol etc.

The infra-red data [30a] refers to solutions in carbon tetrachloride. They show a considerable difference between ortho nitro phenols and m- and parainitro derivatives.

A number of authors [78–81] examined the intramolecular hydrogen bonds between NO₂ and NH₂ in o-nitroaniline.

**TABLE 22. Chemical shifts δOH ppm and infra-red frequencies in cm⁻¹ for nitrophenols**

<table>
<thead>
<tr>
<th>Compound</th>
<th>δOH ppm</th>
<th>IR bands cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Nitrophenol</td>
<td>10.67</td>
<td>3250</td>
</tr>
<tr>
<td>2,4-Dinitrophenol</td>
<td>11.12</td>
<td>3210</td>
</tr>
<tr>
<td>2,5-Dinitrophenol</td>
<td>10.76</td>
<td>3270</td>
</tr>
<tr>
<td>2,6-Dinitrophenol</td>
<td>11.41</td>
<td>3170</td>
</tr>
<tr>
<td>Picric acid</td>
<td>9.16</td>
<td>3100</td>
</tr>
<tr>
<td>m-Nitrophenol</td>
<td>4.87</td>
<td>3615</td>
</tr>
<tr>
<td>p-Nitrophenol</td>
<td>5.14</td>
<td>3615</td>
</tr>
</tbody>
</table>


As pointed out in Vol. I, trinitrobenzene and its derivatives possess the ability to form addition compounds, especially with aromatic hydrocarbons composed of condensed rings, such as naphthalene, anthracene, phenanthrene, acenaphthene etc. Addition compounds of picric acid have been known since 1858 [82] and those of sym-trinitrobenzene since 1882 [83]. Complexes of sym-trinitro-benzene with aromatic amines were also described in 1882 [84].

Currently problems connected with CT or EDA complexes form one of the topics of physical–organic chemistry. A few excellent monographs and review articles have appeared [85–90]. After the remarkable work of Briegleb, Weiss, Brackman and other authors (Vol. I, p. 220) the most important treatment of the nature of bonds keeping donor and acceptor together, was given by Mulliken [91] on the basis of quantum mechanical assumption of the electron transfer from the donor to the acceptor.

Here are the main points deduced by Mulliken. The electronic ground state wave functions of the complex ΨN are a combination of a 'no-bond' wave
function $\psi_0$ and one or more 'dative bond' functions $\psi_1, \psi_2$ etc.: 

$$\psi_N = a\psi_0 + b\psi_1 + c\psi_2 + \ldots,$$

where $a, b$ and $c$ are coefficients with $a > b > c$.

The no-bond function includes the electronic energy of the component molecules, plus terms representing the effect of dipole interactions, dispersion forces, hydrogen bonding and other intermolecular forces. The dative bond functions represent states where an electron has been transferred from the donor molecule to the acceptor, introducing electrostatic interactions and forming a weak covalent link between the resulting radical ions:

$$\begin{align*}
A^- + D^+ \xrightarrow{\text{EDA Complex}} AD \\
\downarrow \text{hr} \\
A^+ + D^- \xrightarrow{\text{EDA Complex}} AD
\end{align*}$$

Excited states with a dative structure as the main contributor, have the same form with the coefficients varied to give predominance to the dative bond contribution.

The Mulliken treatment provided the theoretical basis for interpretation of spectroscopic and formation constant data and initiated research on semiconductivity and magnetic properties of molecular complexes.

According to McGlynn [85] and Briegleb [87] the complex addition compounds should be called 'EDA-complexes' for Electron–Donor–Acceptor–Complexes and the term 'Charge–Transfer' should be reserved for the absorption band characterizing the complex. The symbol hν_{CT} is given to the energy of the 'charge–transfer band' characterizing the complex. Thus the term 'Charge–Transfer', according to Briegleb, is reserved in this particular instance.

According to Dewar and Lepley [92] the following are CT-bands of complexes of sym-trinitrobenzene and hydrocarbons (Table 23). Also they calculated the energy $E_m$ of the highest occupied MO.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>CT-band $\lambda$ nm</th>
<th>$E_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>284</td>
<td>1.000</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>365</td>
<td>0.618</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>353</td>
<td>0.637</td>
</tr>
<tr>
<td>Anthracene</td>
<td>460</td>
<td>0.414</td>
</tr>
<tr>
<td>Naphthacene</td>
<td>520</td>
<td>0.294</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>370</td>
<td>0.605</td>
</tr>
</tbody>
</table>

The electron affinity of trinitrobenzene which characterizes the ability of the compound to form charge–transfer complexes is not very high and is estimated to be equal to 0.6 eV, whereas stronger electron acceptors such as tetracyanoethylene and chloranil show values of 1.6 and 1.35 eV respectively [86].

The Mulliken treatment provided a simple classification of molecular complexes according to the type of orbitals involved in charge–transfer [93]. The complexes of nitro compounds with hydrocarbons belong to $\pi$–$\pi$ complexes i.e. $\pi$-donors and $\pi$-acceptors.

For maximum charge–transfer interaction the relative orientations of the two molecules must provide maximum overlap of the filled donor orbital and the vacant acceptor orbital. This is known as Mulliken's 'Overlap and Orientation principle' [94].

X-ray examination of $\pi$–$\pi$ molecular complexes shows that the crystals of the complexes are formed from stacks of alternate donor and acceptor molecules in agreement with theoretical analysis of Mulliken.

This was described by a number of authors (Vol. I) for example, Powell and Huse, Rapson, Sauder and Stewart and Wallwork [95] subjected a few complexes of $s$-trinitrobenzene to X-ray analysis. Wallwork concluded that the structure can be summarized and plane-to-plane packing of the components. The relative dispositions of the components are such as to allow the maximum degree of overlap between their molecular $\pi$-orbitals. Figure 12 gives a diagrammatic presentation of the complexes of sym-trinitrobenzene with naphthalene, and Fig. 13 – with anthracene [96].

**FIG. 12. CT–complex of sym-trinitrobenzene with naphthalene (according to Brown, Wallwork and Wilson [96]).**
FIG. 13. CT - complex of sym-trinitrobenzene with naphthalene (according to Brown, Wallwork and Wilson [96].)

Particular cases of EDA complexes are those of nitrophenols and bases, for example, dinitrophenols with aniline described by Zeegers-Huyssens [96a], mono-, di-, and trinitrophenol with hexamethylenetetramine of Vanganescu and Ionescu [96b]. The complexes show the presence of hydrogen bonds in addition to the existence of π-π complexes. High nitrated aromatic compounds have been used for the identification of multi-ring aromatic hydrocarbons and various amines. Thus Willstätter and M. Fischer [97] used styphnic acid, an acceptor to detect porphyrins, and later a few papers were added on similar detection of chlorophyll and other porphyrin-like molecules with 1,3,5-trinitrobenzene and 2,4,7-trinitrofluorenone [98–100]. Some alkaloids and drugs can be detected and subjected to quantitative analysis by measuring the intensity of the charge-transfer band produced in the spectrum of complexes with 1,3,5-trinitrobenzene or picric acid [101, 102].

Also highly nitrated compounds can be detected and identified by means of donors, such as hydrocarbons. Their identification was suggested by the method of thin-layer chromatography [103]. A method of rapid detection of explosives such as TNT, TNB, Picryl chloride, m-DNB, Tetrayl in the form of charge-transfer complexes with aromatic amines, such as aniline, dimethylaniline, toluidines, anisidines, naphthylamines, benzidine etc. was developed by Dwivedy et al. [104]. The authors used for identification thin-layer chromatography establishing \( R_f \) values for model complexes.

An original approach to the stereostructure of complexes on the basis of infra-red spectra was given by Severin [105]. He examined the complexes of sym-trinitrobenzene with phloroglucinol or nitrophloroglucinol and of picric acid with phloroglucinol and came to the conclusion that the approach of the acceptor molecule can be sterically hindered if the donor molecule is non-planar. Hence complex formation is difficult as the non-planarity increases the distance between the components. For example, trans-stilbene forms a picrate, but the cis-isomer does not. The planar molecule of 2-phenylnaphthalene also forms a picrate, while its non-planar isomer, 1-phenylnaphthalene, fails to do so.

A number of papers have appeared which describe absorption spectra of charge-transfer complexes in solutions without however isolating the actual complexes.

Thus Foster and Thomson [106] examined complexes of \( p \)-phenylene-
diamine and its \( N \)-methyl derivatives, and bis(dimethyamine) derivatives, of diphenyl and stilbene with 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, 1,3- and 1,4-dinitrobenzene and 1,3,5-trinitrobenzene. Similarly Waclawek and Hurvic [107] described complexes formed in solutions by 1,3,5-trinitrobenzene with pyridine, picolines, aminopyridines and cyanopyridines. They also used dielectric titration, refractive index and density measurements to establish the formation of the complexes. Aliphatic nitro compounds can also be electron acceptors. Thus Lewańska and Lipczynska [108] established the existence of a complex of tetranitrobutane with dimethylaniline in molar proportion 1:1 by measuring electronic spectrum of solutions with different proportions of the donor and acceptor, according to the method of constant dilutions of Job [109].

Hammond and Burkardt [142] described the electron accepting properties of tetranitromethane. They came to the conclusion that tetranitromethane interacts only weakly with aromatic hydrocarbons and does not form isolable complexes.

Hetnarski [110] in a number of papers has described a new donor – ferrocene. It gives EDA complexes with sym-trinitrobenzene, picric acid, picryl chloride while using Job's method [109] to establish the ratio between the acceptor and donor.

More recently T. Urbaniński, Hetnarski and Pofudnikiewicz [111] established that nitrate esters form EDA complexes with a strong donor – \( N,N' \)-tetramethyl-p-phenylenediamine. Particularly interesting are nitrate esters with five or six \( \text{ONO}_2 \) groups, such as \( \text{D-arabitol pentanitrate, D-mannitol and D-sorbitol hexanitrate} \). A particular stereochemistry of such complexes was suggested with nitrate esters coiled in pseudo-rings. Complexes of erythritol tetranitrate with biologically important pyrimidine and purine bases were examined by T. Urbaniński, Waclawek and Pofudnikiewicz [112]. The ratio donor:acceptor was established by examining NMR spectra.

T. Urbaniński, Krasiejko and Pofudnikiewicz [113] suggested using \( N,N' \)-tetramethyl-p-phenylenediamine to detect nitrate esters: a magenta colour makes the detection easy.

Like most EDA complexes, those of sym-trinitrobenzene, for example, with \( N,N \)-dimethylaniline show a semiconducting property [114].

**X-Ray Structure**

A considerable number of X-ray examinations of nitro compounds have been done over the last two decades. They will be given in the description of particular compounds. However, the following are reviews which should be mentioned: X-ray analysis of aliphatic nitro compounds, nitrate esters and nitramines were described by Novikov and co-workers [7], nitramines by G. F. Wright [115], polynitroaromatic addition compounds by Hall and Poranski [116]. The X-ray
THERMOCHEMISTRY

Thermochemical data of explosives will be given in the description of particular compounds. General problems of thermochemistry of nitro compounds was given in the monograph by Lebedev, Miroshnichenko and Knobel [117]. In recent years a considerable number of contributions have been given by Pepekin and co-workers [118] on such problems as the enthalpy of formation of nitro and nitramino compounds and nitrates esters and enthalpy of detonation. Also Pepekin and co-workers [119] contributed considerably to the solution of problems of the energy of dissociation of the bond C–N.

A very important review article on thermal analysis of explosives was given by Collins and Haws [140]. The results of thermal analysis will be described in properties of particular compounds.

MASS SPECTROGRAPHY

A number of papers have appeared on the fragmentation of nitro compounds by mass spectroscopy. They were reviewed by Beynon [120] and recently by Khmel'nitskii and Terentiev [121] therefore only main outlines will be given here. Three main molecular ions have been found: M–O⁺, M–NO⁺ and M–NO₂⁺. The first one was present in a small yield 1–2%. There are two schools of thought, as far as the mechanism of rearrangement of the molecular ion prior to its dissociation. According to some authors [122] the molecular nitro-ion is first rearranged into a nitrite. McLafferty and Bursely [123] found a marked distinction between compounds having meta and para positions of the nitro group relative to other substituents.

Beynon, Saunders and Williams [122], Fields, Meyerson and co-workers [124] compared mass-spectra of isomeric dinitrobenzenes (Table 24) and came to the conclusion that meta and para isomers give similar fragments, whereas ortho differ considerably.

The fragmentation of negatively charged molecular ions of mono- and dinitrobenzenes does not differ from that of the positive ions [125, 126].

Meyerson et al. [127] examined the fragmentation of sym-trinitrobenzene. A much more complicated picture appeared from the spectrum with one particular feature: the most prominent is the elimination of NO₂ as the first step of the fragmentation.

Experiments with isomeric nitrotoluenes show that the fragmentation of meta- and para-isomers is similar to that of nitrobenzene [122].

Both isomers are characterized by the high presence, ca. 70%, of the molecular ion, while nitrobenzene shows 49% and o-nitrotoluene only 25%. The spectrum of o-nitrotoluene shows a high peak with a mass of 120 which is not present in meta- and para-isomers. According to Beynon et al. [122] it corresponds to the ion M–OH⁺ with the structure according to scheme (5).

\[
\text{O} \quad \text{N} \quad \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array}
\]

(4)

\[
\text{O} \quad \text{N} \quad \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array}
\]

(5)

The ion 20 is losing CO to be transformed probably into the azatropolium ion 92. The mass spectra of m- and p-nitrotoluenes yielded only M–NO⁺ and M–NO₂⁺ ions. Nitroxylenes and polynitrotoluenes yielded ions M–OH⁺ [122].

Mass spectrum of TNT yielded ion (M+H)–OH₂⁺ [128].

The peak (M–OH)⁺ is present in the mass spectra of all three nitroanilines [122, 129].

Benoit and Holmes [130] examined a number of o-nitro compounds, such as o-nitroanisol, o-nitrobenzoic acid, o-nitrobenzamide etc. to study the ortho-effect. They came to the conclusion that two ortho-effects exist. One is marked by the migration of hydrogen from one substituent to another. The second effect consists in migration of an atom or a group of atoms from the substituent of a vacant place in ortho position. Particular attention is now being paid to elucidating different features of the ortho effect. Among interesting facts a similar effect was recorded in peri-position in 1-nitronaphthalene [131, 132].

The following mechanism was rationalized by labelling position 8 of the naphthalene ring with 13C [133]:

<table>
<thead>
<tr>
<th>Ions</th>
<th>ortho</th>
<th>Isomers of DNB</th>
<th>meta</th>
<th>para</th>
</tr>
</thead>
<tbody>
<tr>
<td>M⁺</td>
<td>6.98</td>
<td>11.00</td>
<td>10.30</td>
<td></td>
</tr>
<tr>
<td>M–O⁺</td>
<td>0.24</td>
<td>0.63</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>M–NO⁺</td>
<td>0.07</td>
<td>0.21</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>M–NO₂⁺</td>
<td>0.41</td>
<td>4.76</td>
<td>4.12</td>
<td></td>
</tr>
<tr>
<td>M–NO₃⁺</td>
<td>0.03</td>
<td>0.04</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>M(NO)₂O₂⁺</td>
<td>1.66</td>
<td>5.82</td>
<td>3.64</td>
<td></td>
</tr>
<tr>
<td>M(NO)₂O₂⁺</td>
<td>3.94</td>
<td>11.20</td>
<td>9.18</td>
<td></td>
</tr>
<tr>
<td>M–NO₃⁺+HNO₂⁺</td>
<td>2.03</td>
<td>10.80</td>
<td>11.30</td>
<td></td>
</tr>
<tr>
<td>NO⁺</td>
<td>26.70</td>
<td>17.20</td>
<td>21.30</td>
<td></td>
</tr>
</tbody>
</table>
Nitroalkanes: nitromethane, nitroethane and nitropropanes were examined by Collin [134].

**ELECTROCHEMICAL PROPERTIES**

**Galvanic Cells**

Nitro compounds and metals as reducing agents can form galvanic cells [134]. Particularly interesting are results with 2-nitrobenzene [135]. The system 2-nitrobenzene and magnesium gave a rather high yield of 160 wh/kg through the reaction:

\[
\text{RNO}_2 + 4\text{Mg} + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{RNNH}_2 + 4\text{Mg}^2+ + 2\text{H}_2\text{O}
\]

in a neutral medium.

**Photoconductivity.** It has been found that the conductivity of nitrobenzene increases when irradiated with ultraviolet light [136]. This will be discussed in the paragraph on the photochemistry of nitro compounds.

**Lasers.** Chelates of europium with some aromatic nitro compounds with phenolic and aldehydic function can be used to produce laser beams [137].

**BIOLOGICAL ACTIVITY OF NITRO COMPOUNDS**

Nitro compounds possess strong biological activity. Moncieriff [138] has given a first monograph of such properties as sweet and bitter or pungent taste, musk odour. A review by Venulet and Van Etten [139] described the biochemistry and pharmacology of nitro compounds and included a description of antibiotics containing the nitro group such as naturally occurring nitro compounds, toxic substances with their practical use as insecticides, molluscidcides, fungicides and herbicides. A separate chapter is dedicated to the toxicity of commercially important nitro compounds.

Reactive aromatic nitro compounds were successfully used as antitumour agents. Such is chlorodinitrobenzene [143] and some 2,4-dinitrophenyl derivatives, such as 5-aziridino-2,4-dinitrobenzamide [144].

**PHYSICO-CHEMICAL PROPERTIES OF NITRO COMPOUNDS**

The toxicity of nitro compounds was discussed in Vol. I in the description of particular compounds. This method will be followed in the present volume: any novel information on the toxicity of compounds, were available, will be given in the description of the compounds.

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133. T. H. KINSTLE, R. A. ALTHAUSS, J. G. STAM and J. BECKER, according to D. H.
CHAPTER 4

REACTIVITY OF AROMATIC NITRO COMPOUNDS

(Vol. I, p. 192)

A great number of reactions of nitro compounds were described in the well-known monograph edited by H. Feuer which forms a part of the monographs edited by S. Patai [1]. Reference will therefore be made to these and some other books and only the most important and more recent papers will be given here.

SUBSTITUTION (HETEROLYTIC AND HOMOLYTIC)

It is well known that heterolytic substitutions occur through 'electrophilic' and 'nucleophilic' attacks produced by cation $E^+$ ('electrophile') and anion $Nu^-$ (nucleophile) respectively. Homolytic substitutions involve the action of uncharged free radicals.

In electrophilic and nucleophilic substitution of aromatic nitro compounds different directing effects are dictated by electron distribution. The simple case of nitrobenzene $\pi$-electron distribution is given in diagram Fig. 14a [2], and the free valence of aromatic cations of nitrobenzene $C_6H_5NO_2^+$ is given in Fig. 14b [3].

Both diagrams show that electrophilic substitution should occur mainly in meta position, whereas the nucleophilic one should yield mainly ortho and para substituted products.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig14.png}
\caption{Nitrobenzene: (a) $\pi$-electron density (see also Fig. 7); (b) free valencies; (c) localization energy.}
\end{figure}

Another approach consists of the calculation of relative rates for substitution from the atom localization energies of Wheland. It gives a more qualitative insight. However, in the instance of homolytic reactions at 80°C the relative reaction rates are better approaching the experimental results (Fig. 14c).

ELECTROPHILIC SUBSTITUTION

A few monographs have been dedicated to the description of electrophilic substitution of nitro compounds in general [2, 5–7] and a review has been published on the subject [8]. The mechanism of nitration was discussed in Chapter II. Nitrination with $NO_2^+$ containing agents belongs to the mechanism SE 2 as already mentioned in Chapter II.

Diagrams – Fig. 14a–c – shows that substitution can occur not only in meta, but also in ortho and para positions. According to the diagrams it should be expected that the proportion of ortho isomer should be superior to that of the $p$-dinitrobenzene. Indeed this is in agreement with the experiment: the proportion of $o$-dinitrobenzene is larger and at high temperature of nitration much larger than that of $p$-dinitrobenzene (Vol. I, p. 243, Tables 38 and 39).

Also in the homologues of benzene the influence of alkyl groups should not be neglected, their directing influence being ortho and para.

NUCLEOPHILIC ADDITION AND SUBSTITUTION (Vol. I, p. 197)

One of the characteristic features of aromatic nitro compounds, particularly those with two or more nitro groups is their ability to react with bases and in many instances the reaction is accompanied by an intense colour. The colour had caught the attention of chemists by the late nineteenth century and initiated a considerable amount of research on the nature of the formed substances. Thus considerable literature appeared on reactions known as Janovsky or Jackson–Meisenheimer or Meisenheimer reactions which are discussed later. They are nucleophilic reactions and are not only of theoretical but also of practical importance. Thus the Janovsky reaction became an important analytical method, and reactions of di- and trinitrobenzene and their homologues with bases, are of great importance in the problem of the safety of manufacture and of the stability of these nitro compounds.

The reactions of nitro compounds with bases are nucleophilic reactions and recently have received much attention. Numerous monographs include chapters on nucleophilic substitution of nitro compounds and review articles have been published. Such are the excellent reviews by de Boer and Dirkx [9], Hall and Poranski [10]. References in [9] are brought up to 1966, and it seems appropriate to complete the list of review articles by mentioning the later review papers: Challis [11], Buncel and co-workers [12], Miller [13], Pietra [14], Buck [15], Crampton [16], Strauss [17], Bernasconi [18], Sekiguchi and Yuki [19].
suggested the same formula for potassium salt. Jackson and Earle [27] supplied analytical proof of the structure. Jackson–Meisenheimer compounds are now recognized as \( \sigma \)-complexes. Currently their mode of writing is given in Fig. 15b, and the formation presented in diagram (1):

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{OC}_2\text{H}_5 \quad \text{NO}_2 \\
\text{O}_2\text{N} & \quad \text{OC}_2\text{H}_5 \quad \text{NO}_2 \\
\text{C}_2\text{H}_5\text{O}^- & \quad \text{H}^+ \\
\end{align*}
\]

(1)

This can be classified as a SNAr mechanism.

Attention should be drawn to the fact that the reaction is reversible and under the action of an acid, the starting nitro compound is formed.

Naphthalene analogues of Jackson–Meisenheimer complexes were described [28, 42] and 9-anthracene derivative has already been discussed by Meisenheimer [26].

A few heterocyclic Jackson–Meisenheimer complexes were recorded, viz.: I [29]; II [30]. Vickery [31a] rationalized the structure of the complex (III) obtained in 1883 by Lobry de Bruin [31b] while acting with potassium cyanide on n-dinitrobenzene.

Similar \( \sigma \)-complexes (IV) can be obtained by acting with \( \text{CH}_3\text{O}^- \) on picramide and its derivatives [32–34, 37].

Gold and Rochester [32] and Pollitt and Saunders [35] examined electronic spectra, Dyall [36] infra-red spectra of \( \sigma \)-complexes. NMR spectra were studied in the pioneering work of Crampton and Gold [37], the works were reviewed by Hall and Poranski [10] and Crampton [38]. More recent works were done by Norris [39] and Epitots [40]. Kinetic studies of \( \sigma \)-complexes were made by a number of authors [41, 42] and thermodynamic control by Fendler and co-workers [43]. Bernasconi [18] reviewed the work on kinetic behaviour of \( \sigma \)-complexes.

In their recent work Crampton and Gibson [33] used a modern technique of
stopped flow and T-jump spectrometry in their study of the reaction of \(N\)-alkyl picramide and \(\text{CH}_3\text{O}^-\).

All of these works confirmed in principle the structure of Jackson–Meisenheimer complexes. It was also supported by X-ray analysis by Simonetta and co-workers [44] and Ueda and co-workers [45] with one correction: the length of the bonds between carbon atoms 2–3 (and 5–6) is relatively short (1.35 \(\text{Å}\)), close to the length of the olefinic bond. Subsequently the original formula – Fig. 15a – with quinoid structure should be preferred. Crompton and Gold [37b] arrived at a similar conclusion.

However, Heilbronner, Zollinger and co-workers [46] came to the conclusion that the existing formula of Jackson–Meisenheimer complexes is insufficiently exact in the light of the present theories of molecular orbital calculation. By using HMO method a shifting of \(\pi\)-electrons by the nitro groups should be considered. Thus the reaction of trinitroanisol with the methoxy anion can be depicted by diagram (2):

\[
\text{NO}_3^+ \xrightarrow{\text{CH}_3\text{O}^-} \text{NO}_2^+ \xrightarrow{\text{OCH}_3} \text{CH}_3\text{O}^- \xrightarrow{\text{OCH}_3} \text{NO}_2^+ \xrightarrow{\text{OH}^-} \text{NO}_3^+ \xrightarrow{15.8 \text{ M KOH/60°C/N}_2} \text{OH}^- \xrightarrow{\text{N}_2} \text{NO}_2^+ \xrightarrow{\text{CO}_2} \text{OCH}_3 \xrightarrow{15.8 \text{ M KOH/60°C/N}_2} \text{OH}^- \xrightarrow{\text{N}_2} \text{NO}_2^+ \xrightarrow{\text{CO}_2} \text{OCH}_3
\]

Practical Significance and Application of Jackson–Meisenheimer Reaction

The Jackson–Meisenheimer reaction is of considerable theoretical and practical significance for analytical and preparatory work in the laboratory and in industry. The latter refers to replacing halogen or allyloxy groups in nitroaromatics by acting with bases and it received full attention in Vol. I (pp. 197, 453, 461, 467, 484, 545, 547, 549, 559, 563, 571) and Vol. III (pp. 47, 61).

The reaction should be rationalized in terms of the formation of intermediate \(\sigma\)-complexes [21, 42]:

A free-energy contour diagram of reaction (5a) is given in a review paper [18].

Fluoro-2,4-dinitrobenzene is extensively used in the determination of \(N\)-terminal groups in peptides. A number of other nitro compounds reacting with
nucleophiles are in use in biochemical work. A very wide description of the structure, kinetic properties and equilibrium of Jackson–Meisenheimer complexes was recently given by Terrier [223]. For review see [50].

J. Urbalski [51] developed a nucleophilic colour reaction of dinitroarenesulphonic esters with primary and secondary amines and quaternary ammonium hydroxides. The reaction was originally used to determine small quantities of epoxy groups in polymers. The coloured products possess the structure of $\sigma$-complexes, for example V:

\[
\begin{align*}
\text{V} & \\
\text{VI} & 
\end{align*}
\]

Jackson–Meisenheimer complexes can serve in obtaining nitro derivatives of diphenyl. An original approach to this type of reaction was given by Wennerström [52]. He reacted a derivative of phenylsulphur with 1,3,5-trinitrobenzene in the presence of pyridine. The oxidation of the $\sigma$-complex yielded compound VI.

**REACTION POTENTIAL MAP (RPM)**

The calculation of the Reaction Potential Maps (RPM) [215] is a new kind of molecular reactivity index which is very helpful in elucidating the site selectivity observed in some chemical reactions. This was a development of the original calculation of electrostatic potential maps (EPM) by Bonaccorsi and co-workers [216].

The RPM method was proposed by Klopman et al. [215] to elucidate the reaction of ambient nucleophilic agents such as S$^-$CN with hard and soft electrophiles: picryl chloride and iodide respectively. The products contain the groups C–NCS and C–S CN respectively.

**MYCELAR NUCLEOPHILIC REACTIONS**

Bunton and co-workers [53] made a significant contribution to reaction (6, $X = \text{halogen}$) by introducing cationic surfactants (detergents) which effectively catalysed the reaction of dinitrohalobenzenes with nucleophiles in aqueous solution by forming cationic mycelles. Cetyltrimethylammonium bromide and chloride (CTABr and CTACl) were used. Thus Bunton and co-workers [54] reported that the reaction of 2,4-dinitrofluorobenzene with C$_6$H$_5$O$^-$ and C$_6$H$_5$S$^-$ was catalysed by CTABr by factors 230 and 1100 respectively. Also

\[
\begin{align*}
\text{VII a} & \\
\text{VII b} & \\
\text{VIII} & 
\end{align*}
\]

the reaction of arene sulphonates with amines can be catalysed by cationic mycelles [55] (6):

\[
\begin{align*}
\text{X} = \text{NO}_2, \text{CF}_3 \\
\text{VII} a & \\
\text{VII} b & \\
\text{VIII} & 
\end{align*}
\]

It should be pointed out that the reaction is inhibited or unaffected by anionic surfactants.

**JANOVSKY REACTION (Vol. I, p. 207)**

The Janovsky reaction became an important analytical test which could be used to detect both reagents: di- or trinitro-compounds or ketones and aldehydes. The modification of the reaction consisting in the use of $m$-dinitrobenzene as a test for 17-ketosteroids is sometimes called the Zimmerman reaction [15, 56].

The Janovsky reaction was reviewed by Hall and Poranski [10], Buck [15], Strauss [17] and more recently by Gitis and Kaminskii [57]. The structure given in Vol. I, p. 209 is now regarded as incorrect. Instead formulæ VIIa, VIIb and for $1,3,5$-trinitrobenzene VIII (see also Vol. I, pp. 210–211) are now accepted. They were suggested by Hantzsch and Picton [58] as early as 1909 and more proof was given in their favour by Gitis and Kaminskii [59], Foster and Fyfe [60], Severin and Schmitz [61] and Kimura [62].

Similar to the reaction by Jackson–Meisenheimer the formation of compounds VII–VIII is reversible and acids reproduce the substrates.

These compounds however form the first step of the Janovsky reaction. They can further react to yield bicyclic products (IX) according to Strauss and Schran [17, 63], Kohashi, Ohkura and Momosa [64] (7)
The mechanism of formation VII and IX was rationalized by Sosonkin and co-workers [65] using ultraviolet, infra-red and ESR techniques.

**ACTION OF BASES IN NUCLEOPHILIC REACTIONS OF NITRO COMPOUNDS**

Nitro compounds can react with carbanion through the nucleophilic mechanism. Carbanions (as well as radical anions and free radicals) can be formed by the action of strong bases on nitrocompounds. Russell and co-workers [66] presented it in scheme (8):

![Scheme 8]

Mąkosza and Jawdosiuk [67] have found that nitrobenzene can react exothermally with nitriles in the presence of such bases as NaOH, NaNH$_2$ and CH$_3$ONa and in various solvents. Substitution in para position can occur. The yield was greatly influenced by the solvent. The highest (15%) was in liquid ammonia and THF at −60 to −30°C.

Mąkosza [20, 68] developed a new two phase nucleophilic reaction which consists in the use of quaternary salt of a cation (Q$^+$) – most frequently tri-

ethylbenzylammonium (TEBA) – chloride suggested originally by Jarousse [126]. The cations of TEBA are present in the aqueous phase containing a concentrated solution of NaOH (usually 50%), whereas organic phase, immiscible in water, contains the nitro compounds and a nitrite, for example 2-phenylproponitrite. The reaction is now known as 'Jarousse–Mąkosza' or 'Mąkosza' reaction.

Thus p-chloronitrobenzene does not react with 2-phenylpropionitril in 50% aqueous NaOH, but the addition of a catalytic quantity of TEBA chloride immediately produces an exothermic reaction with the yield ca. 80% of the substitution product.

A model depicting a variety of reactions is 4-chloro-4-nitrobenzophenon (X).

![Diagram X]

All these positions can be attacked by a suitable nucleophile, as can be seen in schemes (9–12) [69–71].

1. Substitution of the nitro group

\[
\text{CHCN} + A \xrightarrow{\text{Q}^+ \text{Cl}^-} \text{NaOH aq} \rightarrow \text{Cl}^- \text{C} \text{C}_6 \text{H}_4 \text{C} \text{CH}_3
\]

2. Substitution in position 2

\[
\text{CH}_3 \text{CN} + A \xrightarrow{\text{NaOH}} \text{CH}_3 \text{OH} \rightarrow \text{Cl}^- \text{C} \text{C}_6 \text{H}_4 \text{C} \text{CN}
\]

3. Attack of the carbonyl group

\[
\text{CH}_3 \text{CN} + A \rightarrow \text{Cl}^- \text{C} \text{C}_6 \text{H}_4 \text{C} \text{CN}
\]
4. Substitution of chlorine

\[
\text{NH} + \text{A} \rightarrow \text{NH-C}_6\text{H}_4\text{NO}_2
\]

(12)

Another kind of substitution of nitro compounds was 'vicarious' substitution [72, 73], which takes place when the attack is carried out by a nucleophile

\[
\begin{align*}
\text{X} & : \text{a leaving group in a form of anion} \\
\text{Y} & : \text{a group stabilizing carbonium}
\end{align*}
\]

An example of such a substitution is reaction (13):

\[
\text{ClCH}_2\text{CN} + \text{C}_6\text{H}_4\text{NO}_2 \rightarrow \text{ClCH}_2\text{CN} + \text{C}_6\text{H}_4\text{NO}_2
\]

(13)

An example of nucleophilic substitution combined with a partial reduction of the nitro group was given by Davis and co-workers [74–76]. They examined the action of phenylacetonitrile anion on nitrobenzene and found that it formed a substitution compound with a p-quinoid ring according to scheme (14):

\[
\begin{align*}
\text{C}_6\text{H}_4\text{NO}_2 & + \text{C}_6\text{H}_5\text{CH}_2\text{CN} \\
\text{1. KOH + CH}_3\text{OH} & \\
\text{2. C}_6\text{H}_5\text{COOH + H}_2\text{O} & \\
\end{align*}
\]

(14)

Cine-nucleophilic substitution is an interesting example of nucleophilic substitution with the loss of a nitro group. This was reviewed [77] and a few new examples were given by Barnett, Dickens and West [78] and by Markwell [79]. The latter work gives an example of such substitution (15):

\[
\text{OH} \rightarrow \text{NHR}_2
\]

(15)

REACTIVITY OF AROMATIC NITRO COMPOUNDS

A nucleophilic introduction of an amino group into p-nitrobenzenophenone through the action of potassium amide in liquid ammonia was recently reported [80]. The substitution occurred in the ortho position to the nitro group with a yield of 17%.

Important for industry is the reaction of the substitution of a nitro group by a sulphonate group as was described in Vol. 1 (pp. 201, 207). The mechanism of the reaction is now given in the chapter dedicated to the manufacture of TNT and other higher nitrated aromatics.

Salts of TNT (and strictly speaking salts of the products of decomposition of TNT through the action of strong bases) were described in Vol. 1, pp. 303–304. They possess interesting pyrotechnic properties such as ease of burning. They seem to be the base of delay compositions described in a patent by du Pont de Nemours [220].

ACTION OF GRIGNARD REAGENT ON NITRO COMPOUNDS

(Vol. 1, p. 186)

In addition to a few rather confusing papers on the action of Grignard reagent on nitro compounds (see 15), two papers should be mentioned: on the reduction of the nitro group to an amino group [81] and advice on how to carry out the reaction at low temperature (e.g. –70°C) otherwise undefined resinous products can be formed [82].

As it was stated, Severin (Vol. 1, p. 187) obtained 1,3,5-trialkyl-2,4,6-trinitrocyclohexane from 1,3,5-trinitrobenzene and Grignard reagent followed by acidification with acetic acid of the originally formed o-complex, Severin and R. Schmitz [83] described fully the reaction as below (16):

\[
\begin{align*}
\text{O}_2\text{N}_2 & \rightarrow \text{O}_2\text{N}_2 \\
\text{CH}_3\text{COOH} & \\
\end{align*}
\]

(16)

Similarly m-dinitrobenzene yielded a cyclohexene derivative (XI) [84]
Recently Bartoli and co-workers [85–87] have published a number of papers dedicated to the systematic study of the reaction of aromatic nitro compounds with Grignard reagent. They confirmed the nucleophilic character of the alkylation of the ring. They also found that under their experimental conditions the nitro group was reduced to the nitroso group (17):

However p-nitroanisole gave an 'anomalous' reaction (in the findings of Bartoli et al.). The main product was 3-alkyl-4-nitroanisole and only a small quantity of nitroso compound was found (18):

Bartoli and co-workers pointed out that their results did not contradict those of Severin and the differences were due to the different substrates and different experimental conditions.

Interesting cases of reactions of metal salts of secondary amines with nitrobenzene have also been recorded. Thus Montmollin [142] reacted potassium salt of carbazol with nitrobenzene. The nucleophilic substitution of nitrobenzene occurred in para position to the nitro groups. A similar reaction with diphenylamine [143] has also been described.

The reaction of 1,3,5-trinitrobenzene with diazomethane was carried out as early as 1898–1900 [88, 89], but only recently de Boer rationalized it as a nucleophilic addition leading to seven-member ring condensed with two cyclopropane rings when the molar ratio of trinitrobenzene to diazomethane was 1:3. The first step of the reaction was a type of Jackson–Meisenheimer complex (A₁) and the final product was trimethylene-trinitrobenzene (A₃) [90–92a] (19). The reaction is temperature dependent: at −80°C compound (A₃) was formed.

With an excess of diazomethane (molar ratio 1:4) the last double bond can enter the reaction forming a stable pyrazoline ring not a cyclopropane (20).

A similar reaction was given by picric acid which in the first instance was methylated to trinitroanisol [93].

MECHANISM OF RICHTER REACTION (Vol. I, p. 205)

In Richter reaction m-bromobenzoic acid may be obtained by reacting potassium cyanide with p-nitro-bromobenzene. The original mechanism of the
NUCLEOPHILIC SUBSTITUTIONS IN GAS PHASE

Nucleophilic substitutions can be carried out in gas-phase. Such reactions are much faster than in solution. They were recently reviewed by Bowie [47]. Some of these reactions are produced by radical anions.

REACTIVITY OF AROMATIC NITRO COMPOUNDS

The treatment of o- and p-nitrotoluenes with a basic agent (e.g. potassium tert-butoxide) in the absence of air can give rise to oxidation of nitrobenzyl radical anions which further react to yield dinitrobenzyl [102]. The reaction can proceed through a radical chain mechanism [103] (23):

\[
p-\text{NO}_2C_6H_4\text{ClHCH}_2 \quad \underset{\text{N}}{\text{H}} \quad \rightarrow \quad p-\text{NO}_2C_6H_4\text{ClHCH}_2^- \quad \text{(a)}
\]

\[
p-\text{NO}_2C_6H_4\text{Cl}^- + p-\text{NO}_2C_6H_4\text{CH}_2 \quad \rightarrow \quad [p-\text{NO}_2C_6H_4\text{ClHCH}_2]^+ + p-\text{NO}_2C_6H_4\text{Cl}_2 \quad \text{(b)}
\]

\[
p-\text{NO}_2C_6H_4\text{Cl}^- + p-\text{NO}_2C_6H_4\text{Cl}_2^- \quad \rightarrow \quad [p-\text{NO}_2C_6H_4\text{ClHCH}_2H_2\text{ClNO}_2]^+ \quad \text{(c)}
\]

Russell and co-workers [104] also examined the action of potassium tert-butoxide on p-nitrotoluene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, m-dinitrobenzene and 1,2,5-trinitrobenzene. The higher the nitrated hydrocarbons the slower the oxidation.

Hass and Bender [105] described a reaction of p-nitrobenzyl chloride with salts of nitroalanes, for example, 2-nitropropane. The mechanism of the action was rationalized by Kornblum and co-workers [106] and Russell and Danen [107] as a sequence of chain reactions:

\[
p-\text{NO}_2C_6H_4\text{Cl} + (\text{CH}_3)\text{C} = \text{NO}_2 \quad \rightarrow \quad (\text{CH}_3)\text{CNO}_2 + [p-\text{NO}_2C_6H_4\text{Cl}]^- \quad \text{(a)}
\]

\[
[p-\text{NO}_2C_6H_4\text{Cl}]^- \quad \rightarrow \quad p-\text{NO}_2C_6H_4\text{ClHCH}_2^- \quad \text{(b)}
\]

\[
p-\text{NO}_2C_6H_4\text{Cl}^- + (\text{CH}_3)\text{C} = \text{NO}_2 \quad \rightarrow \quad [p-\text{NO}_2C_6H_4\text{ClHCH}_2\text{CH}_2\text{ClNO}_2]^+ \quad \text{(c)}
\]

\[
[p-\text{NO}_2C_6H_4\text{ClHCH}_2\text{CH}_2\text{ClNO}_2]^+ + p-\text{NO}_2C_6H_4\text{ClHCH}_2\text{Cl} \quad \rightarrow \quad p-\text{NO}_2C_6H_4\text{ClHCH}_2\text{H}_2\text{ClNO}_2 + [p-\text{NO}_2C_6H_4\text{ClHCH}_2\text{Cl}]^- \quad \text{(d)}
\]

Another example of chain reactions with radical anions was described by Shein and co-workers [108]; that is the reaction (25) between 2,4-dinitrochlorobenzene and trialkylamines:

Radical anions of nitro compounds

The radical anions of nitrobenzene and substituted nitrobenzenes may be formed by electrolytic or metal reduction [100].
An interesting example of a radical anion reaction is the action of oxygen negative ion formed in chemical ionization in a mass spectrometer [109]:

\[
p\text{NO}_2\text{C}_6\text{H}_4\text{Cl} + \text{O}_2^- \rightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{O}^- + \text{ClO}. \quad (26)
\]

Nitroaromatics can act as catalysts of some oxidation reactions, such as the oxidation of benzoil [110] and polynitroaromatics in the oxidation of 'hindered' phenols [111]. Russell and co-workers [112a, b] rationalized it in terms of radical ion reactions where the radical ion \( \text{Ar NO}_2^- \) activates oxygen (27):

\[
\text{Ar NO}_2^- + \text{O}_2 \rightarrow \text{Ar NO}_2 + \text{O}_2^-. \quad (27)
\]

**FREE RADICAL REACTIONS** (Vol. I, p. 212)

A few monographs have been dedicated to free radical reactions including substitutions. The most important are those by Williams [113] and Sosnovsky [114] and a review article has appeared concerning the homolytic substitution of nitro compounds [115].

The nitro group activates aromatic rings towards a homolytic substitution. As previously pointed out, the nitro group directs a substitution into ortho and para positions through the greater availability of an unpaired electron at the ortho and para positions and a greater stability of ortho and para quinoid which can be regarded as intermediates of some homolytic substitutions.

Some of the main reactions of aromatic nitro compounds with free radicals are given here [116]. Nitrobenzene reacts with hydroxyl produced by hydrogen peroxide ferrous salt reaction (28)

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^-. \quad (28)
\]

The reaction furnished \( o-, m\)- and \( p\)-nitrophenols with yields of 25–30%, 30–25% and 50–55% respectively.

Another typical free radical reaction is that of mercurication of nitrobenzene with mercuric acetate in a non-polar solvent [117] (29):

\[
R\text{NO}_2 + \text{Hg(OOCCH}_3)_2 \rightarrow R\text{Hg(OOCCH}_3)_2 + \text{NO}_2^- \quad (29)
\]

**REACTIVITY OF AROMATIC NITRO COMPOUNDS**

Ortho and para isomers are formed in proportion in 57%, and meta in 43%. A relatively large proportion of meta isomer is probably due to the lack of a clear demarcation line between the electrophilic and the radical substitution.

A partial radical substitution may be responsible for the nitration of nitrobenzene to dinitrobenzenes by nitric acid in the presence of mercuric oxide reported by Ogata and Tsuchida [118]. They found 26% of \( o\)- and only 24% \( m\)-dinitrobenzenes.

Hey and co-workers [119–124] studied the arylation of nitrobenzene through the action of various sources of aryl radicals \( p\)-\( R\text{C}_6\text{H}_4\text{H}_4\text{ONa} \) generated from such sources as diazotates \( (p\text{-RC}_6\text{H}_4\text{N}_2\text{ONa}) \), nitrosocarbazylamines \( (p\text{-RC}_6\text{H}_4\text{NCOCH}_3) \) and acyl peroxides \( (p\text{-RC}_6\text{H}_4\text{CO}_2\text{O})_2 \). The average substitution in the \( \text{meta} \) position for \( R = \text{Br} \) and \( \text{CH}_3 \) was only 12.1 and 8.6% respectively and was independent of the source of aryl radical.

The phenylation of nitrobenzene gave the figures shown in Table 25.

<table>
<thead>
<tr>
<th>Source of phenyl radical</th>
<th>ortho</th>
<th>meta</th>
<th>para</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium benzenediazotate</td>
<td>54</td>
<td>9</td>
<td>37</td>
</tr>
<tr>
<td>Benzoil peroxide</td>
<td>59.5</td>
<td>8.5</td>
<td>32</td>
</tr>
</tbody>
</table>

However, when the free radical is \( p\)-nitrophenyl, the proportion of \( \text{meta} \) isomer increases. This is explained by the fact that the radical \( p\text{-NO}_2\text{C}_6\text{H}_4\text{H}_4^+ \) is somewhat electrophilic in character.

Hey and Grieve [125] found in 1934 that the nitro group activates the aromatic ring towards homolytic substitution. For example, the competitive phenylation of toluene and nitrobenzene by phenyl radicals showed that the yield of nitrophenyls was about four times greater than the yield of methylphenyls.

Hey and co-workers [119, 121, 124] gave a quantitative analysis of the rate of homolytic attack on nitrobenzene as compared with that on chlorobenzene. The phenylation of nitrobenzene gave proportions of \( \text{ortho, meta and para} \) products: 58, 10 and 32% respectively, whereas the phenylation of chlorobenzene yielded 62, 24 and 14% respectively. However when the entering group is more electrophilic than benzene (e.g. \( o\)- and \( p\)-nitrophenyl radicals) the proportion of \( \text{meta} \) substituents increased.

Fields and Meyerson [127] have described in numerous papers the formation of free radicals from aromatic nitro compounds at temperatures of 400–600°C. Their work has been summarized in a review paper [128]. They found that the C – N bond in nitroaromatics breaks above 400°C generating phenyl and similar
aromatic radicals. The decomposition at 600°C seems to be closely paralleled to its decomposition under electron impact in a mass spectrometer. Nitrobenzene at 600°C, gave within 20 s. a 30% yield of phenol, biphenyl, dibenzofuran, benzene, hydroxypiphenyl, nitrophenyl and in some instances of naphthalene.

In the presence of benzene, toluene, pyridine and triphene, considerable proportions of biphenyl and terphenyl and their homologues and analogues were formed.

The mechanism of the reactions is rationalized by the authors, as follows (30):

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NO}_2 & \xrightarrow{\text{fast}} \text{C}_6\text{H}_6 + \text{NO}_2 \\
\text{C}_6\text{H}_5\text{ONO} & \xrightarrow{\text{slower}} \text{C}_6\text{H}_5\text{O}^+ + \text{NO} \\
& \xrightarrow{\text{[11]}} \text{C}_6\text{H}_5\text{OH} \\
& \xrightarrow{\text{[O]} \text{OH}} \text{biphenyl and terphenyl.}
\end{align*}
\]

Naphthalene can be formed, according to the authors, through the intermediate formation of benzene.

A few more free radical reactions of nitro compounds should be mentioned. Some of these reactions are photo-induced and are described in the chapter on photochemistry of nitro compounds.

In 1866 Kekulé [129] described the reaction of nitrobenzene with bromine at 250°C which under pressure yielded tetra- and hexabromobenzene [130], thus the replacement of the nitro group by bromine occurred. Later it was found [131] that chlorobenzene was the main product when acting with chlorine on nitrobenzene at 375°C in 48 s contact time with only a small proportion of chloronitrobenzenes. The substitution of nitro groups in m-dinitrobenzene by chlorine in gas phase at 200–300°C appears to be a commercial method of manufacturing m-dichlorobenzene [132]. Ponomarenko [133] studied this reaction and found the yield to be 92%. He also stated that aromatic nitro compounds are transformed into chloro derivatives by acting on nitro compounds with carbon tetrachloride at 220–310°C under pressure.

A similar, but probably nucleophilic substitution was studied by Lobry de Bruin and van Leent [134]. By acting with hydrochloride at 250°C they replaced nitro groups in dinitrobenzenes and s-trinitrobenzene to obtain dichlorobenzenes and s-trichlorobenzenes respectively.

Gerstman and Bickel [111] observed that polynitroaromatics can act as catalysts in the oxidation of hindered phenols.

The mechanism of the catalytic action of aromatic nitro compounds was not clear until Russell and co-workers [136] rationalized it in terms of free radical reactions. Their particular study was dedicated to the oxidation of fluorene by molecular oxygen in tert-butoxide in the presence of potassium tert-butoxide.

The reaction is catalyzed by aromatic nitro compounds, such as nitrobenzene and particularly m- and p-dinitrobenzene and p-bromo- and p-chloronitrobenzene.

A rather unusual free radical reaction should be mentioned here: aryl free radicals produced by heat or copper powder can displace and substitute a nitro group [172, 173].

ACTION OF AROMATIC NITRO COMPOUNDS ON POLYMERIZATION (Vol. I, p. 214)

Aromatic nitro compounds inhibit radical polymerization. However, they do not seem to inhibit ionic polymerization [137]. On the contrary Rumanian authors reported [190] that nitrobenzene as well as nitromethane and nitromethane increase the rate of cationic polymerization of N-vinylcarbinol.

With regard to radical polymerization some controversial results have also been obtained. Thus Mondai and co-workers [138] have shown that o-dinitrobenzene was a stronger retardant of radical polymerization of methyl methacrylate than other isomers. On the contrary Hammond and Bartlett [139] found that o-dinitrobenzene was a weaker retardant than other isomers of polymerization of allyl acetate.

T. Urbanski and Buźniak [140, 141] undertook the task of a systematic study of the action of mono-, di- and trinitro derivatives of benzene and toluene (a few dozen compounds) on the polymerization of unsaturated polyester resin 'Polymar 109'. The polymerization was initiated with benzoyl peroxide at 12°C. It was found that nitro compounds with an ortho substituent are particularly active as inhibitors of polymerization.

The strongest inhibitor was found to be o-nitrotoluene.

Steric factors, such as those produced by the two methyl groups in ortho position reduces the inhibitory activity of the nitro compounds.

Tudós and co-workers [175] described inhibition of polymerization of styrene by sym-trinitrobenzene.

All these studies may have a certain significance in the technology of solid propellants for rockets.

REDUCTION OF AROMATIC NITRO COMPOUNDS.
FORMATION OF NITROSO COMPOUNDS

The reduction of the nitro group to amino and hydroxyamino groups is well known and described in textbooks dedicated to intermediates and dyestuffs.
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Less known is the reduction of nitro to nitroso group. It was reviewed by Boyer in a chapter ‘Reduction and Deoxygenation of Nitro Compounds’ [147]. The following are methods giving good yields of nitroso derivatives:

- Electrolytic reduction [148],
- Catalytic reduction in the presence of iron powder in CO₂ at 220°C [149],
- Deoxygenation of nitro group by free radicals [150].

Reduction of a nitro group can lead to a ring closure to form furuoxane derivatives [151]

\[
\text{NO}_2\quad\text{Cl} \\
\begin{array}{c}
\text{O} \\
\text{C}_2\text{H}_5\text{OH}
\end{array} \\
\begin{array}{c}
\text{NH}_2\text{OH}
\end{array} \\
\text{O} \\
\text{NO}_2
\]

(31)

Another interesting reaction was reported by Willgerodt [152] on the action of potassium iodide in acetic acid on N-1,3,5-trinitrosophenyl-N-phenylhydrazine (from picrylazobenzene) (32):

\[
\begin{array}{c}
\text{NO}_2 \\
\text{O}_2\text{N} \quad \text{N} = \text{N} \quad \text{C}_2\text{H}_5\text{OH} \\
\text{KI} \\
\text{CH}_3\text{COOH}
\end{array} \\
\text{H}_2\text{N} \quad \text{NH} \quad \text{H}_2\text{N} \quad \text{H}_2\text{N}
\]

(32)

The classical photochemical reaction of Ciamicin and Silber [153] of o-nitrobenzaldehyde transformed into o-nitrosobenzoic acid is described in the chapter on photochemistry of nitro compounds. o-Nitrophenyl azide can readily yield benzofuroxane [154].

\[
\begin{array}{c}
\text{NO}_2
\end{array} \\
\begin{array}{c}
\text{N}_3
\end{array} \\
\text{H}_2\text{O} \quad \text{or heat}
\]

(33)

It is highly probable that a nitroso intermediate is formed in the Richter reaction (p. 109).

Reduction of Aromatic Ring

A remarkable reaction was discovered by Severin and co-workers [155, 156] (Vol. I, p. 252). He succeeded in reducing the aromatic ring of nitro compounds without reducing the nitro groups. The reducing agent was sodium borohydride. s-Trinitrobenzene was dissolved in tetrahydrofuran and NaBH₄ in aqueous methanol was added at 0°C. 1,3,5-Trinitrocyclohexane resulted in a yield of 40% [155]. 1,8-Dinitronaphthalene was reduced by the same method to 1,4-dihydro-1,8-dinitronaphthalene (78% yield).

m-Dinitrobenzene was partially reduced [156] to 3,5-dinitrocylohexene (XI) and picric acid to 1,3,5-trinitropentane (XII) through the ring opening.

\[
\begin{array}{c}
\text{NO}_2 \\
\text{O}_2\text{N} \quad \text{NO}_2 \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2
\end{array} \\
\begin{array}{c}
\text{XI}
\end{array} \\
\begin{array}{c}
\text{NO}_2 \\
\text{O}_2\text{N} \quad \text{NO}_2 \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2
\end{array} \\
\begin{array}{c}
\text{XII}
\end{array}
\]

The reaction has been studied by a number of authors [157, 158], who came to the conclusion that the hydride reacts initially on the electron-deficient carbon atom at position 3 and forms a kind of Jackson–Meisenheimer adduct, the latter is eventually subject to reduction.

Okamoto and Attarwala [159] brought an improvement to the reaction of Severin, by adding a cationic surfactant (as a phase transfer catalyst) to the reaction medium. They examined the reduction of unsymmetrically substituted 2,4,5- and 2,3,4-trinitrotoluenes by sodium borohydride in methylene dichloride at 23–24°C in the atmosphere of nitrogen in the presence of ethylhexadecyl-dimethylammonium bromide.

An interesting instance of oxido-reduction of a nitro compound was given by Forbes and Gregory [180]. 2,4-Dinitrobenzaldehyde when warmed with a concentrated solution of sodium hydroxide yielded 2-nitro-4-nitrosophenol instead of the expected acid and alcohol according to the Cannizzaro reaction.

\[
\begin{array}{c}
\text{CHO} \\
\text{NO}_2
\end{array} \\
\begin{array}{c}
\text{NaOH}
\end{array} \\
\begin{array}{c}
\text{OH} \\
\text{NO}_2
\end{array} \\
\begin{array}{c}
\text{+ HCOCNa}
\end{array}
\]

(34)

The reaction is similar to that of Ciamicin and Silber – a classical photochemical reaction (Chapter V).

A partial reduction of the aromatic ring of trinitrobenzene was recently described by Ohno, Yamamoto and Oka [160]. By acting with 1,4-dihydroxytocimic acid derivatives, 1,3,5-trinitrobenzene was reduced to dihydrotrinitrobenzene at room temperature in dry acetonitrile in the atmosphere of argon and away from light.
Sodium amide can reduce the nitro group of aromatic nitro compounds to give a small yield of diazo compounds [161, 162].

Kemula and co-workers [163] developed the polarographic reduction of the nitro group as an analytical method.

The case of the reduction of nitro compounds leads to their use as oxidizing agents. The use of nitrobenzene in the Skraup reaction is well known. α-Dinitrobenzene was reported to be a good agent for oxidizing ascorbic acid to diketone [164].

A nitro group can yield N-heterocycles (see Vol. I, p. 195) through the action of various reducing agents such as metal oxalates [165, 166], triethyl phosphate [167–169] or iron pentacarbonyl [170] (35):

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{NO}_2 & \quad \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

The reaction of nitro aromatic compounds with carbon monoxide was recently reviewed by Manov-Yvesninskii and Nefedov [221]. Particularly interesting is the formation of isocyanates apparently produced in the same way in Japan [222].

**DIAZOTIZATION OF AMINO NITRO COMPOUNDS**

The NO₂ group reduces the basicity of amino group and makes the diazotization more difficult. Diazotization of dinitro aniline and particularly trinitroaniline requires more drastic conditions, such as use of more concentrated acid medium and higher temperature. This can be found in textbooks on diazotization and on dyestuffs chemistry.

On the other hand the nitro group renders the diazo group more electrophilic and more reactive in the process of coupling to form azo compounds. Thus 2,4,6-trinitrobenzidazonium ion couples with mestylene which is less reactive than anisole and does not react with other diazonium ions [171].

Reactions of the replacement by hydrogen of the tertiary nitro group in aliphatic and cyclic compounds were recently described by Kornblum and co-workers [145]. They occur at room temperature when the nitro compounds are treated with the sodium salt of methyl mercaptan.

Eytko-Krasnousk, Piotrowska and T. Urbaniński [146] described the replacement by hydrogen of tertiary nitro group in 5-nitro-1,3-dioxane by acting with ethylene glycol in KOH at 120–140°C with yields of up to 60%.

An interesting case of the substitution of nitro group by adamantyl radical was reported by Italian authors [188]. Free adamantyl radical was produced from carboxylic acid according to [187].

**1,3-CYCLOADDITION OF NITRO COMPOUNDS**

Nitro compounds can be subjected to the so-called 1,3-cycloaddition which is manifested by adding a system with double bonds to 1,3-dipole.

1,3-Dipole can be represented in two limiting forms: a sextet and an octet:

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{O} & \quad \text{N} \\
\end{align*}
\]

Sextet

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{N} \\
\end{align*}
\]

Octet

Cycloaddition can be represented by schemes (36): (a) and (b)

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{N} \\
\end{align*}
\]

(a)

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{N} \\
\end{align*}
\]

(b)

An excellent review of 1,3-cycloaddition was given by Huisgen [135].

A considerable number of experiments with 1,3-cycloaddition were reported by Tartakowskii, Novikov and co-workers [181–185]. They reacted nitronic acid esters (esters of aciform of primary or secondary nitro alkanes) with dipolephilic such as styrene, vinyl chloride, acrylic esters and methyl–vinyl ketone (36c). The reaction occurs at room temperature (or lower) with an excess of unsaturated compound, the yield is 60–90%.

The reaction of nitronic acid esters with acetylene derivatives yielded aziridines (36d) [186].

\[
\begin{align*}
\text{CH}_2 = \text{CHCOOCH}_3 & + \text{O}_2 \text{N} - \text{CH} - \text{N} - \text{OCH}_3 \\
\text{CH}_3 \text{OOC} & \quad \text{ONO}_2 \\
\end{align*}
\]

(c)

\[
\begin{align*}
\text{R} & \quad \text{C} = \text{CH} + \\
\text{O} & \quad \text{ONO}_2 \\
\text{OCH}_3 & \quad \text{OCH}_3 \\
\end{align*}
\]

(d)
THERMAL STABILITY OF AROMATIC NITRO COMPOUNDS

It is generally accepted that aromatic nitro compounds are thermally stable and are only sensitive to the action of bases which produce deep changes in their structure. Nevertheless the action of high temperature on TNT had already been examined in 1911–12 by Verola (Vol. I, p. 306). He found that an evolution of gases started when TNT was kept at 160°C, and the m.p. of TNT was reduced from 80.75°C to 79.9°C after keeping the substance for 177 hours at 145–150°C. Thus Pasman, Groothuisen and Vermeulen [191] made a statement that fused TNT is unstable at elevated temperatures (>150°C).

The high thermal stability of nitro compounds is manifested by the high activation energy \( E \) of their thermal decomposition. The following are figures referring to mono-, di- and trinitro compounds:

Nitrobenzene \( E = 53.4 \) kcal/mol, \( \log B = 12.65 \) at 395–445°C

\( m \)-Dinitrobenzene 52.6 kcal/mol, \( \log B = 12.7 \) at 345–410°C

1,3,5-Trinitrobenzene 51.9 kcal/mol, \( \log B = 13.6 \) at 270–355°C

as given by Maksimov [192].

Andreev [193] gave figures for:

Picric acid, \( E = 38.6 \) kcal/mol, \( \log B = 11.6 \) at 183–270°C.

Styphnic acid, \( E = 34.6 \) kcal/mol, \( \log B = 11.2 \) at 270–355°C.

Koginskii and Magid [194] found \( E = 27.0 \) kcal/mol and \( \log B = 11.4 \) for the decomposition of TNT.

Similar figures were obtained by Robertson [195], Pasman et al. [191] for the temperatures in the interval of 126–196°C, and for higher temperatures (380–440°C) T. Urbanski [196] found 14.0 kcal/mol.

Pasman et al. [191] carried out experiments on thermal decomposition of TNT using the adiabatic storage test method. They found that the total heat evolved during 120 hours of keeping at 175°C was 74 kcal/kg.

A few accidents which have recently occurred demonstrate that prolonged heating, much below their ignition temperature, (the deflagration point) can produce an explosion even if this is referred to lower nitrate compounds. Such an accident was recorded (probably for the first time) in 1972 when an explosion took place at 218°C in the U.S.A. in a 100 m long pipe filled with dinitrotoluene [197]. Previous experiments determined ignition temperature as being 270°C, although some sources give an even higher temperature of 300°C [198].

The problem revived in 1976 in the United Kingdom when 1300 kg of 3,5-dinitro-o-toluenediamine kept in a closed drier at 118–130°C exploded after 27 hours of heating [199]. In order to create a method which could be used to establish the stability of aromatic and possibly other nitro compounds, Camera and Biasutti [199] developed an ingenious method of “isothermal Pressure Meter” which is a perfection of the method used by Small and co-workers. The method consists in keeping a sample 65 g in a steel pressure vessel in a thermostat (accuracy ± 0.2°C). The induction period is considered to be terminated when the pressure in the vessel increased by 0.2 kg/cm². The experiment was continued until the disc closing the vessel was ruptured.

For DNT (a mixture of 2,4- and 2,6-dinitrotoluene) the induction period was found to be:

- 175000 hours at 100°C
- 1040 hours at 150°C
- 18 hours at 200°C

The calculated energy of activation was 32.2 kcal/mol.

The addition of 2,4,6-trinitrotoluene to DNT reduced the induction time at 235°C, viz.:

- pure DNT: 1.70 hours
- TNT: 1.70 hours
- addition of 5000 ppm TNT: 1.53 hours
- 25,000 ppm TNT: 1.09–1.14 hours
- 50,000 ppm TNT: 0.88–1.00 hours
- 100,000 ppm TNT: 0.20

Similar influence was shown by addition of 2,4-dinitro-o- and 2,6-dinitro-p-cresols.

Attention is also drawn to the paper by Dacons, Adolph and Kamlet [200] who described a spontaneous self-ignition of TNT after being kept for 14–16 hours at 210°C.

A review of kinetic data from low-temperature thermolysis of polynitro compounds was recently given by Zeman [201].

Free Radicals

In the course of thermal decomposition of aromatic nitro compounds free radicals are formed. The ESR signals were detected by Janzen [202], Japanese workers [203] and Soviet workers [204]. The latter authors obtained strong signals from picric acid after an induction period of 30–5 min at 190–210°C respectively.

Janzen reported the formation of free radicals in 2,4-dinitrotoluene, 2,4,6-trinitrotoluene and picric acid at 260°, 240° and 130°C respectively. 2,4-Dinitro- and 2,4,6-trinitroaniline give the signal at room temperature. This can be rationalized by the author of the present book in terms of the intramolecular
FURANOXES (Vol. I, p. 603)

Aromatic nitro compounds which in ortho position have azido group can readily be transformed into benzofuranoxanes (31, 33). An excellent review on furanoxazone was written by Kaufman and Picard [206]. Recent works on the structure of benzofuranoxazone were also published: on X-ray analysis [207, 208], vibrational and Raman spectra [209, 210], nitrogen NMR [211], carbon 13 NMR [212]. Explosive properties were also discussed [213].

Korsunskii and Apina [214] examined the kinetics of the transformation of 1,3,5-triazido-2,4,6-trinitrobenzoic acid into benzofuranoxazone at 70–115°C. The reaction is of the first order with activation energy 26 kcal/mol.

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CHAPTER 5
PHOTOCHEMISTRY OF NITRO COMPOUNDS

(Vol. I, p. 225)

Photochemistry has received much appreciation in the last two decades manifested by several fine monographs and review articles. Most of them have a general character [1–5]. Excellent reviews dedicated to photochemistry of the nitro and nitroso groups were given by Morrison [6], Carless [35] and Kaye [47].

It is assumed that photochemical reactions originate from the lowest energy singlet and triplet excited states. They are due to absorption bands which have been described in Chapter III on the spectroscopy of nitro compounds: the \( \pi \rightarrow \pi^* \) transition (ca. 210 nm) of high intensity and \( n \rightarrow \pi^* \) (ca. 270 nm) of a relatively low intensity; some nitro compounds show the second transition \( n \rightarrow \pi^* \) (ca. 350 nm). It is accepted that the lowest lying singlet and triplet states for nitro compounds are \( n, \pi^* \).

The photochemistry of nitro compounds began with the pioneering work of Clamician and Silber [7, 8] who described two photochemical reactions (1, 2):

\[
\begin{align*}
\text{NO}_2 & \xrightarrow{C_2H_5OH, \text{hr}} \text{NH}_2 + \text{NH}_2 \\
\text{CHO} & \xrightarrow{h^+} \text{COOH} \quad \text{(2)}
\end{align*}
\]

In reaction (1) ethanol is oxidized [9, 10] to acetaldehyde, nitrobenzene is reduced partly to phenylhydroxylamine (which rearranges into \( p \)-aminophenol) and partly to aniline.

Reaction (2) in alcoholic medium was examined by Bamberger and Elger
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[11], who found that it passed through the formation of acetals.

Recently George and Scala [12] examined the reaction of Ciamician and Silber and came to the conclusion that photolysis of o-nitrobenzaldehyde proceeded by a triplet state with a lifetime of 0.6 ns. Laser flash photolysis showed the formation of a transient intermediate according to (3):

\[
\text{CHO} \rightarrow \begin{array}{c}
\text{H} \\
\text{O} \\
\text{N} \\
\text{0}
\end{array} \rightarrow \begin{array}{c}
\text{CHO} \\
\text{NO}
\end{array}
\]

(3)

Similar photochemical reactions were recorded for 2,4-dinitrobenzaldehyde [13] and nitroterephthalaldehyde [14].

o-Nitrobenzyl ester yielded o-nitroso benzaldehyde [48a] by the same mechanism.

A rule of Sachs and Hilpert [15] should be mentioned: “all aromatics which have a hydrogen ortho to a nitro group are light sensitive”. They expressed it by a scheme (4):

\[
R' - C = H \quad R' - C = H
\]

(4)

Photolysis of nitramine derivatives of steroids has also been recently described [16].

Some photoinduced reactions of nitro compounds involving a formation of free radicals or radical ions were reviewed by Traynham [17]. He classified such reactions as occurring through the “ipso” attack, that is, the entering group is (in the first instance) attached to the same carbon as the group to be removed, as in the classical case of replacing the nitro group of nitrobenzene by chlorine under the action of light:

\[
\text{NO}_2 \quad \text{Cl}_2 \quad \text{NO}_2 \quad \text{Cl} \quad \text{Cl} \quad \text{NO}_2
\]

(5)

(see also [18] and [19]).

Some reactions described in [6] merit particular attention, for example:

Havinga, de Jongh and Dorst [20] reported the photoinduced hydrolysis of $m$-nitro phosphoric ester to $m$-nitrophenol. $m$-Nitroanisol was also hydrolysed to $m$-nitrophenol [21] and by the action of potassium cyanide yielded $m$-cyanoamnitrobenzene [22]. Gold and Rochester [23] reported the formation of 3,5-dinitrophenoxy ion from s-trinitrobenzene and hydroxyl ion. Van Vliet [24] obtained a number of nitro derivatives of aniline by acting with liquid ammonia on some aromatic nitro compounds under irradiation with ultraviolet light, viz. (6), (7) and (8):

\[
\begin{array}{c}
\text{NO}_2 \\
\begin{array}{c}
\text{NH}_3 \\
\text{NH}_3
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\text{NO}_2 \\
\begin{array}{c}
\text{NH}_3 \\
\text{NH}_3
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\text{NH}_2 \\
\begin{array}{c}
\text{NH}_2 \\
\text{NH}_2
\end{array}
\end{array}
\]

(6)

(7)

(8)

Photoinduced condensation of $m$-dinitrobenzene and sym-trinitrobenzene to nitro derivatives to azoxybenzene was reported by Stenberg and Holter [36]. The most important factor is the solvent. The reaction does not proceed in benzene but gives a good yield in tetrahydrofurane. In ethanol a smaller yield was obtained and ethanol was partly oxidized to acetaldehyde, as found in other reactions [9, 10].

A few papers by Reid and co-workers [37] and de Boer and co-workers [60, 61] were dedicated to the photochemistry of aliphatic nitro compounds. The photochemistry of 17-nitrosteroïdes was also described [38].

An interesting instance of remote oxidation with photoexcited nitrobenzene derivatives was given in [39].

An excellent review was given by Frolov, Kuznetsov and Eltsov [52] on the photoreduction of aromatic nitro compounds through intermolecular action. Alcohols and hydrochloric acid supply the hydrogen needed for reduction: alcohols are converted into aldehydes, as in reaction (1) and hydrochloric acid
becomes a strong chlorinating agent, for example [53].

Gold and Rochester [54] and Johnson and Rees [55] described a transformation of 1,3,5-trinitrobenzene into 3,5-dinitrophenol under photochemical action of OH⁻ [compare with reaction (11) in Vol. I, p. 251].

Wang and Yates [56] reported the photochemical oxidation of m-nitrobenzyl alcohol in aqueous solution to m-nitrobenzaldehyde and azoxy compounds.

An interesting photochemical reaction of 1,3-cycloaddition (see Chapter IV) was reported by Büchi and Ayer [58] (9):

\[
\text{C}_6\text{H}_5\text{NO}_2 + (\text{CH}_3)_2\text{C}==\text{CH}_3 \xrightarrow{hv} \text{C}_6\text{H}_4\text{O} + \text{CH}_3\text{CHO} \quad (9)
\]

A similar reaction to the addition of nitrobenzene to cyclohexane was reported by Charlton and de Mayo [59].

A heterolytic substitution of 1-methoxy-3,5-dinitrobenzene through the action of ultraviolet light was described by Havinga and co-workers [57]. 3,5-Dinitrophenol resulted, i.e., demethylation occurred.

ALIPHATIC AND ALCYCLIC NITRO COMPOUNDS

A primary photochemical reaction of nitro alkanes is a cleavage of the C — N bond [47, 48]:

\[
\text{CH}_3\text{NO}_2 \xrightarrow{hv} \text{CH}_3^+ + \text{NO}_2^- \quad (10)
\]

followed by recombination to yield methyl nitrite

\[
\text{CH}_3^+ + \text{NO}_2^- \rightarrow \text{CH}_3\text{ONO} \quad (11)
\]

For a full discussion of the reactions see [6] Vol. I, p. 583 and Chapter VIII. Photochemistry of nitromethane and its substituted derivatives (XCH\textsubscript{2}NO\textsubscript{2}, X = CH\textsubscript{3}, NH\textsubscript{2}, F, and F\textsubscript{2}CHNO\textsubscript{2}, F\textsubscript{2}C(NO\textsubscript{2})\textsubscript{2}) was examined by Slovetskii and co-workers [49]. They came to the conclusion that the transition from the ground state to the triplet state leads to an increase of the density of the positive charge at the central carbon atom and decrease at the nitrogen. They also suggested probable conformation of monosubstituted derivatives of nitromethane. Slovetskii et al. [50] also examined the photolysis of tetrinitromethane:

\[
\text{C(NO}_2)_4 \xrightarrow{hv} \text{C(NO}_2)_3^- + \text{NO}_2^+ \quad (12)
\]

The reaction is influenced by solvents and begins by a triplet state.

PHOTOCHEMISTRY OF NITRO COMPOUNDS

An important reaction is the photochemical 1,2-cycloaddition of nitroalkenes [6].

S. T. Reid and co-workers [51] examined the photochemistry of some nitroalkenes. They are depicted by formulae (13) and (14):

\[
\text{ONO}_2 \xrightarrow{hv} \text{ONO}_2^- \quad (13)
\]

\[
\text{ONO}_2 \xrightarrow{hv} \text{ONO}_2^- \quad (14)
\]

Photoconductivity of Nitro Compounds

The phenomenon of photoconductivity, that of nitro compounds was recently reviewed by Jarosiewicz [25].

Photoconductivity of liquid nitrobenzene was described by Brique and Gaspard [26]. They rationalized it as the result of photoionization of the compound. The increase in conductivity occurred in the course of irradiation by the light of the wave-length corresponding to the absorption by nitrobenzene. The process is reversible when irradiation is of short duration, but after prolonged irradiation it can attain a constant value.

Some authors have drawn attention to the fact that photoconductivity can be due to impurities in nitrobenzene [27]. On the other hand it is known that radical ions can be formed in pure nitrobenzene under the action of an electric current [28].

Szczepiński [29] described the same phenomenon and found the influence of the solvent, for example the photoconductivity, is prominent in ethyl ether or
1,4-dioxane but less noticeable in benzene. This author explains it in terms of the formation of CT (EDA) complexes. An important finding was made by Japanese authors [30, 31] that 1,3,5-trinitrobenzene shows a strong photoconductivity. Among other aromatic nitro compounds 2,4,7-trinitro-9-fluorenone possesses similar properties [32].

Also nitroalkanes have demonstrated photoconductivity [33, 34].

An interesting proof has recently been given of photochemical splitting of free radical NO$_2$ from nitroalkane: Marcinak and Paszyce [62] irradiated nitromethane dissolved in cyclohexane and received nitrosocyclohexane dimer:

\[
\text{CH}_3\text{NO}_2 \xrightarrow{\text{hv} (254 \text{ nm})} \text{CH}_3^* + \text{NO}_2 \rightarrow \text{trans-nitrosocyclohexane dimer}
\]

**PHOTOLYSIS**

Flash photolysis of aromatic nitro compounds was carried out by a number of authors: Wettermark [40], Suryanarayanan, Capellos, Porter and co-workers [41–43]. Among various findings the latter authors came to the conclusion that 2,4,6-trinitrotoluene under flash photolysis is transformed into aci-quinoid isomer (I) with an absorption maximum at 460 nm.

![Flash photolysis diagram]

Important contributions to the mechanism of photolysis of aliphatic nitro compounds were made by Bolsman, de Boer and co-workers. In the first paper Bolsman and de Boer [44] examined photolysis of ‘pseudonitro’ 1-nitro-1-nitrosocyclohexane with red light in the absence of oxygen. This is described in Chapter VIII.

In further experiments Bolsman, de Boer and Verhoeven [45] examined the photochemical decomposition of 2-iodo-2-nitroanilinamidate in several hydrogen donating solvents and found the formation of α-nitroalkyl radical. This was extended to simple α-iodonitroalkanes in solution [46].

The formation of α-nitroalkyl radical can be depicted by reaction (15):

\[
\begin{align*}
\text{NO}_2 & \quad \rightarrow \quad \text{NO}_2^* \\
\text{R}^1 \text{C}^* & \quad \rightarrow \quad \text{R}^1 \text{CN}_2
\end{align*}
\]

(15)

**PHOTOCHEMISTRY OF NITRO COMPOUNDS**

The evidence of the formation of the radicals was given by ESR signals. Further reactions of a simple radical in inert solvents can be presented by scheme (16):

\[
\begin{align*}
\text{CH}_3 & \quad \rightarrow \quad \text{CH}_3^* \\
\text{NO}_2^* & \quad \rightarrow \quad \text{H}^+ \quad \text{CH}_3 & \quad \rightarrow \quad \text{CH}_3^* \\
\text{CH}_3 & \quad \rightarrow \quad \text{H}^+ \\
\end{align*}
\]

(16)

For more details on the photochemistry of nitro compounds see *Encyclopedia of Explosives* [47].

**REFERENCES**

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CHAPTER 6
NITRO DERIVATIVES OF BENZENE
(Vol. I, p. 230),
TOLUENE (Vol. I, p. 265)
AND OTHER AROMATICS

The properties of higher nitrated derivatives of benzene and toluene were given in Vol. I (pp. 230, 265) and more detailed and modernised data in the monograph by Meyer [1]. Only those properties which have not been recorded in the said books or given in the literature recently will be mentioned here. With regard to the chemical properties, one of the most characteristic features of polynitro aromatics is their ability to nucleophilic substitution. This is discussed in Chapter IV in general terms and some features will be given here in the description of particular nitro compounds.

NITRATION OF BENZENE TO NITROBENZENE

The heterogeneous nitration of benzene has been reviewed by Albright, Hanson and co-workers [2]. They drew attention to the problem of diffusion control which has already been discussed in Chapter II. The differences between the results of various authors was partly due to insufficient appreciation of the problem of diffusion. It is true that nitration occurs mainly in the acid phase and at the interface between acid and organic phases. However, the role of diffusion and solubility of organic compounds in each phase can be decisive and so is adequate mixing. The authors also described their own work where they used a continuous flow stirred tank reactor of 50 ml capacity made of stainless steel and jacketed for temperature control. The agitator of 2.5 cm diameter was a four-blade operator at 3000 rpm. They found that the solubility of benzene in acids changed almost linearly as the concentration of nitric acid changed in the mixed acids. The solubility of benzene was about four times greater than that of toluene. Subsequently the nitration of benzene is only 5 times slower than the nitration of toluene, although earlier reports gave a figure of 20 times slower. The latter figure was based on one phase nitration systems and can be misleading for industrial reaction.

Nitrobenzene (Vol. I, p. 231)

Although it is not an explosive, nitrobenzene created an interest as an intermediate in the formation of di- and tri-nitrobenzene. Also it was known that at high temperature in the presence of an alkali it is subjected to explosive decomposition.

Powerful liquid explosives mixtures of nitrobenzene and liquid N2O4 were also known and in some use (Vol. III, p. 289). Recently pyrolysis of nitrobenzene was examined in the range of 275–630°C [3]. At lower temperatures nitrobenzene decomposes via direct rupture of the C–N bond to give free radicals C6H5⋅ and ⋅NO2. As the temperature was raised the yield of NO2 considerably decreased and at 625°C the volatile products were composed of:

| 1.2% | NO2 |
| 28.0% | NO |
| 1.2% | N2O |
| 61% | CO |
| 8% | CO2 |

The liquid products contain: benzene (21%), phenol (19%), diphenyl (8%), benzonitrile (5%), dibenzofuran (8.5%), benzoquinoline (2.5%) among other less defined substances. Among earlier papers see also that of Fields and Meyerison [4] (see p. 113). Hand, Merritt and Di Pietro [5] which referred to phenyl free radical and nitrobenzene formed by pyrolysis.

Nucleophilic substitution of nitrobenzene with some carbonations was described in Chapter IV.

The industrial method for the nitration of benzene to nitrobenzene is described in the paragraph dedicated to nitration of toluene.

m-Dinitrobenzene

An early paper on the crystal structure of m-dinitrobenzene should be mentioned [6]. The method of Fourier series and a projection of the electron density gave the following result. Benzene ring is a regular hexagon of side 1.41 Å. C–N bonds do not lie in the plane of the ring but make an angle of 15° with it. The C–N distance is 1.54 Å, the N–O distance has been found to be 1.20 Å and O–O distance in the nitro groups is 2.17 Å.

An interesting synthesis of biaryl systems which is a modification of the Ullmann method was recently given by Comforth and Wallace [7]. It consists in acting upon m-dinitrobenzene with aryl iodides under the influence of copper t-butoxide (1).

The yield of 2,6-dinitrodiphenyl derivatives varied from 10 to 96% depending on aryl.

New data have appeared on the vapour pressure of m-dinitrobenzene [11] – p. 94. This is of importance because of the danger of handling this highly toxic
A few more charge-transfer complexes have been described of sym-trinitrobenzene with: phloroglucinol and nitrophloroglucinol [9], picric acid [10], ferrocene [11].

Although the compound possesses very good explosive properties an application could not be found for it owing to the difficulty of making it. A new laboratory method was given by Olah and Lin [12] of nitrating m-dinitrobenzene to sym-trinitrobenzene with nitronium tetrafluoroborate in fluorosulphuric acid solution. A short description of the method is given below.

Nitronium tetrafluoroborate and m-dinitrobenzene were added to fluorosulphuric acid and cooled in a dry ice/acetone bath. The temperature was gradually raised to 150°C. After three hours of heating the reaction mixture was poured on to crushed ice. The nitro product was extracted with dichloromethane, washed with sodium hydrogen carbonate solution and dried over magnesium sulphate. The yield of sym-trinitrobenzene was 61.6% with 5% unreacted m-dinitrobenzene.

The reaction time of 2.2 hours gave a 66% yield of sym-trinitrobenzene and 17% of unreacted substrate. A reaction time of 3.8 hours gave a 49.3% yield of high purity sym-trinitrobenzene.

sym-Trinitrobenzene can be subject to a number of nucleophilic reactions. The known reaction for transformation of this compound into 3,4-dinitrophenol under the action of alkalis (Vol. 1, p. 251, reaction 11) was facilitated by irradiation with ultraviolet [27, 28]. Pure 3,5-dinitrophenol without the azoxy compound resulted.

1,2,3,5-Tetranitrobenzene (Vol. 1, p. 257)

1,2,3,5-Tetranitrobenzene was obtained by a new method established by Nielsen and co-workers [13]. In general terms it consists in the oxidation of an amino group of polynitroanilines with concentrated (98%) hydrogen peroxide in 100% sulphuric acid. The reaction of picramide was carried out below 30°C with an excellent yield:

\[
\begin{align*}
\text{NO}_2 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2 + \text{NO}_2
\end{align*}
\]

\[
\begin{align*}
\text{O}_2\text{N} + \text{H}_2\text{SO}_4 \rightarrow \text{O}_2\text{N} + 93.5\%
\end{align*}
\]

Electrochemical properties

The ease of reduction of the nitro group of aromatic nitro compounds suggested using aromatic nitro compounds for electrochemical cells. The electrochemical cell Mg/m-DNB seems to be particularly suitable giving a high yield of 160 Wh/kg. The reaction requires an acid or neutral medium [85].

Isomeric dinitrobenzenes

High purity o- and p-dinitrobenzene can be obtained by the oxidation of o- and p-nitroaniline respectively. The oxidation was carried out with hydrogen peroxide (30%) in acetic acid [36].

Some attention was paid to o-dinitrobenzene as an oxidizing agent (Chapter IV).

sym-Trinitrobenzene (Vol. 1, p. 248)

Some new data have been published [1] on the physical properties of sym-trinitrobenzene such as vapour pressure between 122°C (m.p.) and 270°C.
According to Nielsen [16] the method consists in the action of peroxydisulphuric acid \( \text{H}_2\text{S}_2\text{O}_8 \):

\[
\text{H}_2\text{O}_2 + 2\text{H}_2\text{S}_2\text{O}_8 \rightarrow \text{H}_2\text{S}_2\text{O}_6 + 2\text{H}_2\text{O}.
\]  

(3)

Murto [14] examined the action of sodium ethoxide on 1,2,3,5-tetranitrobenzene. It produced a red colour attributed to the formation of a quinoid structure and eventually sodium picrate. A more detailed study of the action of nucleophiles on 1,2,3,5-tetranitrobenzene was made by Crampton and El Gharani [15]. They obtained o-complexes of Jackson–Meisenheimer type.

1,2,4,5-Tetranitrobenzene (Vol. I, p. 259)

Crampton and El Gharani [15] examined the behaviour of 1,2,4,5-tetranitrobenzene (m.p. 188°C) towards nucleophile and found that o-complexes were being readily formed. Nielsen and co-workers obtained [16] the same product of higher purity (m.p. 190–191°C) by the oxidation of 2,4,5-trinitroaniline with 90–98% \( \text{H}_2\text{O}_2 \) in oleum or 100% sulphuric acid.

1,2,3,4-Tetranitrobenzene

The new compound – 1,2,3,4-tetranitrobenzene was obtained by Nielsen and co-workers [16] by the oxidation of 2,3,4-trinitroaniline with hydrogen peroxide (98%) in sulphuric acid (100%) at 10–18°C with a 78% yield. Oxidation with concentrated hydrogen peroxide in the presence of sulphuric acid forms a new modification of the method for the introduction of a nitro group, described earlier by Nielsen and co-workers [13], where no sulphuric acid was used.

Pentanitrobenzene

Other high nitrated derivatives of benzene obtained by the method of Nielsen [16]

Tetranitroaniline (Vol. I, p. 560) was used by Nielsen and co-workers [13] to oxidize it with 98% \( \text{H}_2\text{O}_2 \) in the presence of 20% oleum at a temperature below 30°C. Pentanitrobenzene resulted.

Hexanitrobenzene (HNB) (Vol. I, p. 259)

![Hexanitrobenzene](image)

m.p. 246–262°C

The method given in Vol. I could not be repeated. Also no data on the preparation were given and the only paper published until recently was on crystal structure [17] and some data on the properties [18]. It decomposes in air to yield trinitrophloroglucinol. Its density is \( \alpha \), 2.0 and the rate of detonation (at \( \rho = 1.9 \)) is 9500 m/s.

Nielsen and co-workers described in their remarkable papers [13, 16] the formation of hexanitrobenzene by oxidation of pentanitroaniline.

The reaction was carried out either (1) in fuming (20% \( \text{SO}_3 \)) sulphuric acid at 25–30°C by adding 98% \( \text{H}_2\text{O}_2 \) or (2) in trifluoromethanesulphuric at 45–55°C with 90% \( \text{H}_2\text{O}_2 \). The product was extracted with dichloromethane and dried over magnesium sulphate (which also removed trifluoromethane sulphuric acid). Method (2) gave 90% yield.

A lower yield (58%) was obtained by method (1).

Also a relatively low yield was produced with potassium persulphate instead of hydrogen peroxide.

Wide range of m.p. is explained in terms of the formation of a few decomposition products in the course of heating near the m.p. of the substance. At 100°C nitro groups are transformed into phenolic groups yielding pentanitrophenol, tetranitrosoresorcinol and eventually trinitrophloroglucinol. In the absence of light HNB shows good stability at room temperature, but irradiation produces an interesting isomerization of nitro groups to nitrites which in turn are hydrolysed to phenolic groups [120]:

\[
\text{NO}_2 \xrightarrow{\text{hv}} \text{ONO} \rightarrow \text{OH}
\]

The following were the compounds obtained by oxidation of the nitro derivatives of aniline:
1,2,3-trinitrobenzene (Vol. I),
1,3-difluoro-4,5,6-trinitrobenzene (m.p. 88–90°C)
1,3-difluoro-2,4,5,6-tetranitrobenzene (m.p. 99–100°C)
fluoro-pentanitrobenzene (m.p. 152–154°C)

The latter three compounds are new to the literature.

NITRO DERIVATIVES OF TOLUENE

Nitrated of Toluene to Nitrotoluenes (Vol. I, p. 265)

Formation of nitrotoluenes is an important step in the manufacture of the trinitro product and has been the subject of some review articles: [19, 20] which were dedicated to the kinetics of mononitration.

Giles, Hanson and Ismail [19] found that in mononitration of toluene with a standard nitration mixture of nitric–sulphuric acid and water, the organic phase contained nitric and nitrous acids, but did not include sulphuric acid and water. The authors also studied the role of agitation. Their conclusion was similar to that reported previously [2] that mass transfer between the phases plays an important role, and a fast reaction takes place in a zone in the aqueous phase adjacent to the interface. It is important to know the diffusivity of the aromatic substrate in the aqueous phase which depends on the design of the nitrat. The paper by Strachan [20] also points out the importance of mass transfer in agreement with a previously described statement (Vol. I, p. 49).

As has been already pointed out (Vol. I, p. 265) and Chapter III, in the mononitration of toluene, nitroresols are formed [21]. They can be further nitrated to yield trinitroresol and oxidized to oxalic acid. The presence of trinitroresol is most undesirable (formation of sensitive salts) and therefore mononitrotoluenes should be washed with alkali to remove the nitroresols (Vol. I, p. 359).

Some efforts have been made to reduce the proportion of undesirable m-nitrotoluene. A general rule is that the lower the temperature of nitration the smaller the proportion of meta isomer (Vol. I, p. 273). Also the use of nitric acid acetic anhydride mixture at 0°C can assure a lower proportion of m-nitrotoluene, for example to reduce it to 1.6% [22]. This is in agreement with former findings (Vol. I, p. 274).

Isomer control in the mononitration and dinitration of toluene was studied by Harris [23, 24]. Both papers were dedicated to the increase of p-nitrotoluene which is an important intermediate in dyestuffs and pharmaceuticals manufacture, where both α- and m-isomers are waste products and the high proportion of 2,4-dinitrotoluene is desirable for isocyanate production. This aim was achieved by adding phosphoric acid to the nitration mixtures.

A number of papers (in addition to those mentioned in Vol. I) were given by Kobe, R. M. Roberts and co-workers [122–125] on the determination of the isomer distribution of the nitration of α-, m- and p-nitrotoluenes by the method of isotope dilution analysis.

The nitrination of toluene to trinitro products will be presented in a separate paragraph.

Mononitrotoluenes

A few unexpected reactions of nitrotoluenes have been recorded in recent years. Such is the reaction described by Hakanson and Nielsen [25] of the oxidation of o-nitrotoluene with dilute (35%) nitric acid at 190°C to yield (30%) picric acid. On the contrary m- and p-nitrotoluenes yield m- and p-nitrobenzoic acids. In addition to picric acid also nitro- and dinitrobenzoic and 3,5-dinitrosalicylic acids were formed. A large quantity of nitrogen was evolved and this led the authors to rationalize the reaction as passing through the formation of a diazo compound.

p-Nitrotoluene under action of ammonia in the presence of catalysts (Si-Mo-V-Bi-Base) at elevated temperature (4) was converted to p-cyanoaniline in addition to aniline and the expected p-toluidine.

\[ \text{CH}_3 \quad \text{OH} \quad \text{CN} \quad \text{NH}_2 \quad \text{H} \]

INDUSTRIAL METHODS OF MONO-NITRATION OF BENZENE

Industrial methods of mono-nitration of benzene and toluene are either periodical or continuous. More attention is now given to continuous methods – safer and more economic when applied to a large, continuous production. Nevertheless, periodic nitration is still in use for smaller and less regular production.

Matsa and Matsa [29] in their monograph collected technical data on the nitration of benzene and toluene (Table 26).

<table>
<thead>
<tr>
<th>Components*</th>
<th>Nitrating acid</th>
<th>Benzene</th>
<th>Spent acid</th>
<th>Nitrating acid</th>
<th>Toluene</th>
<th>Spent acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>32</td>
<td>1</td>
<td>28</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>60</td>
<td>83</td>
<td>56</td>
<td>69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>8</td>
<td>15</td>
<td>16</td>
<td>29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>2</td>
<td>2</td>
<td>–</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature °C</td>
<td>40</td>
<td>60</td>
<td>60</td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction time min.</td>
<td>60</td>
<td>75</td>
<td>100:100</td>
<td>100:100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ratio HNO₃ : hydrocarbon</td>
<td>100:100</td>
<td>100:100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yield in % of theoretical</td>
<td>98</td>
<td>97</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* In weight per cent.
Removal of Phenolic Byproducts

To free the aromatic mononitro products from phenolic by-products the usual industrial procedure consists in washing the nitro compound with water to free it from acids and then washing with dilute sodium hydroxide (concentration 1–5% NaOH and an excess of 5–15%). The process is efficient as regards to purification of the nitro compound but produces a considerable amount of water containing sodium phenates and is an obnoxious effluent. This can be dealt with by acidification and extraction of phenols with organic solvent immiscible with water (such as benzene or more costly solvents). The method is expensive and led to the search for another method. Hanson and co-workers [30] developed a method of extracting phenolic compounds with a weak basic regent such as phosphate salts. A mixture of trisodium and disodium hydrogen phosphate, for example 64.2 g/l of Na$_2$HPO$_4$·2H$_2$O with 21.9 g/l of Na$_3$PO$_4$·12H$_2$O. After separation from the purified nitro compound the aqueous solution of phosphates and sodium phenates is mixed with benzene which dissociates the phenates and the liberated phenols are dissolved in benzene. The main constituent (ca. 80%) of phenolic fraction is 2,6-dinitro-p-cresol.

Periodic Nitration

Little can be added to the design of periodic nitrators as given in Vol. I, p. 155 (contrary to the continuous nitrators). An interesting innovation (which can also be used in continuous nitrators) deals with the control of the efficiency of stirring as given in the monograph by Chekalin, Passet and Ioffe [31]. It consists of a T-shaped glass tube on the lid of the nitrator. The tube is connected with a steel tube reaching the bottom of the nitrator (Fig. 16). The U-tube is filled with a coloured electrolyte solution and connected to an electric circuit. When the stirrer is in motion the pressure inside the nitrator increases and this is manifested by the difference of the levels in the U-tube. As a consequence the electric circuit is disconnected. When mixing stops (or is inadequate) the levels in the U-tube equalize, the circuit is closed and an acoustic or light signal gives a warning.

The emulsion of the nitro product and spent acid enters a separator which is designed on the principle of a laboratory separating funnel [31].

The nitro compound forms the upper layer. The spent acid is taken through the bottom valve and switched to another container when the upper layer appears in the 'lantern' situated just above the valve. The spent acid is further treated with a fresh hydrocarbon which goes to the nitrator and the nitro product is washed with aqueous alkaline solution to remove acids and phenols.

Continuous Nitration

The advantages of continuous method have already been pointed out in Vol. I, p. 306. It should be added that continuous nitration does not involve losses in time used for loading, emptying the nitrator and heating and cooling its contents as in periodic nitration. According to Soviet authors [31] the production of nitrobenzene can be increased 15 times, by changing periodic into continuous nitration.

One of the popular designs for nitrators was given by Bizzari (Vol. I, p. 108, Fig. 47), originally designed for the nitration of glycerine and adapted with small changes for the nitration of aromatic compounds.

SOVIET METHOD (ACCORDING TO CHEKALIN, PASSET AND JOFFE [31])

The following is a diagrammatic presentation of a continuous nitrator made of stainless steel (Fig. 17).

The hydrocarbon enters through the top of the central, wide diameter tube where it is cooled, driven down and at the bottom meets the nitrating acid. Through energetic mixing the emulsion is formed and driven upwards through the stainless steel tube. Continuous outflow of the emulsion is achieved from the upper part of the nitrator.
It is of great importance that the continuous nitrator should be completely airtight.

The emulsion enters the continuous cylindrical separator (Fig. 18) near the middle of its height. The place of entrance is changed depending on the nitrated substance; it should correspond to the surface of the separation of phases.

The lighter nitro compound flows to the upper part of the cylinder and the heavier spent acid flows out through a syphon tube. It is advisable to fill the cylinder with Raschig rings.

A general diagram of continuous nitration of benzene (and also toluene) according to Soviet sources (Chekalin, Passet and loffe [31]) is given in Fig. 19. The nitrator is provided with a cooling mantle, two cooling coils of different tube diameters, the stirrer has an upper turbine mixer driving the liquids downwards and a lower propeller. The supply of hydrocarbon, nitrating acids, spent acid and cooling liquid (usually water) is regulated in such a way as to keep the temperature of nitration at 65-68°C in the case of nitration of benzene. The concentration of nitrobenzene in the acid remains constant ca. 5%. The emulsion enters two spiral 'coolers' where the reaction is ended: 90% of nitric acid is used in the nitrator and 9-9.5% in the coolers; thus 98-99.5% of nitric acid is used for the

FIG. 17. Continuous nitratror according to Chekalin et al. [30]. 1. Stirrer, 2. tubular cooler and heater, 3. stainless steel plate, 4. regulation valve.

FIG. 18. Continuous separator according to Chekalin et al. [30].

FIG. 19. General scheme of nitration of benzene or toluene according to Chekalin et al. [30]. 1. benzene or toluene storage tank, 2. measuring tanks for the hydrocarbon, nitration acid, spent acid, 3. continuous separator, 4. spent acid tank, 5. spiral coolers, 6. nitrator of continuous action.
nitration. In the second spiral cooler the reaction mass is cooled to 30°C. It should be understood that the spiral coolers are provided with stirrers. From there the emulsion enters the continuous separator. Due to the great difference of the density of nitrobenzene (or nitrotoluenes) and the spent acid, the separation takes 5–10 min.

Every 1000 kg of nitrobenzene gives 900–1000 kg of spent acid containing 70–73% H₂SO₄, 1.5–2.2% nitrobenzene and 0.25–0.5% nitric acid. Nitrobenzene is extracted from the spent acid with benzene. The latter is partly nitrated with the residual nitric acid and the content of nitrobenzene and nitric acid after the extraction falls to 0.1–0.15% and 0.01–0.03% respectively. Benzene with a small quantity of nitrobenzene is sent to the storage tank and from there to the nitrator.

It is strongly emphasised that perfectly faultless automation is necessary for the safe and efficient process. Thus the ratio: hydrocarbon/acid is under automatic control according to the temperatures of the reaction, cooling liquid inflow is regulated according to the temperature of the cooling liquid leaving the nitrator. The cooling water entering the spiral coolers is also automatically controlled. If the mixing in the nitrator and supply of cooling liquid becomes inadequate, the flow of hydrocarbon into the nitrator is automatically stopped and the whole plant ceases to operate.

**BOFORS NOBEL-CHEMATUR METHOD OF NITRATING BENZENE AND TOLUENE TO MONONITRO PRODUCTS (FIG. 20) [32]**

An innovation in the nitration technique was introduced by Boftors-Nobel-Chematur (Sweden). This is the so-called “Nitrator Circuit.” It consists in the ingenious use of a centrifugal pump as a nitrator. A cooler and a gravimetric separator are included in the circuit. Cooled acids and hydrocarbons are injected into the circuit. Hydrocarbons are: benzene or toluene used for the extraction of spent acid together with fresh hydrocarbons. The nitro compound and the spent acid overflow to the gravimetric separator and are split into streams of spent acid and a nitro compound. The spent acid is mixed with fresh hydrocarbon and subsequently the latter enters the circuit as mentioned above. The spent acid containing 70% H₂SO₄ is removed and can be used for fertilizer production or can be concentrated and recycled for nitration. The nitro compound is washed with dilute NaOH solution to remove phenols.

The advantages of the nitrator circuit method are as follows: low oxidation due to the short contact time of the hydrocarbon with the acid, full nitric acid utilization, safety due to a very small quantity of the nitro compound in the circuit.

The following is the material balance given by Boftors-Nobel-Chematur (Table 27) [32]:

**TABLE 27: Consumption of materials in kg for production of 1000 kg of nitrobenzene and nitrotoluene**

<table>
<thead>
<tr>
<th>Material</th>
<th>Nitrobenzene</th>
<th>Nitrotoluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>650</td>
<td>686</td>
</tr>
<tr>
<td>toluene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric acid 98% as HNO₃</td>
<td>537</td>
<td>486</td>
</tr>
<tr>
<td>Sulphuric acid 96% as H₂SO₄</td>
<td>460*</td>
<td>390*</td>
</tr>
<tr>
<td>Sodium hydroxide as NaOH</td>
<td>5</td>
<td>10.4</td>
</tr>
</tbody>
</table>

* If the spent acid is concentrated the consumption is only 5% of the above figure.

**DINITROTOLUENES (Vol. I, p. 281)**

As is known dinitrotoluenes are not explosives by themselves but they are of course intermediates in the manufacture of TNT and are in use as ingredients of:

(1) mining explosives,
(2) some smokeless powders.

For mining explosives a low melting mixture of isomer is used. It is readily
miscible with nitroglycerine and dissolves soluble nitrocellulose. For smokeless powder a relatively pure 2,4-dinitrotoluene is used. For further nitration, dinitrotoluene—a mixture (m.p. ca. 35°C) is used and after nitration to trinitroproduct, the latter is purified.

**Physical (including thermochemical and explosive) Properties**

The following are figures for main isomers of dinitrotoluene according to Meyer [1].

<table>
<thead>
<tr>
<th></th>
<th>2,4-</th>
<th>2,6-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.521 g/cm³</td>
<td>1.538 g/cm³</td>
</tr>
<tr>
<td>Melting enthalpy</td>
<td>261 kcal/kg</td>
<td>225 kcal/kg</td>
</tr>
<tr>
<td>Enthalpy of formation</td>
<td>-89.5 kcal/kg</td>
<td>57.6 kcal/kg</td>
</tr>
<tr>
<td>Heat of detonation</td>
<td>1056 kcal/kg</td>
<td>1538 kcal/kg</td>
</tr>
<tr>
<td>Ignition temperature</td>
<td>360°C</td>
<td></td>
</tr>
<tr>
<td>Volume of detonation gases</td>
<td>6.02 l/kg</td>
<td></td>
</tr>
<tr>
<td>Lead block test</td>
<td>240 cm³ 10 g</td>
<td></td>
</tr>
</tbody>
</table>

The same source [1] gives vapour pressure of the 2,4-isomer:

at

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>35° C</th>
<th>70° C (m.p.)</th>
<th>100° C</th>
<th>150° C</th>
<th>200° C</th>
<th>300° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (mmHg)</td>
<td>0.014</td>
<td>0.111</td>
<td>0.83</td>
<td>8.5</td>
<td>50.5</td>
<td>300</td>
</tr>
</tbody>
</table>

The MAK-value (maximum permitted concentration in air at a workplace) is 1.5 mg/m³.

The specification of commercial product is as follows:

- moisture: no more than 0.25%
- benzene insoluble: no more than 0.10%
- acidity (as H₂SO₄): no more than 0.02%
- tetratinotmethane: absent
- solidification point
  - for smokeless powder grade: 68.0 ± 2.5°C
  - for commercial explosives: liquid solid mixture

Data for isomeric dinitrotoluenes are given in Vol. 1, pp. 281–282.

**Formation of Dinitrotoluenes from mononitrotoluenes** (Vol. I, p. 285)

It is generally known that 2,4-dinitrotoluene is formed by nitration of o- and p-nitrotoluene and 2,6-dinitro isomer by nitration of o-nitrotoluene. It is accepted that 2,3-, 3,4- and 3,6-isomers are produced from m-nitrotoluene. Nevertheless it was firmly established that the nitration of o- and p-nitrotoluene can also produce a small proportion (below 0.5%) of 2,3- and 3,4-dinitrotoluene respectively [33]. Also small proportions of other isomeric dinitrotoluenes, such as 3,3-, 3,5- and 3,4- was proved from o- and p-nitrotoluene respectively [34]. Hill and co-workers [39] have found that the nitration of pure o- and p-nitrotoluene at −10°C with a nitrating mixture containing SO₃ yields only 0.1% dinitro- and trinitroproducts deriving from m-nitrotoluene.

The formation of m-nitrotoluene derivatives from o- and p-nitrotoluene can be understood on the basis of the electron densities, free valencies and localization energies as depicted in Fig. 14. Also the formation of 3,5-dinitrotoluene seems to be possible by direct nitration of m-nitrotoluene [34].

The exact analysis of the nitration product has almost been perfected since the advent of chromatographic methods (i.e. gas chromatography) and exact and reliable detection of isomers and impurities of lower and higher nitrated hydrocarbons [25–37] has been possible.

French authors [118] isolated pure isomeric dinitrotoluenes: 2,3, 2,5 and 3,4 from the product of the nitration of m-nitrotoluene by fractional distillation and repeated crystallization. 2,6-Dinitrotoluene was isolated by distillation of crude dinitrotoluene.

The following are setting points and distillation temperatures of isomeric dinitrotoluenes:

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Setting Point</th>
<th>Distillation Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,4</td>
<td>58.3</td>
<td>166–168°C, 10 mmHg</td>
</tr>
<tr>
<td>2,5</td>
<td>50.3</td>
<td>175–177°C</td>
</tr>
<tr>
<td>2,3</td>
<td>59.3</td>
<td>181–183°C</td>
</tr>
</tbody>
</table>

Recently 2,5-, 2,3- and 3,4-dinitrotoluenes were obtained by oxidation of 2-methyl-4-nitroaniline, 2-methyl-6-nitroaniline and 2-methyl-6-nitroaniline respectively [38]. The oxidation was carried out by hydrogen peroxide in acetic acid at 65–75°C. The yields were around 70% of theoretical.

As mentioned earlier low temperature nitration of toluene favours the reduction of the yield of m-nitrotoluene. This was examined in detail by Hill and co-workers [39]. They found that while lowering the nitration temperature from −5° to −35° a reduction of 3,4-, 2,3- and 2,6-dinitrotoluenes occurred from 2.06% to 1.40% and the setting point of the product raised from 61.0 to 63.7°C. According to the same authors the use of trifluoromethanesulphonic acid with nitric acid made it possible to use a very low temperature on mononitration (−110° to −60°C) and the temperature 0° to 25°C on dinitration. When mono-
Nitration was carried out at $-110^\circ C$ and dinitration at $0^\circ$ to $25^\circ C$, the content of isomeric dinitrotoluenes was as low as 0.33%. This figure is the lowest that has been recorded for dinitrotoluenes derived from toluene.

A problem was recently raised again on the production of high purity 2,4-dinitrotoluene not only because of its use in the manufacture of TNT but also for reduction to p-toluiledenediamine which is an important starting material for polyurethane. The general tendency is to use high purity p-nitrotoluene to introduce the second nitro group. Thus Vinnik and co-workers [95], Leitman and Fedorova [96], found that the nitration of pure p-nitrotoluene produces pure 2,4-dinitro product. Nevertheless Žižko and Matyš [97] stated on the grounds of their experiments that the nitration of pure p-nitrotoluene yielded 2,4-dinitrotoluene containing 0.3 % 0.5% 3,4-dinitrotoluene. The conditions of the nitration were as follows:

Nitration acid contained 25% $\text{HNO}_3$
70% $\text{H}_2\text{SO}_4$
5% $\text{H}_2\text{O}$

An excess of the acid over theoretical was 5%, the temperature of nitration between 75 and $95^\circ C$. The yield of 96% of the product with setting point over 69.5ºC was obtained. Crystallization from ethanol or trichloroethylene yielded practically pure 2,4-dinitrotoluene.

INDUSTRIAL METHODS OF DINITRATION OF BENZENE AND TOLUENE

Matasă and Matasă [29] collected the technical data on dinitration of mono nitro derivatives of benzene and toluene.

Modemized Pilot-plant and Industrial Production of DNT

Three modern methods of dinitration will be given here:

1. Pilot-plant method by Haas and co-workers [40] of low temperature nitration of toluene.
2. Continuous method of Bofors-Nobel-Chematur two-step process with a pump nitratior [32, 41].

Low Temperature Nitration of Toluene to DNT [40]. - Fig. 21

The principle was based on the nitration of toluene by anhydrous mixtures composed of nitric acid and oleum at temperatures between $0^\circ$ and $-10^\circ C$ (freezing point of the solution) [39]. The dinitration was nearly quantitative (over 99%) when the molar ratio $\text{HNO}_3$/toluene was 2:1. 2:2. With the increase of the ratio (e.g. to 4) the yield decreased (ca. 98%). The optimum was obtained with molecular proportion of reagents

- Toluene: 1.0
- $\text{HNO}_3$: 2.11
- $\text{SO}_3$ (as 20% oleum): 1.97
- $\text{SO}_3$/HNO$_3$ ratio: 0.93

The yield at $-10^\circ C$ was 99.4%.

These experiments served as a basis for DNT pilot plant development [40]. Toluene has a low solubility in nitric acid, subsequently, toluene is added just
ahead of the centrifugal pump. Toluene is dispersed into the anhydrous acid at 
$-8^\circ$C.

The dinitration is carried out in four recycle nitrators. The acid stream moves 
through the reactors and toluene is added to each of the first three. The effluent 
from the last nitrator has the composition in wt%:

<table>
<thead>
<tr>
<th>Compound</th>
<th>12.5</th>
<th>5.5</th>
<th>0.2</th>
<th>68.9</th>
<th>12.8</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dinitrotoluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trinitrotoluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitroylsulphuric acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The effluent is heated from $-8^\circ$ to $35^\circ$C in a tank where the product is 
divided into two phases. The upper phase enters the trinitrator and the lower 
acid phase is diluted with water to reduce the concentration to 70% H$_2$SO$_4$. The 
nitro compounds are separated and sent to the trinitrator and spent acid to the 
concentration unit.

The diagram of the system is given in the paragraph on trinitration.

**Bofors-Nobel-Chematur Method of Manufacture of DNT (Fig. 22) [134]**

This method is based on the principle of a circuit nitrating pump for the 
production of nitrobenzene and dinitrotoluene, as described already (p. 151). Each 
circuit is comprised of the nitrating pump, cooler, separator and acid overflow 
vessel. The toluene led to the mononitrating circuit leaves the separator, is 
pumped as mainly mononitrotoluene to the dinitration circuit and leaves the 
separator as DNT ready for washing. The sulphuric acid led to the dinitration 
step flows downstream and leaves the mononitrating circuit acid to overflow as

spent acid. Nitric acid is fed to both circuits meeting the requirements of fully 
nitrated dinitro product and possibly complete consumption of nitric acid. The 
spent acid contains ca. 70% H$_2$SO$_4$ and less than 0.5% HNO$_3$ and does not 
require denitrification.

An important innovation is the use of Bofors-Nobel centrifugal separator 
which minimizes the volume of the circuits and the size of the plant (Figs 23 and 
24). It was originally designed in the 1960s for nitroglycerine manufacture, now

![Figure 23: Bofors-Nobel Centrifugal Separator](image-url)

**FIG. 23. Bofors-Nobel Centrifugal Separator. Courtesy A. B. Bofors-Nobel-Chematur.**

...it is accepted for DNT and TNT production. It changes the classical static separator, considerably reduces the amount of the explosive in the apparatus and is 
particularly suitable for use in continuous methods. It can be used to separate 
the nitro product from the spent acid and in the process of purification and 
washing of the nitro product. According to the manufacturer it can be easily 
cleaned. A relatively low operating speed of 500 - 1000 rpm is much below the 
critical figure. The separator can be installed in the nitrator - this design is 
described in the paragraph dedicated to the manufacture of TNT.

**Biauzzi S.A., Vevey Continuous Method (132)**

The continuous Biauzzi nitration process was used for the first time in 1935 
for the manufacture of nitroglycerine. It soon became clear that many advantages 
were offered by this system such as the increased reaction speed, the high

![Figure 22: Bofors-Nobel-Chematur method of manufacture of DNT (diagrammatic presentation)](image-url)

heat transmission coefficient, the new method of separating the phases, washing by counter-current flow could be applied to the nitrations of other organic products such as aromatic compounds.

A general scheme is presented in Fig. 25.

The reaction takes place in nitrators into which toluene and mixed acid is introduced continuously in exact proportion. The number of nitrators in the series varies from two to four. The temperature in each nitrator is kept constant.
by a thermostatic system. The stirring is achieved by a turbine acting as a pump. The emulsion from the nitrator enters a 'semistatic' Biazzi separator. The separated product is nitrated in next nitrators followed by a second separator.

The spent acid from the second separator is used as nitrating acid for the previous stage.

The final spent acid is generally mixed with toluene to extract dissolved nitro-bodies and use up the small remaining quantity of nitric acid.

The separated DNT is washed with water, with an alkaline solution and finally with fresh water. The water from the last wash is used again for the next wash. Between each wash the product is separated in a Biazzi separator.

The plant is made of stainless steel.

The manufacturing parameters are kept constant by automatic remote control. Among recorded parameters is the Redox value of the spent acid fully described in Chapter XI. In case of any irregularity the plant is automatically stopped and an alarm given in the control room.

TRINITROTOluene (Vol. I, p. 290)

2,4,6-Trinitrotoluene (TNT) remains the most popular explosive because of its stability, low sensitivity to impact, friction and high temperature and well-developed methods of manufacture. It is widely used in commercial explosives as a good sensitizer and is much safer in production and handling than nitroglycerine. For commercial explosives lower grade purity of TNT is being used whereas the military grade TNT must be a highly pure compound.

Physical (including thermochemical and explosive) Properties

The setting point of TNT for military purposes should not be lower than 80.2°C. Chemically pure substance shows 80.8°C. TNT recrystallized from nitric acid is commercially available; its setting point is 80.6...80.7°C [1a].

The following are figures related to properties of TNT according to Meyer [1].

Thermal conductivity of 2,4,6-trinitrotoluene was determined by Belayev and Matushko [43]: \( \lambda \times 10^4 = 4.8 \text{ cal/cm sec degree} \) for pressed substance and 3.5 \( \text{cal/cm sec degree} \) for powder. The temperature conductivity \( a \times 10^4 = 8.5 \text{ cm}^2/\text{sec and 11.5 cm}^2/\text{sec} \) respectively.

The following are data for the velocity of detonation calculated for the infinite diameter and density \( \rho \) [42]:

\[
D_{\infty} = 1872.7 + 3187.2 \rho
\]

when \( \rho = 0.9 \) to 1.5343.

At higher densities:

\( \rho = 1.5543 - 1.636 \)

<table>
<thead>
<tr>
<th>Density (crystals), g/cm³</th>
<th>1.654, molten 1.47 g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point, °C</td>
<td>254.3°C</td>
</tr>
<tr>
<td>Specific heat at 20°C, J/g</td>
<td>3.33 J/g</td>
</tr>
<tr>
<td>Enthalpy of formation, kJ/mol</td>
<td>42.8 kJ/mol</td>
</tr>
<tr>
<td>Heat of detonation, kJ/mol</td>
<td>1080 – 1210 kJ/mol</td>
</tr>
<tr>
<td>Ignition temperature, °C</td>
<td>300°C</td>
</tr>
<tr>
<td>Volume of detonation gases, L</td>
<td>3.62 L</td>
</tr>
<tr>
<td>Lead block test, kg</td>
<td>100 g</td>
</tr>
<tr>
<td>Impact sensitivity, m/s</td>
<td>1500 m/s</td>
</tr>
<tr>
<td>Friction sensitivity, kgf</td>
<td>120 kgf</td>
</tr>
</tbody>
</table>

Critical diameter in steel tube, mm

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Critical Diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.57</td>
</tr>
<tr>
<td>150</td>
<td>2.2</td>
</tr>
<tr>
<td>200</td>
<td>5.5</td>
</tr>
<tr>
<td>250</td>
<td>8.5</td>
</tr>
</tbody>
</table>

(room temperature) 100°C

\[
D_{\infty} = 6752.2 + 3187.2 (\rho - 1.5342) - 25102 (\rho - 1.5342)^2 + 115056 (\rho - 1.5342)^3
\]

The figures are valid for diameters from 0.7 to 7.8 cm. Meyer [1] gives 6900 m/s for \( \rho = 1.60 \).

The specification for commercial product is according to [1]:

Appearance: light yellow coloured flakes or crystals

Setting point for TNT of highest purity min 80.6°C

for some commercial explosives 80.2...80.4°C

ammonium nitrate commercial explosives various lower setting points

Volatile: none

Tetranitromethane: no more than 0.1%

Acidity (as H₂SO₄): no more than 0.005%

Alkalinity (as Na₂CO₃): no more than 0.001%

Benzenes insolubles: no more than 0.05%

Minerals (as ash): no more than 0.01%

For a long time the setting point was the most common criterion of the purity of TNT. However, it has also been recognized for some time that it does not answer all the problems of the practical use of the explosive. One of the important problems is the exudation of a multicomponent eutectic mixture of isomeric trinitrotoluenes and dinitrotoluenes. Even a minute quantity of these substances can produce an inconvenience through the exudation.

This can occur in the course of the storage of projectiles with TNT particularly in summer time. The problem was recently reviewed by Reitsma [76]. Here are the main disadvantages produced by the exudation:

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CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

(1) it may affect the functioning of some components of the ammunition (e.g. initiators).
(2) cavities and cracks may be formed in the TNT casting and create a danger of premature detonation,
(3) the migration of explosive mixture to the screw thread of the fuse also creating a danger.

In the Federal Republic of Germany the exudation test consists in placing a cylinder of cast TNT on filter paper and keeping it at 70°C for 20 hours. The diameter is then determined by the stain on filter paper and also the loss of weight of the cylinder.

Reitsma examined different factors influencing the test, for example higher humidity favours the exudation. The test is not only influenced by impurities of TNT but also by the crystal size of the cast. Pressed cylinders of TNT do not show the exudation.

His conclusion is that the practical value of the test in its present form is limited.

Attention should be drawn to the microscopic examination of cast TNT. Thorpe and Connick [126] suggest polishing the cast sample with MgO powder and direct observation by reflected light. The previously suggested ‘peal’ method by Williamson [127] does not reveal sufficient structural detail.

Thorpe and Connick suggested:
(1) preliminary polishing with wet silicon-carbide paper,
(2) intermediate polishing by hand on nylon velvet using MgO powder,
(3) finishing by vibratory polishing,
(4) an etch with bromoform shows up the grain orientation of the TNT matrix.

Among the properties of 2,4,6-trinitrotoluene related to its explosive character, very important is the sensitivity to high temperature. High sensitivity of molten TNT to impact was described in Vol. I, pp. 319–320.

Another problem is its thermal decomposition. T. Urbanski and Rychter [44] examined the decomposition at temperatures near 400°C and above. The energy of activation between 380–440°C was of the order of 14 kcal/mol. Between 490 and 750°C trinitrotoluene took spherical shape and decomposed slowly with the evolution of a considerable amount of soot. The energy of activation in the range of temperatures 490–750°C was of the order of 8 kcal/mol and the shape of the curve: induction period against temperature was analogous to that shown for nitroglycerine in Vol. II, p. 50, Fig. 13.

Kamlet and co-workers [45] undertook the task of elucidating chemical changes of 2,4,6-trinitrotoluene which occurred during its isothermal decomposition at 200°C. 75–90% of TNT remained unchanged after 16 hours. The main products were: 4,6-dinitroanthranil (I) (2–4%), 2,4,6-trinitrobenzaldehyde (1–2%), 2,4,6-trinitrobenzyl alcohol (ca. 0.2%) and a minute amount (ca. 0.1%) of an azoxy compound of a probable structure (II).

Camera and Biasutti [121] developed an interesting method of isothermal pressure metering for the determination of chemical stability of aromatic nitro compounds, as described in Chapter IV. It showed that a temperature as low as 200°C could be dangerous if DNT pure, or with TNT, is kept for less than 16 hours (e.g. 18 hours) at this temperature.

Also the addition of many foreign substances to molten TNT can create a great danger (see the paragraph on safety of manufacture and handling aromatic nitro compounds).

The formation of an azoxy compound is not surprising considering the ease of transformation of nitro compounds into benzazoxy derivatives. Among them is known an important by-product of the continuous methods of making TNT known as ‘white substance’ (p. 169). A few unidentified products of oxidation and reduction were isolated, all of which had high melting points. In up to 15% a polymeric substance was formed, insoluble in benzene, which did not melt below 300°C and burned when ignited by a flame. The substance was named ‘explosive coke’. No sym-trinitrobenzene was found by Kamlet et al., contrary to the statement by Rogers [46]. Kamlet suggested that a minor quantity of TNB could be produced through the oxidation of TNT to trinitrobenzoic acid followed by a loss of CO₂ (the usual reaction leading to TNB) and after that TNB was lost in the ‘explosive coke’.

An important finding of Kamlet and co-workers was that at 210°C a spontaneous self-ignition of TNT occurred after 14–16 hours (or less) of heating.

The thermal decomposition of TNT is accompanied by the formation of free radicals, Jantzen [108] found free radicals at 240°C.

Hara, Kamei and Osada [109] described a detailed study of the thermal decomposition of TNT. They examined the decomposition by differential thermal analysis, thermogravimetry, infra-red spectroscopy, ESR and mass spectrometry. One of their most important findings was that TNT produced free radicals already in the vicinity of the melting point, that is 80°C. The substances which promote the decomposition of TNT are free radicals which are stable at room temperature. They are insoluble in benzene or chloroform and are partly oxidized polymeric substances.
Chemical Properties of 2,4,6-Trinitrotoluene

**Acid properties.** The acid properties of 2,4,6-trinitrotoluene were discussed in Vol. I (p. 300). This problem was reviewed with the reactions of the formation of \( \alpha \)-complexes (Chapter IV). Acid properties were also examined by modern methods. Thus Schaal [47] gave the following figures for \( pK_a \) of trinitrotoluene, as compared with dinitrotoluenes:

\[
\begin{align*}
2,4,6\text{-trinitrotoluene} & \quad pK_a = 14.45 \\
2,4\text{-dinitrotoluene} & \quad 17.12 \\
2,6\text{-dinitrotoluene} & \quad 19.00
\end{align*}
\]

Therefore, 2,6-dinitrotoluene is the weakest acid.

Buncel and co-workers [48] also came to the conclusion that 2,4,6-trinitrotoluene has acid properties. They based it on their report of a ready exchange of \( CH_3 \) protons of the compound in basic medium of deuterium oxide.

Fyfe, Malkiewich and Norris [94] examined intermediates formed by the action of bases on TNT using high resolution NMR spectroscopy. Within 0.5 sec of mixing equimolar proportions of TNT and methoxide in DSO and \( CH_3OH \) the Jackson Meisenheimer complex is formed. It decayed over 8 sec and the spectrum of anion according to (5) slowly appeared.

Salts of TNT were described in Vol. I, p. 304. A patent [79] claimed the use of salts of TNT for delay compositions.

**Action of light.** This was described in Chapter V on the photochemistry of nitro compounds.

**Reaction with Sodium Sulphite**

Reaction of 2,4,6-trinitrotoluene with sodium sulphite was extensively studied and reviewed by Crampton and co-workers [49], Strauss [50], Buncel and co-workers [51], Bernasconi and co-workers [52].

\( \alpha \)-Complexes with sulphonic groups are the products of the reaction of 2,4,6-trinitrotoluene \( (X = H) \) or trinitrobenzyl chloride \( (X = Cl) \) with one and two moles of sodium sulphite at \( 25^\circ C \): IIIa and b respectively.

According to Crampton [49b, d] dimethyl sulphoxide stabilizes the adduct 1:1. The compounds are soluble in water with a deep colour (440–460 nm and 550 nm).

---

NITRO DERIVATIVES OF BENZENE, TOLUENE AND AROMATICS

The reaction of sodium sulphite with unsymmetrical trinitrotoluenes is much more vigorous replacing \( meta \) nitro with sulphonic group (Vol. I, p. 332).

**Oxidation of 2,4,6-Trinitrotoluene**

Kamlet and co-workers [53] made an interesting and important observation that the oxidation of 2,4,6-trinitrotoluene with dichromate-sulphuric acid in the presence of nitric acid gave a high yield of para nitric acid, that is the methyl group is replaced by phenolic group, whereas the oxidation with pure dichromate-sulphuric acid yields, as known (Vol. I, p. 255), 2,4,6-trinitrobenzoic acid. The formation of picric acid was rationalized according to Kamlet as the result of oxidative aromatic nucleophilic substitution which passes through the intermediate formation of 2,4,6-trinitrobenzoic acid.

Thus, the oxidation of 2,4,6-trinitrobenzoic acid with dichromate -0.2% oleum in acetic acid solution yielded 71% picric acid.

Using acetic acid instead of nitric acid Kamlet et al. [53b] was also able to obtain picric acid from 2,4,6-trinitrotoluene. The yield was 70% by using chromium trioxide-sulphuric acid in acetic acid medium.

The oxidation of 2,4-dinitrotoluene [53a] with sodium dichromate in sulphuric acid in the presence of nitric acid yielded up to 45% of picric acid together with ca. 18% of 2,4,6-trinitrobenzoic acid. These authors found that 2,4-dinitrotoluene is more sensitive than 2,4,6-trinitrotoluene.

The oxidation-reduction process is involved in the formation of the 'white compound', a by-product of continuous production of TNT [54]. The formation of this compound is discussed in the paragraph on by-products of nitration of toluene to TNT.

**Reduction of 2,4,6-Trinitrotoluene**

An extensive study of the reduction of 2,4,6-trinitrotoluene was made by Nielsen, Coon and co-workers [55]. They also reviewed the existing literature. So far the use of different reducing agents produced mainly 4-amino-2,6-dinitrotoluene. Nielsen, Coon et al., examined the use of hydrogen sulphide in the presence of a catalytic amount of ammonia and found the reaction to be solvent dependent: in dioxane both 4-amino-2,6- and 2-amino-4,6-dinitrotoluenes being
formed. In ethanol the attack at position 4 is favoured but incomplete reduction to hydroxylamine derivatives also occurred.

The results can be summarized as follows (6):

\[
\begin{align*}
\text{Nitration of 2,4,6-Trinitrotoluene} & \quad (\text{Vol. 1, p. 212}) \\
\end{align*}
\]

In addition to the reaction of nitration reported by Fieser (Vol. 1, p. 212), a more recent observation was reported by Sauermilch [56]. It consists in warming 2,4,6-trinitrotoluene and sym-trinitrobenzene with an aqueous 50% solution of acetic acid and Ce(IV) ammonium nitrate. At 90–95°C an evolution of CO₂ occurred with the formation of 2,4,6-trinitro-m-xylene with yields of 67% and 84% respectively.

Nitro Derivatives of Benzene, Toluene and Aromatics

Components of waste waters which are formed through ammonolysis and reduction of TNT isomers, and to determine their toxicity.

The method of Hepp (Vol. 1, p. 331) was also used: the action of ethanolic solution of ammonia.

The mechanism consists of the initial formation of o-adduct followed by splitting off NO₂ group in the form of the anion NO₂⁻ as depicted in scheme (8). It is referred to as the main unsymmetrical product 2,4,5-trinitrotoluene:

Unsymmetrical Isomers of Trinitrotoluene and By-products of Nitration of Toluene

A number of analytical papers have been dedicated to the detection of isomers of trinitrotoluene and by-products by gas chromatography [57], NMR [58] and by TLC [59].

Some new reactions have been reported of unsymmetrical trinitrotoluenes. Okamoto and Attarwala [60] described the reaction of denitrification of meta nitro group by acting with sodium borohydride in the atmosphere of nitrogen at 23–24°C in CH₂Cl₂.

Another extensive paper on the reaction of unsymmetrical trinitrotoluenes with ammonia leading to aminodinitrotoluenes was that by Nielsen, Coon and co-workers [55]. The main purpose of this work was to identify the major com-
**Nitro Derivatives of Benzene, Toluene and Aromatics**

Aromatic ring carbons with over 50% being contributed by the ring carbon attached to CH$_3$ group. The distribution of carbon atoms taking part in the formation of TNM is given in diagram IV.

It was found that over 80% of all the TNM can be traced to the dinitrotoluene isomers deriving from m-nitrotoluene. The ultimate formation of TNM is attributed to DNT oxidation reactions in competition with the reaction of nitration.

**White Compound**

It was found as early as 1950 that continuous methods of making TNT produce an as yet unknown compound named "white compound".

It was characterized by high m.p., white colour and a low solubility in nitric acid. It readily crystallized out in various parts of the apparatus. Joshi and Patwardhan [54] established its structure as being 2,2'-dicarboxy-3,3',5,5'-tetrinitroazoxybenzene (V). They established it by synthetic route from 2,4,6-trinitrobenzaldehyde which was subjected in the light to the known reaction of Ciancian and Silber (Chapter V) yielding 2,4-dinitro-6-nitrosobenzoic acid. The latter on warming with water gave V (10).

The synthetic product was identical to that produced by continuous nitration.

The structure of V was confirmed by Kamlet and co-workers [53]. Kotarski, Krasičko and co-workers [64] also confirmed the structure V given by Joshi and Patwardhan by using infrared, NMR spectroscopy and mass spectroscopy. Recently Ziołko, Krasičko and Dębski [65] established that 'white compound' exists in two crystalline forms differing by their m.p.: 268–269°C and...
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239–240°C. The raw product is also accompanied by a monocarboxylic azo compound (VI) [53b] which can further be decarboxylated to tetranitroazoxybenzene while boiling in ethylene glycol [65].

![Chemical structure of VI]

Table 30. Solubility of white compound in organic solvents (in 100 g of solvents)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>20°C</th>
<th>Temperature (°C) Higher</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>13.58</td>
<td>15.40 at 40°</td>
</tr>
<tr>
<td>Ethanol</td>
<td>6.80</td>
<td>7.85 at 50°</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.0003</td>
<td>0.04 at 75°</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.018</td>
<td>0.081 at 95°</td>
</tr>
</tbody>
</table>

Table 31. Solubility of white compound in water and acids (in 100 g of solvents)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature (°C) Higher</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.22</td>
</tr>
<tr>
<td>Sulphuric acid (96%)</td>
<td>0.433</td>
</tr>
<tr>
<td>Nitric acid (91%)</td>
<td>0.162</td>
</tr>
<tr>
<td>Nitration acid:</td>
<td></td>
</tr>
<tr>
<td>HNO₃</td>
<td>41.5%</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>54.5%</td>
</tr>
<tr>
<td>H₂O</td>
<td>4.0%</td>
</tr>
<tr>
<td>Spent acid:</td>
<td></td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.2%</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>79.7%</td>
</tr>
<tr>
<td>H₂O</td>
<td>20.1%</td>
</tr>
</tbody>
</table>

Nitro Derivatives of Benzene, Toluene and Aromatics

The white compound was examined by the same authors with regard to its sensitivity to impact and high temperature.

The results are as follows:
Sensitivity to impact is of the order of that of PETN and much above TNT, thus:
- 5 kg from a height of 10 cm gave 100% explosion.
- 2 kg from a height of 25 cm gave 100% explosion.
(allowing for PETN are: 10 cm and 23 cm respectively)

At 300°C the explosion occurred after 10 s.
At 320°C the explosion occurred after 1 s.
(allowing for PETN are 95 and 60 s respectively).

An attempt was made to establish in which stage of nitration white compound is formed. According to de Cazanove and co-workers [66] the amount of white compound increases with the time of the reaction. Ziołko, Krasiejko and Dęhowsk [65] established that white compound composed mainly of V with a possible admixture of VI is formed in the course of trinitration and is dissolved in the acid which passes to di- and mononitration. There, in more dilute acids it is precipitated in various parts of nitrators, pipes, valves etc. The precipitate can disturb the regular trend of the process.

It is advisable to determine the presence of white compound in the products of nitration of toluene. It is also advised [65] to use the TLC technique on silica gel: the solution of nitro compounds in acetone is put on the starting line and the chromatogram is developed with vapours of benzene–acetone–methanol–dioxane (50:5:30:15 vol.%). The chromatogram is treated with ethylene diamine solution in acetone (50:50). White compound can be detected as a magenta coloured spot of \( R_f = 0.68 \). (Nitro derivatives give a reddish-brown coloured spot at \( R_f = 0.80 \)).

Impurities of TNT

As previously mentioned, Yasuda [59] examined TNT by TLC. Among unsymmetrical trimitrotoluenes he found dimitrotoluenes: 2,4-, 2,6-, 2,5- and 3,5.

Gehring [67] undertook the task of examining non-volatile impurities of TNT by NMR technique. He found compounds in crude TNT as given in Table 32.

None of these substances were detected in purified TNT in quantities over 0.03%.

Special attention should be paid to 'o-Nitro-TNT' which appears to have been detected by Yasuda [59], but no structure was given. Gehring [67] suggests the structure (VII):


**Table 32. Impurities of crude TNT [67]**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Quantity present in TNT in weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,5-TNT</td>
<td>1.80 2.20</td>
</tr>
<tr>
<td>2,2,4-TNT</td>
<td>1.50 1.70</td>
</tr>
<tr>
<td>2,3,6-TNT</td>
<td>1.25 1.40</td>
</tr>
<tr>
<td>2,3,5-TNT</td>
<td>0.05 - 0.06</td>
</tr>
<tr>
<td>4,4-DNT</td>
<td>0.20 0.25</td>
</tr>
<tr>
<td>α-Nitro-TNT</td>
<td>0.30 0.35</td>
</tr>
<tr>
<td>2,4,6-Trinitrobenzoic acid (TNBA)</td>
<td>0.20 0.22</td>
</tr>
<tr>
<td>2,4-Dinitrobenzoic acid</td>
<td>0.05 0.06</td>
</tr>
<tr>
<td>3,4-Dinitrobenzoic acid</td>
<td>0.01</td>
</tr>
<tr>
<td>2,4,6-Trinitrobenzaldehyde (TNBA)</td>
<td>0.20 0.24</td>
</tr>
<tr>
<td>m-DNB</td>
<td>0.003 0.005</td>
</tr>
</tbody>
</table>

Kohlsbeck and co-workers [68a] detected by TLC trinitrobenzaldehyde, trinitrobenzylalcohol, hexanitrobenzyl and azoney benzene derivatives related to the 'white compound': tetranitroazoxybenzene and dimethyl tetranitroazoxybenzene.

**Sulphitation of Crude TNT (‘Sellite’ Process)**

As known (Vol. I, p. 332) the reaction of sodium sulphite with unsymmetrical trinitrotoluene is a major reaction in the purification of crude TNT, known under the name of ‘Sellite Process’ – ‘sellite’ being the name of sodium sulphite solution. Sodium sulphite solutions have pH > 8.0. It is known how sensitive higher nitrated aromatic compounds are to bases and sodium sulphite (particularly at a temperature, for example, above 40–45°C) can produce a damaging effect on TNT. It is therefore advisable to add a certain amount of sodium bisulphite to sodium sulphite to keep the pH value as low as possible. According to Clift and Fedoroff [71] 0.1–0.3% NaHSO₃ was added in the U.S.A. as a buffer to keep the pH value down.

**Nitro Derivatives of Benzene, Toluene and Aromatics**

By-products Formed in the Course of Purification of TNT with Sodium Sulphite

The excellent paper by Chandler, Kohlsbeck and Bolletier [68b] has drawn attention to the possible formation of the 'new' by-products in the course of sulphitation of crude TNT (‘sellite purification’). The authors noted a high reactivity of sulphonic group in meta position which derives from the sulphitation of unsymmetrical trinitrotoluene. They explain the formation of 3-methyl-2,4,4',6,6'-pentanitrodiphenylethane (MPDM) (VIII) from 2,4,5-trinitrotoluene by the reactions (11):

![Reaction (11)](image)

Another impurity previously reported [67, 68a] is 2,2',4,4',6,6'-hexanitrobenzyl (HNB)(II). The same authors [68b] also reported the difference between the quantity of both products – MPDM and HNB – in continuous and batch processes of the manufacture of TNT:

<table>
<thead>
<tr>
<th>Continuous methods:</th>
<th>Batch processes:</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPDM</td>
<td>0.1 0.3%</td>
</tr>
<tr>
<td>HNB</td>
<td>0.1 –0.5%</td>
</tr>
</tbody>
</table>

Industrial nitration of toluene to trinitrotoluene (Vol. I, p. 312) is described in the next paragraph.


In the widely used sellite process vast amounts of aqueous sulphite effluents ('red waters') are present. Some efforts were made to recover the compounds and at the same time to remove them from red waters, as they are harmful to the environment.

Red water is alkaline (pH 8.4) [98] and the products dissolved, slowly decompose on standing. Stabilization was achieved by acidifying with 25% sulphuric acid, allowing to stand for one week and then filtering [99]. The filtrate was extracted successively with benzene and ether and the solvent was evaporated. The precipitate from filtration and solid from evaporation amounted to 0.47% of the weight of the red water and proved to be mainly 2,4,6-trinitro-
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toluene. The stabilized (acidified) red water contains ca. 20% dissolved substances:

inorganics 5–8%
dinitrotoluene-sulphonic acids 4.5%
‘Red Tar’ 8.5%

According to Hall and Lawrence [99] Red Tar is composed mainly (90%) of sulphates. Gilbert [98] found that ca. 60% is composed of 2,4-dinitro-5-sulphonic and 40% of 2,4-dinitro-3-sulphonic acid.

In another series of experiments [98] desulphonation was carried out on dinitrosulphonic acids. It is known that aromatic sulphonic acids can be desulphonated by heating with aqueous sulphuric and phosphoric acid but the data for dinitrosulphonic acid are very controversial and it appears that dinitrosulphonic acid cannot be readily desulphonated [98].

Subsequently reductive desulphonation was tried by methods which do not involve the reduction of nitro groups. A small yield (ca. 5%) was obtained [100] of 2,4-dinitrotoluene on desulphonation of 2,4-dinitro-5-sulphonic acid with sodium borohydride.

Reductive desulphonation was reported for 2,6-dinitrobenzenesulphonic [101] and 2,4,6-trinitrobenzensulphonic to m-dinitrobenzene [101] and trinitrobenzene [102] respectively. In both reactions N-benzylidihydromicotinamide (the nicotinamide co-enzyme) was used.

Among the most important methods of transformation of the sulphonic group the following were reviewed by Gilbert [98].

Amination with ammonia under pressure [103] (12):

\[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{NH}_2 \\
\text{CH}_3 & \quad \text{H}_2\text{N} \\
\text{NO}_2 & \quad \text{H}_2\text{N} \\
\text{NO}_2 & \quad \text{H}_2\text{N} \\
\text{NO}_2 & \quad \text{H}_2\text{N} \\
\end{align*}
\]

This method seems to be too expensive owing to the use of butyl nitrate as a diazotization and reduction agent. Substitution of the sulphonic group with hydrazine [104, 105] gave poor yield and was not economically justified owing to the expensive hydrazine.

Substitution of SO$_3$H with chlorine by reacting with POCl$_3$ and then removing chlorine with copper. The method was described for 2,4,6-trinitrobenzene [106] and 2,4-dinitrobenzenesulphonic [107] acids but it does not give the desired results with dinitrotoluene sulphonic acids [98].

More promising is the reduction of the nitro groups followed by hydrolysis of the sulphonic group [98] (13):

\[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{NH}_2 \\
\text{CH}_3 & \quad \text{H}_2\text{N} \\
\text{NO}_2 & \quad \text{H}_2\text{N} \\
\text{NO}_2 & \quad \text{H}_2\text{N} \\
\text{NO}_2 & \quad \text{H}_2\text{N} \\
\end{align*}
\]

Reaction (13) may possess a commercial significance owing to the value of m-toluidinediamine as a starting substance for urethane manufacture.

Another promising reaction is the partial reduction of the dinitro compounds followed by hydrolysis of the sulphonic group [98] (14):

\[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{NH}_2 \\
\text{CH}_3 & \quad \text{H}_2\text{N} \\
\text{NO}_2 & \quad \text{H}_2\text{N} \\
\text{NO}_2 & \quad \text{H}_2\text{N} \\
\text{NO}_2 & \quad \text{H}_2\text{N} \\
\end{align*}
\]

The reaction was tried with stabilized red water. The yield was 43% of the reacted sulphates present in the waters.

Recently a work has been reported on the treatment of red water with surfactants containing amino and quaternary ammonium groups which can form insoluble products with TNT (and probably with sulphonic acids salts formed in the course of the sellite process) [75].

So far an adequate economic solution for the problem of utilization of sulphonic acids present in red water has not been found (see manufacture of TNT by Bofors-Chematur method [72] p. 177).

PENTANITROTOLUENE (PNT)

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{NO}_2 \\
\text{O}_2\text{N} & \quad \text{NO}_2 \\
\text{m.p.225-240°C} \\
\end{align*}
\]

The compound was prepared by Nielsen, Coon and co-workers [16] by oxidation of 3,5-bis (diacetylamino)-2,4,6-trinitrotoluene in 30% oleum with 90% hydrogen peroxide at 20–25°C (15):
3,5-Diamino-2,4,6-trinitrotoluene was made according to the improved method of Palmer [69].

The wide range of melting points of HNB and PNT has recently been explained by Coon [110] as the result of the isomerization of some of the nitro groups in the course of melting (NO₂ ↔ ONO). Subsequently a lower melting mixture occurred.

TNT MANUFACTURE (Vol. I, p. 345)

Continuous methods are now prevalent in the industrial methods of the manufacture of TNT. A general tendency is to use:

(1) relatively low temperature,
(2) high concentration of acids.

The first requirement ensures less by-products and particularly those produced by oxidation, and the second can help to obtain higher yield at lower temperature.

Nevertheless, batch processes are still in use. Matasă and Matasă [29] give parameters for the trinitration of dinitrotoluene Table 33.

<table>
<thead>
<tr>
<th>Composition of the acid</th>
<th>Nitrating mixture</th>
<th>Spent acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>49</td>
<td>1.5</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>49</td>
<td>9.0</td>
</tr>
<tr>
<td>H₂O</td>
<td>2</td>
<td>4.0</td>
</tr>
<tr>
<td>NO₂</td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>Temperature °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ratio HNO₃ : DNT</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>Yield in % of DNT</td>
<td>120 : 100</td>
<td>92</td>
</tr>
</tbody>
</table>

It should be mentioned here that a paper on the nitration of DNT to TNT by anhydrous nitrating mixtures was given by Heertjes as early as 1953 [70]. He used nitric acid mixed with 40–72% SO₃ and a very good result was obtained by using the composition of the nitrating acid:

With an excess of 103% HNO₃ (i.e. 203% HNO₃ as compared to theoretical 100%), he obtained a yield of 98% while the temperature of nitration was kept at 81°C on mixing for 100 min, followed by heating at 109°C for a further 210 min.

**Bofors-Chematur Continuous Method**

The Bofors-Chematur method is now widely in use in many parts of the world. It emerged from Swedish-Norwegian Chematur and Norsk Sprangstoffindustrie (Vol. I, p. 371) incorporated by Bofors in 1968 [72].

The principle was given in Vol. I, but it is being continuously improved. The present process includes:

1. **Nitrination.** Raw materials: toluene or o-nitrotoluene, nitric acid (98% and 55%) oleum and sulphuric acid are stored in tanks from which they are fed to the process by metering pumps. Nitrination can start from toluene or o-nitrotoluene, p-nitrotoluene being isolated as an important intermediate for dyes and medicinal products — (Vol. I, p. 277). Nitrination is carried out continuously in a series of nitrators through which the toluene or o-nitrotoluene and the nitrating acids flow in a countercurrent. In front of the first nitrator is placed an extraction vessel (not shown on the diagram) in which the residual nitric acid and nitro compounds are extracted from the spent acid by toluene. After extraction, the spent acid/toluene mixture enters the cooling unit. Toluene which now contains some nitrotoluene and acid is separated from the spent acid and enters the nitrator. The spent acid is sent for distillation.

   All nitrators, extractors and spent acid coolers are equipped with ’dynamic’ separators which have been described above — Fig. 23.

2. **Presellite washing.** TNT is continuously washed, in several washing vessels, by pure water to remove the acids. The washers are equipped with dynamic separators. The waste water, known as ‘Yellow Water’ is either sent to the washing system or to the absorbers, retaining the acids and organic products.

3. **Sellite purification.** The TNT is continuously treated with sellite solution
in a series of washers. The pH level is controlled by pH meters. The washers are equipped with dynamic separators. The waste water, called 'Red Water' is transferred to a special destruction unit where water is evaporated and the remaining organic material is burnt.

4. Post sellite washing. The purified TNT is treated continuously in a washing system with pure water. The washers are equipped with dynamic separators. The waste water is transferred to Sellite purification. The washed TNT is transferred either in water emulsion or in molten form to the drying unit.

5. Drying. TNT is dried by heating with steam to 85–90°C and passing hot (75°C) air to agitate the molten substance.

6. Flaking. The dried TNT flows by gravity to the flaker which is a standard apparatus (Vol. I, p. 380, Fig. 38). It consists of an iron or steel drum rotating at constant speed and cooled inside by cold running water. By regulating the depth of immersion of the drum in the molten TNT the thickness of flakes can be controlled.

Design of Nitrators equipped with Centrifugal Separators.

The centrifugal separators which are usually given as an addition to the nitrators or washers (Fig. 23, 24), can be installed inside the reactor or washer. This is depicted in Fig. 26. It can be used for the capacity of the nitrator below 1250 kg/hr.

**TABLE 34**

The raw materials required for the production of 1000 kg of TNT are:

<table>
<thead>
<tr>
<th>Material</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>485 kg</td>
</tr>
<tr>
<td>Oleum 20%</td>
<td>2250 kg</td>
</tr>
<tr>
<td>Nitric acid 55% and 98% calculated as 100%</td>
<td>1100 kg</td>
</tr>
<tr>
<td>Sodium sulphite</td>
<td>65 kg</td>
</tr>
<tr>
<td>Sodium bisulphite</td>
<td>10 kg</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>1 kg</td>
</tr>
</tbody>
</table>

Energy consumption per 1000 kg TNT are:

- HT Electricity and LT Emergency: 135 kWh
- Cooling water 28°C: 50 m³
- Cooling water 15°C: 50 m³
- Steam: 1150 kg
- Processed water: 2 m³

**Low Temperature Process for TNT Manufacture**

Haas, Yee and co-workers [40] developed a method of low temperature production of TNT. The main features of the method consist of:

1. Co-current flow of single phase the anhydrous acid and the nitro compounds,
2. Low temperature (−10°C) of dinitration,
3. Crystallization and filtration of TNT from the anhydrous nitrating acid.

A diagram of the system is given in Fig. 27. Dinitration has already been described and a diagram of the nitrating system given in Fig. 21. Trinitration occurred at 90°C, below 60°C it was insignificant, at 90°C the complete reaction of trinitration of DNT occurred at a batch process in ca. 1 hour. At 90°C an excess of oxidation occurred. The following feed material is added at a continuous rate to produce ca. 22 kg TNT/hr:

- 93 kg/hr of mixed acid,
- 85 kg/hr of dinitrotoluene containing DNT,
- 13 kg/hr of DNT from the dinitrator.

The composition and flow rate in the continuous method are given in Table 35.
Crystallization. A diagrammatic presentation of the process is given in Fig. 28. The solvent was the trinitration acid of the composition: 10.6% HNO₃, 75.8% H₂SO₄, 10.6% SO₃. The solubility at different temperatures is collected in Table 36.

The process is diagrammatically depicted by a scheme. Fig. 28. The first three vessels are cooled with water of 30, 30 and 10°C and the last two with a brine containing 25% NaNO₃ at temperatures of −5 and −15°C. The acid for the crystallization should not be too cold, as it would produce crystals which were too small and could block the pipes connecting the vessels.

The acid flowing from the crystallizer contains ca. 5.3% dissolved TNT and ca. 9.7% HNO₃, the rest being sulphuric acid, SO₃ and nitrosylsulphuric acid. It passes to the first (hot) crystallizer, after the draining of TNT, it is washed with 70% sulphuric acid, followed by washing with water.

### Table 35. Composition of trinitration effluent

<table>
<thead>
<tr>
<th>Compound</th>
<th>Flow kg/kg TNT</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>1.4</td>
<td>16.5</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.65</td>
<td>7.7</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>4.6</td>
<td>64.3</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.8</td>
<td>9.5</td>
</tr>
<tr>
<td>NOH₂SO₄</td>
<td>1.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

The filtrate removed from TNT contains ca. 60% of nitric and sulphuric acid and SO₃, used for the trinitration and is recycled to trinitration after the addition of acids.

**Manufacture of TNT in the U.S.A. during World War II**

Fedoroff [73] reviewed the methods of the manufacture of TNT in the U.S.A., after the description was declassified in the late 1960s. Some parts of the description possess an historical significance, but can create a good insight into the development of technology of one of the most important explosives.

**One-stage Nitration of Toluene**

During World War I, one stage nitration of toluene to TNT was carried out using a Hough nitrator (Vol. 1, p. 157, Fig. 31). The nitrator was filled with...
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

25,000 lb of the nitrating mixture (no composition was given). Toluene (2500 lb) was slowly introduced through a spray at 50°C. Gradually the temperature was raised to 110°C. The total time was 3 hours giving 5300 lb of TNT (85% yield).

Two-stage Process of Nitrination

This method was in use at the Barksdale, Wisconsin plant, of the du Pont Co., the only TNT factory in the country between the two world wars. It consisted of mononitrination and combined bi-tri-nitrination.

Mononitrination: toluene in a very thin stream was introduced to mono-mix for 3 hours at ca. 57°C. The charge was ‘cooked’ for 1 hour and then settled to separate mono-oil from the acid.

Combined bi-tri-nitrination: mono-oil was added very slowly to a mixed acid containing 16% HNO₃, 82% H₂SO₄ and 2% H₂O. The ratio acid/mononitro was 9:5. During 2.5 hours of mixing, the temperature gradually rose to 120-125°C. The separated crude tri-oil was washed by agitating with hot water, dried and purified by crystallization with carbon tetrachloride.

Three-stage Process

This method was used from 1941 at Glen Wilton, Virginia and did not deviate from, at that time, the existing practice. The mono-nitrination and di-nitrination were carried out with the spent acids of dinitration and trinitration respectively mixed with 60–62% nitric acid. Mononitrination was usually carried out in two stages to avoid the vigorous reaction of toluene with nitric acid. The idea was similar to that used in Germany (Vol. I, pp. 357–359). In Glen Wilton toluene was ‘pre-mixed’ in a mononitrator with a large quantity of acid composed of 7% HNO₃, 55% H₂SO₄ and 38% H₂O. After that mononitrination acid was added to complete the nitration. The spent acid from mononitrination was sent to the ‘Recovery House’ where nitric acid was distilled off (see Chapter on Denitrination).

Trinitration was achieved with mixed acid composed of 97–100% nitric acid, sulphuric acid and oleum. It contained ca. 60% H₂SO₄, ca. 40% HNO₃ and a small amount (ca. 0.3%) of NO₂.

Direct Nitrination Process

The so-called ‘Direct Nitrination’ method was developed during 1942–45 in Beloel, Quebec under collaboration between Canadian Industries Ltd and du Pont Co. (It was erroneously described [74] as being placed in Plum Brook Ordnance Work.) This is a three stage process using essentially the method with three concentrations of mixed acid. The factory in Beloel was making over 450,000 t of

TABLE 37. Compositions of acids

<table>
<thead>
<tr>
<th>Type of acid</th>
<th>HNO₃</th>
<th>H₂SO₄</th>
<th>Nitrosyl-sulphuric acid</th>
<th>Nitro compounds soluble in ether</th>
<th>H₂O</th>
<th>Density at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mononitrination</td>
<td>14.2</td>
<td>48.2</td>
<td>16.6</td>
<td>1.8</td>
<td>19.2</td>
<td>1.68</td>
</tr>
<tr>
<td>Spent acid after mononitrination</td>
<td>3.5</td>
<td>55.1</td>
<td>16.8</td>
<td>0.3</td>
<td>24.0</td>
<td>1.67</td>
</tr>
<tr>
<td>Dinitration</td>
<td>13.0</td>
<td>54.3</td>
<td>16.9</td>
<td>9.0</td>
<td>7.8</td>
<td>1.78</td>
</tr>
<tr>
<td>Spent acid after dinitration</td>
<td>4.4</td>
<td>62.4</td>
<td>15.8</td>
<td>2.7</td>
<td>14.7</td>
<td>1.78</td>
</tr>
<tr>
<td>Trinitration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Oleum</td>
<td>4.9</td>
<td>103.7</td>
<td>0.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2. ‘Semi-mix’</td>
<td>62.0</td>
<td>43.0</td>
<td>0.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3. Final Composition</td>
<td>23.3</td>
<td>82.7</td>
<td>0.4</td>
<td>0.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Spent acid after trinitration</td>
<td>3.4</td>
<td>63.5</td>
<td>17.6</td>
<td>13.5</td>
<td>2.0</td>
<td>1.87</td>
</tr>
</tbody>
</table>

* Maximum amount of water which can be added to obtain a mixture free of water. It can be used as a criterion of the concentration of water in the acid mixture.

TABLE 38. Main parameters of the nitrination

<table>
<thead>
<tr>
<th>Type of acid</th>
<th>Weight ratio</th>
<th>Temperature of nitrination (°C)</th>
<th>Time of nitrination (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mononitrination</td>
<td>Acid/Toluene</td>
<td>1.35–38°C (2.54–57°C cooling to 38°C)</td>
<td>40–45</td>
</tr>
<tr>
<td>Dinitration</td>
<td>Acid/MNT</td>
<td>1.82°C (2.84–86°C cooling to 65°C)</td>
<td>45</td>
</tr>
<tr>
<td>Trinitration</td>
<td>Acid/DNT</td>
<td>1.79–80°C (2.90–91°C 3.110–111°C cooling to 93–96°C)</td>
<td>90</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Material for 100 kg TNT</th>
<th>Yield of TNT in kg for 100 kg of toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>47.66</td>
<td>209.84 kg</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>211.67</td>
<td></td>
</tr>
<tr>
<td>Nitric acid</td>
<td>145.19</td>
<td></td>
</tr>
<tr>
<td>Seline*</td>
<td>18.29</td>
<td></td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>5.02</td>
<td></td>
</tr>
</tbody>
</table>

Acid consumed and lost for 100 kg TNT

<table>
<thead>
<tr>
<th>Acid consumed and lost</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric acid consumed and lost</td>
<td>105.72</td>
</tr>
<tr>
<td>Nitric acid recovered</td>
<td>37.45</td>
</tr>
<tr>
<td>Sulphuric acid consumed and lost</td>
<td>1.72</td>
</tr>
<tr>
<td>Sulphuric acid recovered</td>
<td>209.95</td>
</tr>
</tbody>
</table>

Mean setting point of TNT | 80.4

* Sodium sulphite.

TABLE 40. Acid consumption and losses per 100 kg toluene

<table>
<thead>
<tr>
<th>Acid consumption</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric acid in mononitration</td>
<td>90 kg</td>
</tr>
<tr>
<td>Nitric acid in dinitration</td>
<td>90 kg</td>
</tr>
<tr>
<td>Nitric acid in trinitration</td>
<td>125 kg</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>450 kg</td>
</tr>
</tbody>
</table>

The surface of the acid layer, of large quantities of uninitrated organic compounds. Every new portion of organic substance introduced under the surface of acid, nitrates almost completely, except in trinitration, before it rises to the surface. If the feed is too fast and the temperature starts to rise above permissible limits, overheating may be easily checked by simply halting the addition of organic substance. Also the proportion of organic compounds to acids at any time during nitration, except at the end of nitration, is much smaller than in the older methods. This is especially important at the beginning of nitration, when the reaction is most vigorous.

4. Dangerous foaming often observed at the beginning of trinitration by the older methods is practically eliminated by the new method.

5. ‘Burned’ charges, often occurring in the older procedures and caused by too rapid temperature rise during nitration, were not as numerous after the new method was introduced.

6. The new method is easier to operate and does not require such highly skilled workers as in the older methods. Because of increased production per line, labour requirements are much reduced.

7. The introduction of strong downward agitation and the use of undersurface toluene or MNT feed to the nitrating acid results in rapid and practically complete (except in trinitration) nitration during the time that the oil phase is below the surface of the acid in the nitrator. This type of ‘bubble nitration’ is particularly efficient when a strong downward agitation is used, and the time for the oil to rise to the surface is increased by the correct design of the organic substance feeder tube. In the old process, nitration occurred at the interface between the acid and oil layers—and delayed reactions (‘sleepier charges’), excessive heats, etc., were rather common. At the same time improvement in uniformity of nitration was obtained, the improved agitation allowed better temperature control by more efficient distribution of the heat of reaction.

8. The advantage obtained by increased production and decreased cost of TNT was important.

It is interesting to note that the direct method of nitration was attempted in Europe as well as in the U.S.A. (Barksdale Plant), long before the Canadian and Keystone Ordnance Works trials indicated the great benefits derived from this process. However, the early European experimentation indicated that the method was unsafe and that it was difficult to control the important temperature and time factors. It seems highly probable that the difficulties encountered were due to improper feeding of toluene or MNT or DNT to the acid in the nitrator, poor agitation, inefficient cooling and the use of incorrect acid compositions.

Purification of Crude TNT

Three methods of crude TNT purification were in use in the U.S.A.
(1) 'Soda-Ash' (sodium carbonate) process introduced by du Pont Co.,
(2) Ammoniacal 'Sellite' (ammonium–sodium sulphite) process introduced
by the West Virginia Ordnance Works of General Chemical Co.,
(3) The alkaline 'Sellite' (sodium sulphite) process of Hercules Powder Co.

All three methods were designed to shorten the time of the operation and to
reduce the quantity of water used. The latter requirement was dictated by the
necessity to reduce the pollution of streams and waterways with toxic sulphite
solutions. To accomplish this completely the sulphite solutions were evaporated
in a quadruple-effect evaporator to a thick syrup, the syrup was then fired in a
rotary kiln incinerator to give an ash which was harmless to fish and animal life.
The number of water washes of TNT was also reduced.

Soda-Ash Process

Crude 'Tri-oil' was washed with a small amount of hot water, followed by
adding cold water to reduce the temperature in the wash-tank to 68°C. TNT
solidified as fine crystals.

Sodium carbonate 20% solution was added to neutral (on litmus) reaction and
care was taken to avoid an excess of alkali harmful to TNT. A solution of
16–17% Na₂SO₄ and 0.1–0.3% NaHSO₃ was added. The sodium–hydrogen
sulphite was used to avoid alkaline reaction and also served as a buffer. Cold
water was added to thicken the charge, the whole operation lasted 45 min. The
product was screened through a 10 mesh sieve, centrifuged and washed with
water. Larger particles were returned for reworking.
The washed TNT was dried (at 110°C) and flaked (Vol. I, p. 380. Figs 93,
94). The 'Flaker' is a steel drum rotating at constant speed and cooled on the
inside by cold running water. By regulating the immersion of the drum in the
molten TNT in the pan, the thickness of the solid product on the drum is
controlled. A steel scraper removes the adhering TNT. It seems however (for safety
purposes) preferable to use a bronze scraper as in the French method (Vol. I,
p. 379).

Ammoniacal Sellite Process

This method is similar to the 'Soda-Ash' process. The difference consisted of
using a solution of sodium sulphite (16–17% Na₂SO₄) added with ammonia gas
by bubbling it to 2% free NH₃. The solution should have pH = 5. The pH value
rose to 8.5 after mixing the solution with TNT (15 min). The solution contains:
ammonium nitrate, sulphate and sulphite. Free sodium sulphite causes the formation
of a red colour in the slurry of TNT with the aqueous solution. TNT made
by this method is slightly darker owing to the action of ammonia on β- and
γ-trinitrobenzene producing traces of 2,4- and 4,6-dinitro-3-toluidine. Traces of

these impurities have not been found to adversely affect the quality of TNT.
The aqueous solution removed from TNT was not evaporated to incinerate
owing to the presence of explosive ammonium nitrate in the solution.

Alkaline Sellite Method

Crude TNT is mixed with hot water and cold water is added to crystallize the
product at 71°C. After washing to reduce the acidity to ca. 0.3% H₂SO₄, a
calculated amount of Sellite solution was added containing 14.8–15.2% Na₂SO₃
and 1.1–1.6% Na₂CO₃. Mixing at 71°C lasted for 6 min after which the TNT
was filtered. The washing, remelting, drying and flaking operations were carried
out in the usual manner.

SAFETY OF MANUFACTURE AND HANDLING OF AROMATIC
NITRO COMPOUNDS, PARTICULARLY OF BENZENE AND TOLUENE
(Vol. I, p. 391)

Although the number of accidents in the nitrations of aromatic hydrocarbons
is relatively small, the danger of the processes should not be underestimated.

As regards benzene and toluene the first and last steps of the reaction are
particularly dangerous, i.e. the vigorous reaction of the hydrocarbon and the
final nitration to introduce the second and third nitro group into benzene and
toluene respectively.

An instructive description of a considerable number of accidents is given by
Biausti [76b].

In addition to those reported in Volume I, two accidents are described here.

In 1944 in a German factory which was built to the pattern of that of Krümmel
(Vol. I, p. 357) an explosion took place during the nitrations of benzene to
nitrobenzene for the further nitration to dinitrobenzene. The reaction was
carried out in a nitrator of 15 m³ capacity. The nitrating mixture was added to
benzene.

The explosion took place at the beginning of the reaction and demolished the
building, although the nitrator suffered only slight damage. The conclusion of
the investigation was that the explosion was produced by a gas mixture of
benzene/air due to benzene leaking from the nitrator. This was probably the
result of overheating the surface of the liquid in the nitrator. This in turn was
the result of inadequate mixing produced by the incorrect design of the propellant
stirrer (too small and too slow) and leaks from the nitrator which filled
the building with explosive vapours of benzene/air.

The explosion took place through the discharge of static electricity.
As a result of the accident it was decided:

(1) to change the design of the stirrer to achieve better efficiency;
to introduce nitric mixture to the hydrocarbon.

(3) in both systems of adding acid to the hydrocarbon or vice versa it is advisable to introduce the acid and hydrocarbon respectively well below (0.5–1.0 m) the surface of the liquid in the nitrator. In this way, the hydrocarbon will be nitrated below the surface and its vapour pressure over the surface will be diminished.

(4) If acid is added to hydrocarbon a neutral gas (e.g. nitrogen) should be introduced into the nitrator to give a non-inflammable mixture over the surface of the liquid.

In another factory which used the same kind of nitration system as in Krümmel, a major accident occurred in 1952. The whole building was destroyed together with several nitrators used solely for the nitration of DNT to TNT. Altogether ca. 80 tons of DNT/TNT exploded. The nitrators were at different stages of the process, in some of them the nitration proceeded at 95°C, in others with the stirrer stationary separation of the nitro compounds from the acid occurred. The accident began when a fire started in one of the nitrators where the separation of ca. 5 tons of TNT was in progress. The operators tried to quench the fire with a carbon dioxide fire extinguisher. This was unsuccessful and the whole team left the building. A fire brigade arrived and at that moment the detonation occurred, 6 min after the fire started. A detailed examination of the cause of the fire and the detonation and an examination of analogous nitrators in other buildings led to the conclusion that the fire was caused by drops of paraffin oil, which was used as a lubricant to impregnate asbestos washers tightening the axis of the stirrer. Laboratory experiments have shown that at a temperature of 95°C the vapours of nitric acid, containing of course nitrogen dioxide, can readily ignite paraffin oil present in a suspended string of asbestos. Burning gave a temperature of over 260°C which was sufficiently high to bring molten TNT (temperature 95°C) to an explosive decomposition.

A few laboratory experiments have shown that fire in the nitrator separator can be extinguished by resuming the work of the stirrer. This is due to a considerable amount of mixed acid which can act as a cooling and extinguishing liquid.

In a few instances disastrous effects have been produced by foreign bodies entering the nitrator or spent acid of trinitration. Such was the case of a rubber glove which had fallen into spent acid (Vol. I, p. 391) or rubber tubing which entered the nitrator (Radford, 1974) according to [76].

In a factory a small explosion occurred when turning a stop-cock of the apparatus for sublimation of molten TNT. It was found that deposits of picric acid or trinitrocresols and metal picrates (or trinitrocresates) were present in similar stop-cocks. An instruction was given that careful periodic cleaning of stop-cocks should be implemented.

The danger of keeping molten TNT at a high temperature has already been 1700 kg of TNT. It was estimated that the temperature of the molten TNT was 150°C or even 165°C. The melting tank was only used for remelting TNT below 150°C or even 165°C. The melting tank was only used for remelting TNT below 150°C or even 165°C. Cardboard fibres were present in the molten TNT because of the dumping of cardboards. Fibres were present in the molten TNT because of the dumping of the tank. A similar accident with molten TNT occurred earlier (1940) at Bofors. Molten TNT was contaminated with cardboard from cartridges of TNT. The cardboard was impregnated with linseed oil which floated on the surface of the melt. In the presence of air the oxidation of linseed oil could readily occur.

The last two accidents show the danger of contaminants on the behaviour of molten TNT.

The contamination of TNT with various organic substances such as lubricating oil, linseed oil, asphalt and varnishes lowers its ignition temperature [78].

Also contamination of TNT with metals and their oxides can increase the danger of heating TNT (Vol. I, p. 392). It should be borne in mind that TNT is an acid which forms salts with metals, very sensitive to impact, friction and high temperature (Vol. I, p. 364). A patent [79] claims a practical use for TNT salts of Na, K, Cu (II), Ag (I), Ba, Pb (II), Fe (III), Al for delay compositions. Unwanted contamination of TNT with metals may lead to danger.

Although the nitration of aromatic compounds should be regarded as a relatively safe operation some unexpected decompositions and even explosions can occur due to some particular functional groups in the nitrated compounds. It is of course known that nitration of phenols by a direct reaction (Vol. I, p. 380) can bring about decomposition through oxidation. The same applies to o- and p-xylene (Vol. I, p. 395). Relatively recently attention was drawn to the danger of nitration such an apparently harmless compound as phthalic anhydride. The nitration to 3-nitrophthalic anhydride on a laboratory scale becomes very violent, after two hours with very little warming, the entire contents of the reactor were ejected [80]. This fact was rationalized in terms of the formation of phthalic nitrate, dinitrate and nitrate derivatives [81] unstable substances which readily explode.

Häupli [128] carried out extensive experiments on the influence of various "foreign" substances on the decomposition temperature of TNT. Here are some of his results while adding 10% of a foreign substance:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure TNT</td>
<td>297°C</td>
</tr>
<tr>
<td>with cork</td>
<td>257°C</td>
</tr>
<tr>
<td>dry red lead</td>
<td>275°C</td>
</tr>
<tr>
<td>fresh red lead</td>
<td>192°C</td>
</tr>
<tr>
<td>linseed oil</td>
<td>220°C</td>
</tr>
<tr>
<td>asphalt</td>
<td>259°C</td>
</tr>
</tbody>
</table>
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

graphite 289°C
paraffin oil 260°C
mineral oil (lubricant) 249°C

L. C. Smith [129] pointed out that molten TNT can catch fire when mixed with activated charcoal (Norit). The mixture TNT (Norit 50) 50 begins to decompose at 110°C and at 174°C can produce an explosion.

Environmental Problems of TNT Manufacture (Vol. I, pp. 161, 389)

Two environmental problems are connected with TNT manufacture:

1. (1) poisonous of the atmosphere with tetranitromethane (TNT);
   (2) the disposal of organic products formed during the sellite process.

The material balance shows that 0.4 ton of TNM and 4.2 tons of isometric by-products are formed for 100 tons of TNT [98].

With regard to the recovery and use of TNM, its conversion into nitroform was suggested in the U.S.A. [98]. The known method of acting on TNM with aqueous alkali and hydrogen peroxide was recommended (Chapter VIII). Although the demand for nitroform exists and the method was economically justified, the application of the method was discarded as the quantity of nitroform obtainable was insufficient for potential requirements, and the requirement of the Environmental Protection Agency (EPA) can be satisfied by the destruction of TNM with sellite so that the substance will not be vented into the atmosphere.

With regard to solutions from the sellite process (red waters) the problem of recovery of nitro compounds from the solution has already been discussed (p. 173). None of the suggested methods have received practical application and it appears that the best method of dealing with sellite wastes is evaporation to dryness and burning the residue as in Bofors-Chematur method [72].

Also the purification of TNT by crystallization from the acids (see also Vol. I, p. 378) should be considered. It offers the advantage that acids used for crystallization are recycled and enter the production process. However, the impurities present in the acid after crystallization are introduced into the nitrator which is a drawback of the method.

OTHER NITROAROMATICs

Nitro Derivatives of Hydrocarbons

In recent years very little attention has been given to nitro derivatives of higher homologues of benzene. Some of the homologues (e.g. xylenes) have become important starting substances in the production of valuable intermediates.

The only paper of any significance on the homologues of TNT was given by

Desseigne [119]. It referred to 2,4,6-trinitroethylbenzene (Vol. I, p. 414) which was obtained by a three-stage nitration of ethylbenzene. The yield was 77.7% and the setting point of the product 37°C.

Nitro Derivatives of Halogenonitrocarbons

Some halogenonitrocarbons recently achieved importance as intermediates in the formation of important explosives. Such are: 1,3-dichloro- and 1,3,5-trichloro-2,4,6-trinitrobenzene which can serve to obtain high melting explosives: DATB and TATB (Chapter VII).

1,3-Dichlorobenzene can be commercially obtained by chlorination of m-dinitrobenzene (Vol. I, p. 193) and nitratred to the trinitroproduct which can be converted to DATB. A description of the industrial method of making 1,3,5-trichloro-3,4,6-trinitrobenzene was given in Vol. I, p. 469.

Nitrophenols (Vol. I, p. 492)

Relatively little attention is paid to high nitrated phenols as explosives, but some of them (e.g. styphnic acid) became important because of the initiating properties of their salts.

Picric Acid

Picric acid remains the best known highly nitrated phenol.

Some characteristics can be found in the monograph by Meyer [1] and attention was paid to chemical properties of picric acid and its substituted derivatives. Thus Pearce and Simkins [86] determined pKₐ values (by calculation and experiment) of alkyl homologues of picric acid and its methoxy or halogen derivatives. The pKₐ values fit well with data predicted from the Hammett relation. Styphnic acid however shows a deviation.

The mechanism of the substitution of sulphonic groups in phenol by nitro groups was extensively studied by Leśniak and T. Urbaniński [130] and to this purpose the chromatography-polarographic method introduced by Kemula and associates [131] was used. The trend of the nitration of o- and p-phenolsulphonic acids with nitric acid can be depicted by diagram (16a):
Thus the diagram on p. 501, Vol. I remains valid particularly as regards the nitration of p-phenolsulphonic acid.

The mechanism of the attack of nitric acid upon phenolsulphonic acids was rationalized by T. Urbanek and Lesniak as passing through the addition stages forming transient yellow coloured quinoid structures (16b):

Salts of Picric Acid

Salts of picric acid are important for two reasons:

1. for their sensitivity to impact and friction which can be dangerous but can also be of practical importance in initiators and pyrotechnic compositions,
2. they do not possess the undesirable property of picric acid, which is its acidity.

The salt in practical use is ammonium picrate. Its properties were described in Vol. I, p. 528. During World War II and explosive 'Picerol' composed of 52% ammonium picrate and 48% TNT was in use by the U.S. Army.

2,4-Dinitroresorcinol (Vol. I, p. 536)

A semi-industrial method of making 2,4-dinitroresorcinol was given by Ficorouille and Soule [133]. It consists of two stages:

1. Nitration
2. Oxidation.

Nitration. The reactor was filled with 280 l. water and 6240 l. sulphuric acid (65.5 Be). 11,200 kg resorcinol were introduced and 100 kg of ice. A solution of 15 kg of sodium nitrite dissolved in 28 l. of water was added. Yellow coloured dinitro compound was precipitated and immediately the solution was added to 480 g sodium sulphate in 2 l. of water. The precipitate was isolated by filtration, washed with cold water to neutrality (ca. 20 l.), finally it was dried and sieved with ethanol (2 l.).

The yield was 16 kg, i.e. 93.5%.

Oxidation. The reactor was filled with 45 l. of toluene and 10 kg of dinitrosoresorcinol. It was cooled to -5°C and over 8 hours 15 l. of nitric acid (d 1.35) diluted with 15 l. water were added. The product was filtered and washed three times with 30 l. water.

Purification

The dry dinitro compound was dissolved in 80 l. ether. the solution was filtered and ether distilled off. The product was dissolved by boiling with 140 l. water, then cooled and collected on a filter.

From 11,200 kg resorcinol 6500 kg dinitro product was obtained, i.e. the yield was 54-55%.

Styphnic Acid (Vol. I, p. 538)

Two papers [87, 88] have described a novel method of making styphnic acid. Both consist of two steps: (1) nitrosation of resorcinol to dinitroso derivative, (2) oxidation and nitration of the dinitroso compound (17):

Nitrosation. The reactor was filled with 45 l. of toluene and 10 kg of dinitrosoresorcinol. It was cooled to -5°C and over 8 hours 15 l. of nitric acid (d 1.35) diluted with 15 l. water were added. The precipitate was isolated by filtration, washed with cold water to neutrality (ca. 20 l.), finally it was dried and sieved with ethanol (2 l.).

The yield was 16 kg, i.e. 93.5%.

Oxidation. The reactor was filled with 45 l. of toluene and 10 kg of dinitrosoresorcinol. It was cooled to -5°C and over 8 hours 15 l. of nitric acid (d 1.35) diluted with 15 l. water were added. The product was filtered and washed three times with 30 l. water.

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Tetranitrodian

2,6,2',6'-Tetranitrodian was obtained by Szeky [89]. Its salts can be used as potential ingredients of pyrotechnic compositions.
Nitro derivatives of a tribromophenol homologue. Zinke and Breitweiser [116] have found that dinitration of a tribromophenol homologue in the presence of acetic acid yielded two isomeric products. It was recently established (due to modern methods) [117] that nitration can also produce an interesting acyloin rearrangement leading to a five-member ring compound according to scheme (18):

Picric Acid Ethers

Nitration of anisal to o- and p-nitroanisal was studied by Schofield and co-workers [90]. Mononitration in 54–82% sulphuric acid at 25°C gave the ratio of p / o = 1.8–0.7.

Nitro derivatives of diphenyl ether (Vol. I, p. 549). Adamska and Okon [91] prepared a number of methyl derivatives of penta- and hexadiphenyl ether, for example, 3,5-dimethyl-2,2’,4,4’,6,6’-hexanitrodiphenyl ether.

Nitro derivatives of aniline (Vol. I, p. 556). With the exception of hexanitrodiphenylamine, nitro derivatives of aniline are not in use as explosives. Some of them are intermediates of reactions leading to highly nitrated compounds by oxidation NH₂ → NO₂ according to the method of Nielsen, Coon et al. [10, 16]. See also [38].

Hexanitrodiphenylamine (Hexyl) (Vol. I, p. 562)

The data on explosive properties are also collected in the monograph by Meyer [1]. Some relatively new interest was created by salts of hexyl. They possess properties similar to those of picric acid: they burn readily and some of them show initiating properties.

Due to a very low solubility of its potassium salt, hexyl is used as a reagent for potassium. Also a suggestion was made for using hexyl to extract potassium from sea water [92]. The precipitated potassium salt treated with nitric acid yielded potassium nitrate which on evaporation crystallized out.

A considerable number of papers appeared by J. Hirst and co-workers [111] on the reactions of picryl chloride with substituted anilines. They studied the kinetics of the reaction and the influence of the substituents in aniline on Arrhenius parameters and rate constants.

Among other kinetic studies of picryl chloride and 1-chloro-2,4-dinitrobenzene with bases the works should be mentioned of Parker and Read [112] and Zollinger and co-workers [113] which have shown a much higher reactivity of picryl chloride. The reactions are greatly influenced by solvent and in some instances 1-chloro-2,4-dinitrobenzene is more reactive than picryl chloride [114].

The reactions belong to addition–elimination reactions $\text{AE}^{-} \rightarrow \text{S}_{\text{N}} \text{Ar} [115]$. 

Picric Acid (Vol. I, p. 571)

A detailed description was given [93] for making picric acid from picric acid and sodium hydrogen sulphide at 50–55°C with a yield of 88–90%.

Other Aromatic Nitro Compounds with Amino Groups

Some other aromatic nitro compounds such as DATB, TATB and DIPAM are of great practical importance and are described in Chapter VII (Heat Resistant Explosives).

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APPENDIX I

DERIVATIVES OF HALOGENO-BENZENE

The nitro derivatives of chlorobenzene were described in Vol. I, pp. 450–471. More recently, nitro derivatives of fluorobenzene have received some attention. Ohl, Kuhn and Föld [1] described the nitration of halogeno derivatives of benzene with NO₂BF₄ (made of N₂O₅, HF and BF₃) in tetramethylsulphone as a solvent at 25°C and established different reactivities as compared with benzene (Table A1).

<table>
<thead>
<tr>
<th>Relative reactivity</th>
<th>o-</th>
<th>m-</th>
<th>p-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzeno</td>
<td>1.0</td>
<td>8.5</td>
<td>91.5</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>0.85</td>
<td>22.1</td>
<td>76.6</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.14</td>
<td>25.7</td>
<td>33.2</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>0.12</td>
<td>36.3</td>
<td>63.7</td>
</tr>
<tr>
<td>Iodobenzene</td>
<td>0.28</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Also Kuhn and Olah [2] nitratte 2,4-dinitrofluorobenzene with NO₂HSO₄ in 100% sulphuric acid at 120°C for 12 hours and obtained picryl fluoride with the yield of 40%. Fluorine in nitro derivatives of benzene shows a greater reactivity than chlorine in nucleophilic reactions [3]. In view of this attention was paid to 1,3,5-trifluorotriphenylbenzene and its reaction with nucleophiles [3].

1.3.5-TRIFLUOROTRIAROMATIC

An improved preparation was recently described [4]. High reactivity of fluorine excludes the displacement of nitro groups which was a side-reaction of analogous chloro- and bromo-nitro compounds.
ANALYSIS OF NITRATING ACIDS

Although analytical problems are outside the scope of the present book, it is advisable to mention the methods of rapid control of nitration. A considerable attention was recently paid to methods of acids analysis.

A brief description and references are given below. The novel methods are:

1. Injection thermometry of Oehme and Ertl [1].
2. Automation control of nitration by Bel'yanov, Kapustina and Peshekhonov [2].
3. Redox titration of nitric acid in mixed acid [3] (see also Chapter 11).
4. "In-line" analyzer of nitric acid by:
   (a) refractometry
   (b) coulomb-polargraphy [4]
5. High-frequency conductometric titration of mixed acid [5]
7. By adding substances which can readily be nitrated by spent acid and the products of nitration can be quickly determined spectrophotically. One of the methods consists in adding salicylic acid which furnished two isomeric nitro compounds: 3- and 5-nitrosalicylic acid [7]. Their yield was determined by UV spectroscopy.

REFERENCES


APPENDIX 3

Nielsen and co-workers described recently [11] the preparation of decanitrotriphenylamine through a sequence of reactions starting from methyl ester of 4-chloro-3,5-dinitrobenzoic acid:

REFERENCE

CHAPTER 7
HEAT RESISTANT EXPLOSIVES

The last two decades have brought a new line of research in explosives. This is the work on heat resistant explosives.

There was an immense need in industry for an explosive composition which would be safe, reliable and stable at elevated temperatures. For example, it is sometimes necessary to shoot explosive devices in hot wells at temperatures which may reach as high as 200° - 300°C. In the steel industry, open hearth furnaces are tapped with explosive shaped charges in tap holes at temperatures above 500°C. Using the explosives available at present, which have the best possible thermal properties, it is necessary to jacket the shaped charges with heavy insulation. Even so, the charge must be initiated within 3 - 4 min from the time it is set in place or it may fail due to thermal stability. There is also a growing demand in connection with space programmes for explosive compounds which are stable at elevated temperatures and low pressures. The explosive stores carried externally on high speed aircraft at low altitudes are subjected to aerodynamic heating, which may raise the temperature of the filling above 800°C, so that the Torpexes (RDX/TNT/Al) and other conventional explosives are unsuitable for such stores.

Explosives with improved high temperature properties, usually called 'Heat Resistant Explosives' have emerged to meet such requirements. Nitro compounds have been found to be very useful heat resistant explosives. These compounds have received special attention and were reviewed by Danstan [1], T. Urbański and Vasudeva [2]. They were of special interest [3 - 7] because of their ability to withstand the high temperatures and low pressures encountered in space applications. No doubt, the manufacture of these explosives is likely to be on kilogram rather than tonne scale, but the application is highly critical. Sometimes, even complex synthetic routes can be adopted, provided the product exhibits the requisite properties, a low vapour pressure and the ability to function satisfactorily after appropriate environmental trials, which may include heating at temperatures as high as 250°C. A few explosives that have these properties are listed in Table 1.

Bicyclic nitroaromatics, hexanitrostilbene (HNS) and diaminohexanitrodiphenyl (DIPAM) are in use for achieving stage separation in space rockets and for seismic experiments on the moon [7]. Single aromatic ring compounds, such as m-diaminotrinitrobenzene (TATB) have also been found to be of practical value in various space applications.

There has been speculation about the relationship between the exceptional thermal stability of these compounds and their molecular structure. Thermal decomposition studies show that the stability is associated with high melting point and low vapour pressure and there is evidence that the rates of decomposition are enhanced when substances are in liquid or vapour phase; they reach a higher energy level when molten or vaporized [8].

Solid state physical structure appears to be as significant as chemical constitution in determining the stability of explosives, but apart from crystal structure determination on lower molecular weight compounds, such as diamino-trinitrobenzene [9] there is little information available on the magnitude of molecular interactions or crystal lattice effects in these remarkable explosives.

NITRO DERIVATIVES OF BENZENE

1,3-Diamino-2,4,6-trinitrobenzene (DATB) (I) and 1,3,5-trinitro-2,4,6-triaminobenzene (TATB) (II) have qualified as heat resistant explosives among the various nitro derivatives of benzene.

Several complicated procedures for the syntheses of diamino-trinitro benzene (DATB) have been reported. In one of these, the synthesis is accomplished [10 - 12] by vigorously nitrating m-dichlorobenzene at elevated temperatures. 1,3-Dichloro-2,4,6-trinitrobenzene thus obtained is aminated in methanol to yield DATB [13]. The yield has not been reported.

The second approach comprises the preparation of dipyrindium styrphate from styphnic acid in 94% yield. 1,3-Dichloro-2,4,6-trinitrobenzene can be obtained in 98% yield by allowing phosphorous trichloride and dipyrindium styph-
nate to react directly at steam-bath temperature. DATB was obtained by theamination reaction (mentioned above) in 97% yield. The overall yield of DATB (I) is considerably better than that obtainable by the existing procedures.

DATB is a lemon-yellow coloured crystalline substance. It is fairly stable when close to its melting point (286°C) decomposing at a rate of less than 1% per hour at 260°C, but it is transformed into crystal form of lower density at 216°C, which temperature, therefore, represents the limit of its utility. The use of DATB in highly explosive compositions has been described in several patents [14, 15].

DATB forms charge transfer complexes with aromatic hydrocarbons, aromatic amines, quinoline and isoquinoline [37].

**FIGURE 1**

1,3,5-Trinitro-2,4,6-triaminobenzene (TATB) (II) was obtained in 1887 by Jackson and Wing [16] by the route shown in (2) which was substantiated later [16a].

This is a yellow-brown coloured substance decomposing rapidly just below the m.p. (350°C) but it has excellent thermal stability in the range 260–290°C, which represents the upper temperature limit at which it may be used. The molecular structure of TATB was examined by X-ray analysis [44]. TATB possesses also a low sensitivity. However, the compressed or plastic bonded material tends to expand considerably. Subsequently Kolb and Rizzo [45] examined anisotropic thermal expansion between 214 and 377 K by X-ray analysis and found that the unit cell of TATB is formed by the planar sheets of the molecules whereas an amino group interacts with an ortho nitro group of the same benzene ring and with a nearest neighbour molecule. The sheets of TATB are bonded by strong intra- and intermolecular hydrogen bonds. A thermal volume change of 5.1% was found. Expansion was almost exclusively a function of a 4% increase in the axis perpendicular to the sheets of the molecules. The volume coefficient of thermal expansion for crystalline TATB was found to be 30.4 × 10⁻⁵ K⁻¹.

According to both groups of authors [44, 45] TATB is in triclinic form. Two other forms: another triclinic and monoclinic should be assigned to a polymorphic and impure substance respectively.

According to references in [45] a pilot plant for TATB exists in the U.S.A.

**NITRO DERIVATIVES OF DIPHENYL**

**FIGURE 2**

Among the nitro derivatives of diphenyl, 3,3-diamino-2,2',4,4',6,6'-hexanitro-diphenyl (DIPAM) (III) has been found to be a thermally stable explosive. Osterling and co-workers described a method in which the starting material is m-haloanisole. The reaction sequence is shown in (3).

The above method of preparing DIPAM comprises (a) nitration of a m-haloanisole with a mixture of nitric acid and oleum to obtain 3-halo-2,4,6-trinitro-
anisole; (b) condensation of two molecules by reacting with a slurry of copper powder and a diluent to obtain 3,3'-dimethoxy-2,2',4,4',6,6'-hexanitrodiphenyl; and (c) amination to 3,3'-diamino-2,2',4,4',6,6'-hexanitrodiphenyl (III) by introducing ammonia into a solution of hexanitro compound in a diluent which may be methanol, tetrahydrofuran or xylene-methanol-tetrahydrofuran mixture.

In addition to the ability of this explosive to withstand high temperatures, it is extremely insensitive to electrostatic discharge, requiring more than 32,000 J for initiation.

NITRO DERIVATIVES OF BIBENZYL AND STILBENE

Nitro derivatives of bibenzyl and stilbene are of considerable importance for two reasons: (i) some of them are produced by the nitration of toluene in the course of production of trinitrotoluene (TNT) as a result of the oxidation of CH₃ group; and (ii) some of them show very high melting points and can be regarded as classical examples of explosives resisting high temperatures.

Nitro Derivatives of Bibenzyl

2,2',4,4',6,6'-Hexanitrobibenzyl (IV)

This compound was obtained by Will [17] by nitrating 4,4'-dinitrobenzyl. He also claimed to have obtained it by the alkaline oxidation of TNT. A substance of the same melting point was obtained by Rinkenbach and Aaronson [18] as a by-product of the nitration of 2,2',4,4'-tetranitrobibenzyl by fuming sulphuric acid and fuming nitric acid at 85°C for a few days. The main product of nitration was claimed to be pentanitrodiphenyl ethanol: α-2,4,5-trinitrophenyl-β-2,4'-dinitrophenyl hydroxyethane (m.p. 187°C) (V).

Nitration of pentanitrobibenzyl with the same nitrating mixture for 16 hr yielded 30% of hexanitrobibenzyl and unchanged pentanitrobibenzyl. Compound IV when crystallized from acetic acid, had m.p. 213–215°C. Shipp and L. A. Kaplan [20] nitrated bibenzyl using potassium nitrate in 30% oleum in the temperature range 60–120°C for 30 hr and obtained the product in 46.5% yield. After crystallization from hot acetone and water, IV melted at 218–220°C.

Neither Blatt and Rytina nor Rinkenbach and Aaronson were able to obtain hexanitrobibenzyl by the alkaline oxidation of 2,4,6-trinitrotoluene. However, this was achieved by Shipp and Kaplan [20] who found that TNT could be oxidized to hexanitrobibenzyl or hexanitrrostilbene using sodium hypochlorite as the oxidizing agent. Thus, the observation of Will [17] proved to be correct. This was substantiated by Gilbert [51] who used methanol as a solvent at 50°C and a more concentrated hypochlorite solution, the yield was 82%.

Another process [20] consisted in reacting nitro derivatives of benzyl halogenides with trinitrotoluene in sodium hydroxide. In tetrahydrofuran, 2,4,6,6'-tetranitrobibenzyl (m.p. 179–180°C) and 2,2',4,6,6'-pentanitrobibenzyl (m.p. 155°C) were obtained (5).

Recently an Hungarian patent appeared [46] which consists in oxidative coupling of two moles of TNT in the presence of base, oxygen and a transition metal catalyst, for example, cobalt naphthenate at 50°C (in the presence of DMSO as a solvent) or cupric sulphate.

The method was examined by Golding and Hayes [47]. They tried to oxidize TNT in air in the presence of various catalysts, for example, anhydrous CuSO₄/pyridine in the presence of alcoholic KOH and triglyme. A high yield (55.5%) was obtained. Another high yield (53.4%) was given by Radium (5% on alumina) in alcoholic KOH and triglyme.
The authors suggest a mechanism for the formation of the anion $R\text{CH}_2^-$ ($R = (\text{NO}_2)_3C_6\text{H}_4\text{CH}_2^-$) which would react with the catalyst yielding a free radical according to (6):

(a) $\text{RCH}_2 + \text{OH}^- \rightarrow \text{RCH}_2^- + \text{H}_2\text{O}$

(b) $\text{RCH}_2^- + \text{Co(II)} \rightarrow \text{RCH}_2^0 + \text{Co(I)}$

(c) $2\text{RCH}_2^0 \rightarrow \text{RCH}_2^0 + \text{CH}_3\text{R}$

(d) $\text{Co(I)} + \text{O}_2 \rightarrow \text{Co(II)}$

Oxygen (or air) regenerates divalent cobalt.

Also the radical ion reaction of the type given by Russell (Chapter IV) is possible.

**Nitro Derivatives of Stilbene**

The most important nitro derivative of stilbene is hexanitrostilbene (HNS) (VII)

The existing description in the older literature is not exact and requires new information. Very likely the product of m.p. 211°C described in Vol. I, p. 416 was not hexanitrostilbene but hexanitrobenezyl. Also the direct nitration of stilbene does not furnish the required hexanitro derivative, as the double bond is highly vulnerable and oxidation can readily occur to form nitro derivatives of benzil: $C_6\text{H}_5\text{CO.COC}_6\text{H}_4\text{H}_5$. Even nitro derivatives of stilbene on vigorous nitration furnish nitrated products of benzil. Thus Challenger and Clapham [21] nitrated 2,4,6-trinitrostilbene with a mixture of nitric acid (d 1.41) and sulphuric acid at 100°C for 2 hr and obtained 2,4,6,2',4'-pentanitrostilbene (m.p. 198°C). When they applied a nitrating mixture composed of anhydrous nitric acid (d 1.5) and sulphuric acid at 100°C they obtained 2,4,6,2',4'-pentanitrostilbene (VIII) (m.p. 260°C). Blatt and Rytina [19] nitrated 2,2',4,4'-tetranitrostilbene by heating it with nitric acid (90% HNO$_3$), sulphuric acid (95%) and oleum (15% SO$_3$) in a steam-bath for 7 hr and obtained 2,2',4,4'-tetranitrostilbene (m.p. 222°C).

VIII

A few methods exist to produce nitro derivatives of stilbene. They are:

1. Reaction of nitro derivatives of toluene with benzaldehyde.
2. Reaction of nitro derivatives of benzyl halogenides with alkaline agents removing hydrogen halogenide.
3. Oxidation of nitro derivatives of toluene.

**1. Reaction of nitro derivatives of toluene with benzaldehyde and its nitro derivatives.** This type of reaction was first described by Tiele and Pascual [22]. While heating a mixture of 2,4-dinitrotoluene with benzaldehyde at 160-170°C and allowing the reaction mixture to rest for 2 hr, they obtained all the three possible isomers of 2,4,4'-trinitrostilbene using $\alpha$, $m$- and $p$-nitrobenzaldehyde.

In a similar way, Ullman and Geschwind [23] obtained 2,4,6,4'-tetranitrostilbene (m.p. 196°C) from trinitrotoluene and $p$-nitrobenzaldehyde.

Shipp [24] tried the same reaction between trinitrotoluene and trinitrobenzaldehyde and obtained hexanitrostilbene in poor yield.

**2. Preparation from nitrobenzyl halogenides.** This method consists in reacting nitrobenzyl halogenides with alcoholic potassium hydroxide. The reaction was
described for the first time by Krassusky [25] who obtained 2,4,2',4'-tetrynitrobenzyl (m.p. 266–267°C) by warming 2,4-dinitrobenzyl chloride with potassium hydroxide in ethanol. The reaction did not seem to be successful when 2,4,6-tetrynitrobenzyl bromide was used as the starting material contrary to the finding of Reich and co-workers (Vol. I, p. 416).

Shipp [24] obtained 2,2',4',4',6,6'-hexanitrostilbene (HNS) in 30% yield by reacting 2,4,6-tetrynitrobenzyl halogenide with alcoholic potassium hydroxide (8). The product melted at 316°C.

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{CH}_2\text{Br} \quad \text{KOH} / \text{methanol} \quad \text{steat bath} \\
\text{O}_2\text{N} & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NO}_2
\end{align*}
\]

VII

that is, 105°C above the melting point of the product obtained by Reich. The correct structure of the compound follows from the synthetic route given by Shipp [24].

3. Preparation by oxidation of nitro derivatives of toluene. A number of methods involving this approach have been developed. They can lead to derivatives of both bibenzyl and stilbene. Thus, Green and co-workers [26] obtained 4,4-dinitrobenzyl (m.p. 180–182°C) by oxidizing p-nitrotoluene with air in potassium hydroxide solution in methanol at room temperature. When the reaction mixture was warmed 4,4-dinitrostilbene resulted. Green and Baddiley [27] reacted 2,4-dinitrotoluene with diiodine in the presence of pyridine in potassium hydroxide solution in methanol at 40–50°C and obtained 2,2',4',4'-tetrynitrostilbene (m.p. 266–267°C).

Shipp and Kaplan [20] obtained 2,2',4',4',6,6'-hexanitrostilbene (HNS) by oxidizing TNT with sodium hydrochlorite. The method consists in adding 10 parts of 5% sodium hypochlorite solution to a chilled solution of 1 part of TNT in 10 parts of methanol. The solution is allowed to stand at ambient temperature until HNS precipitates as a fine crystalline product. The product is crystallized from nitrobenzene to yield pale yellow coloured needles. The mechanism of the reaction is shown in reactions (9).

\[
\begin{align*}
\text{CH}_3\text{OH} & \quad \text{RCl} \quad \text{ClO}_2^- \quad \text{RCH}_2\text{Cl} \quad \text{O}_2^- \quad \text{RCHCl} \quad \text{RCHCl}_2 \\
\text{Cl} & \quad \text{R}^- \quad \text{CH}^- \quad \text{CH}_2^- \quad \text{R}^- \quad \text{R}^- \quad \text{NO}_2 \quad \text{NO}_2
\end{align*}
\]

IX

It is possible to isolate 2,4,6-trinitrobenzyl chloride or the bimolecular product α-chloro-2,2',4',4',6,6'-hexanitrobibenzyl by stopping the reaction short. This is indeed an excellent preparative reaction for the chloride replacing the tedious series of reactions which had been the only known route for this compound [28].

HNS can form charge-transfer complexes with a number of aromatic amines and phenols [38].

A novel method of producing nitrostilbene derivatives was given by Bethel and Bird [48]. It consists in reacting 4-nitrobenzylhalide with potassium t-butoxide. 4,4-Dinitrostilbene resulted.

According to [47] full scale production of HNS exists in the United Kingdom based on the method of Shipp [24].

NITRO DERIVATIVES OF AROMATIC AZA PENTALenes

Tetranitro derivatives of dibenzo-1,3a,4,6a-tetraazapentalene (TA/COT) (IX):

This is a mixture of isomers with two nitro groups substituted in different positions in each benzene ring. It is a powerful explosive with unusual and outstanding high temperature stability [29]. TACOT, which is comparable to pentathylbenzotetranitrate (PETN) in explosive power, has thermal stability greater than that reported for any known organic explosive compound or composition.

TACOT was described for the first time in 1960 in a patent [30] and later in many papers by Carboni and co-workers [31–36] in which the synthses of this compound and its properties were reported. It can be obtained from α-phenylidendiamine by the sequence of reactions (10).

Tetranitrodibenzol-1,3a,4,6a-tetraazapentalene is generally prepared from tetraazapentalene by direct nitration. The procedure (29) consists in adding 30 parts of fuming nitric acid to 1 part of dibenzo-1,3a,4,6a-tetraazapentalene in concentrated sulphuric acid. After 15 min, the mixture is heated to 60°C and maintained at this temperature for an additional 15 min period. The orange coloured mixture is poured into ice-water to yield TACOT, which can be recrystallized from dimethyl formamide. The product obtained is composed of numerous isomers of tetranitrodibenzol-1,3a,4,6a-tetraazapentalene, depending on the position of the nitro group (ortho, meta or para) in each individual
benzene ring. But these isomers have been found to have similar explosive and thermal properties. Therefore TACOT which is a mixture of the three isomers, is used as such in explosive compositions. Its ignition temperature (494°C) is the highest ever registered for explosives. Its explosive power is equal to 96% and 80–85% that of TNT and RDX respectively. It is highly insensitive to impact and compares favourably with dinitrobenzene in that respect. Despite the insensitivity to impact and static charges TACOT can be readily initiated by lead azide primer containing as little as 0.02–0.03 g of lead azide.

### Table 4. Heat resistant explosives

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Chemical name</th>
<th>m.p. °C</th>
<th>Crystal density g/cm³</th>
<th>Velocity of detonation m/sec</th>
<th>Detonation pressure (cal.) kbars</th>
</tr>
</thead>
<tbody>
<tr>
<td>DATB</td>
<td>1,3-Diamino- 2,4,6-trinitrobenzene</td>
<td>286</td>
<td>1.84</td>
<td>7500</td>
<td>260</td>
</tr>
<tr>
<td>TATB</td>
<td>1,3,5-Triamino- 2,4,6-trinitrobenzene</td>
<td>350</td>
<td>1.94</td>
<td>7500</td>
<td>200</td>
</tr>
<tr>
<td>HNS</td>
<td>2,2',4,4',6,6' hexanitrostilbene</td>
<td>(decomp)</td>
<td>3.18</td>
<td>3740</td>
<td>215</td>
</tr>
<tr>
<td>DIPAM</td>
<td>Hexanitrostilbene 3,3',5-trinitro- 2,2',4,4',6,6'-hexanitrostilbene</td>
<td>1.74</td>
<td>7000</td>
<td>215</td>
<td></td>
</tr>
<tr>
<td>TACOT</td>
<td>Tetranitro- 3,5,6-dibenzo-1,3,4,6-tetrazapentalene</td>
<td>410</td>
<td>1.85</td>
<td>7200</td>
<td>245</td>
</tr>
</tbody>
</table>

NONA is 2,2',2',4,4',4',6,6,6' nonaerphenyl obtained by reacting 2 moles of picryl chloride with 1,3-dichloro-2,4,6-trinitrobenzene in the presence of copper dust at 210°C (Ullman reaction) [55]. It has an exceptional heat stability melting with decomposition at 440–450°C. It has a density of 1.78. No more information is available.

### Potential heat resistant explosives

Some work has been done to obtain new heat resistant explosives. A number of potential products were thus obtained, Buckley, Everard and Wells [58]. They nitrated 2,6-dimethyl-1,3-dinitronaphthalene [40] using nitric acid in acetic anhydride and obtained tetranitro derivatives marked by their high melting points in addition to a small amount of a trinitro compound not shown on formula (11).

It was suggested that the above compounds should be used to produce analogues to hexanitrostilbene by their oxidation.

Buckley and co-workers [56] continued their work on high nitrated naphthalene derivatives. They nitrated 1-methyl naphthalene with dilute nitric acid (d 1.42) in Cl CH₂CH₂Cl at 40°C and obtained 4,8- and 4,5-dinitro-1-methyl naphthalene (I and II respectively).

On further nitration below 2°C with nitric acid (d 1.5) and sulphuric acid
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

(d 1.84) they obtained trinitro- and tetrinitro derivatives, of relatively low melting points:

\[
\begin{align*}
I & \rightarrow 2,4,6\text{-trinitro-}, 4,5,8\text{-trinitro-} & & 2,4,5,8\text{-tetrinitro-1-methyl naphthalene} \\
& m.p. 135^\circ & & m.p. 218^\circ & & m.p. 220^\circ \\
II & \rightarrow 2,4,5\text{-trinitro-1-methyl naphthalene (m.p. 190')}
\end{align*}
\]

The yields of tetrinitro derivatives were low (6%).

Another line of research consisted in producing polynitroacenaphthene [41]: 3-, 4- and 5-nitroacenaphthene were nitrated and yielded di-, tri- and tetrinitroacenaphthenes. Also pentanitroacenaphthene was obtained. None of the substances has shown a very high m.p.; the highest was that of 3,7-dinitroacenaphthene (m.p. 276°C).

However, tetrinitro derivatives obtained by nitration of 3- and 4-nitroacenaphthenes, 3,5,6,8- and 3,5,6,7-tetrinitroacenaphthenes (12a) and (12b) respectively can be of some interest as explosives.

[Diagrams of chemical structures]

Another potential heat resistant nitro compound is 2-amino-4,6,7,9-tetranitroperimidine (X) [42]. The mother substance: 2-amino perimidine can be obtained from perinaphthylene diamine and ammonium cyanate with a good yield [43]. The substance is used in analytical chemistry as a reagent for sulphate ion because of the very low solubility of the sulphate.

It was recently announced [50] that 1,3,5,7-tetranitrodiamantane (TNA) possesses properties which are likely to be of value as a heat resistant explosive. Its m.p. is above 350°C. It is also very insensitive to impact.

HEAT RESISTANT EXPLOSIVES

In some countries Octogene (HMX) is considered as a heat resistant explosive [50, 51]. Its m.p. was found to be between 276 - 277°C (Vol. III, p. 117) and 290°C [51].

Nitro derivatives of 2,5,8-triphenyl-tris-triazolobenzene (XI) are very interesting heat resistant compounds [52]. The substances were obtained by coupling diazotized nitroanilines with 1,3,5-triaminobenzene, followed by oxidation with CuSO₄. Compounds from m-nitroaniline and 2,4-dinitroaniline had m.ps of 369 - 370°C and 400°C respectively.

Resistance to Irradiation

The heat resistant explosives: TACOT, DATB and TATB are remarkably stable towards various irradiations such as gamma radiation from Co⁶⁰ according to Avrami [49].

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HEAT RESISTANT EXPLOSIVES

(1975); Chem. Abstr. 84, 58886 (1976).
47. P. GOLDMING and G. F. HAYES, Prop. & Expl. 4, 115 (1979) and references therein.

APPENDIX

Kubosek and co-workers used phase-transfer catalysis and catalytic two phase system to obtain some heat resistant explosives such as: HNS [1, 21, HNBB [31, Hexanitrodiphenylmethane [4], Hexanitrodiphenylamine [5] and polynitro derivatives of polyphenylethers [6].

REFERENCES

CHAPTER 8

ALIPHATIC NITRO COMPOUNDS

(Vol. I, p. 579)

In the course of the last two decades the chemistry of aliphatic nitro compounds—both nitroalkanes and nitroalkenes has received particular attention. A variety of compounds have been obtained and their properties examined.

Between 1950 and 1960 increased interest in the use of nitroalkanes as potential explosives and propellants has been a major factor in expanding the chemistry of this relatively ignored field.

Evidence of the increasing interest in the field were Symposia on Nitro Aliphatic Chemistry in 1961 [1] on Nitro Compounds in 1963 [2], and in 1968 [3]. Then a few excellent review articles appeared by: Doležel [4], Noble, Borgardt and Reed [5], Shechter [6a], Shechter and R. B. Kaplan [6b], a review on nucleophilic substitution $S_{N}1$ of aliphatic nitro compounds by Belorskaya and Drozd [245], collective volumes edited by H. Feuer [7], monographs by: Perekalin and Sopova [8], Novikov and co-workers [9]. See also [120]. Some books exist where the chemistry of nitroalkanes form important chapters, viz.: by Asinger [10], Matasă and Matasă [11], Sosnovsky [12].

Nitroalkanes have also opened some new fields in organic synthesis. The problems were tackled in a number of monographs and review articles [13–19]—however, most of them are outside the scope of the present book. Such is also the monograph by Krein and Shekhter [233] describing the nitration of lubricating oils to produce anti-corrosion materials.

There are some natural nitroalkane derivatives existing, such as β-nitroproplionic acid present in some plants.

MONONITRO ALKANES

As is known (Vol. I), alkanes can be nitrated in vapour phase by nitric acid or nitrogen dioxide. Nitrination with nitric acid at temperatures of 400–435°C (method of Hass, Vol. I, p. 86) became a well established commercial method of making nitroalkanes. A considerable number of papers mainly by Hass and co-workers (Vol. I) and Titov (Vol. I) gave both theoretical and practical foundations for this remarkable process and subsequently less theoretical work has appeared. Less attention was paid to the nitration of alkanes with nitrogen dioxide (method of T. Urbánski and Słoń, Vol. I, p. 94) which has not been put to industrial use.

The author of this book continued some of his work, for example, nitrating $n$-heptane with a great excess of nitrogen dioxide [20]. It was found that equal distribution of the nitro groups occurred along the chain: ca. 40% were found for positions 2 and 6, 3 and 5, and ca. 20% for position 4. This confirmed the view expressed by Hass (Vol. I, p. 95) and Asinger (Vol. I, p. 95), [10, 21, 22] that the nitration of CH$_2$ groups of longer chain alkanes proceeds according to the statistical rule. This finding was contrary to some views that position 2 in long chain alkanes is the preferred position [23].

Ślebodziński, T. Urbánski and Łukasiewicz [24] nitrated $n$-hexane with nitrogen dioxide at temperatures varying from 120° to 300°C with molar ratios $n$-hexane:NO$_2$ varying from 1:10 to 5:1. The highest yield and safest conditions were obtained with the ratio 3:1 at 300°C. The yield of nitro compounds was ca. 42% in relation to $n$-hexane converted. The composition of the nitroalkane fraction was as given in Vol. I, pp. 94–95.

The identification of nitroalkanes was carried out by coupling nitroalkanes with diazonium salts [25]. The method was based on the work of V. Meyer et al. [26] and used by some authors for the identification of nitroalkanes [27, 28].

With the advent of chromatography the method of gas chromatography was used for the separation and identification of nitroalkanes. This was described in papers by Beebe and Wheelock [29]. The gas–liquid chromatography of C$_1$–C$_4$ nitroalkanes was used by Biernacki and T. Urbánski [30].

Minc, T. Urbanis and Falęcki [96] examined the action of ionizing radiation from Cobalt source (Gamma Cell 220) upon $n$-hexane dissolved in N$_2$O$_4$ in sealed tubes. The reaction was carried out for 200 hr at room temperatures, and the yield of 1-nitrohexane was 1%. The experiments were discontinued when a violent explosion occurred in one of the tubes.

Albright et al. [97] examined the influence of gamma radiation upon the vapour phase nitration of propane with nitric acid at 400–450°C. There was a slight effect of radiation on the yield of nitro products, in agreement with the above finding [96]. The increase of the yield of nitro alkanes was of the order of only 10–15%.

OTHER METHODS OF INTRODUCING THE NITRO GROUP INTO SATURATED COMPOUNDS

The other methods of introducing the nitro group into saturated compounds have been reviewed by Larson [31].

Here are the main outlines for the conversion of oximes to nitro compounds.

Emmons and Pagano [32] used peroxytrifluoroacetic acid to oxidize oximes to nitro compounds with a yield of up to 76%. The reaction is carried out in
acetonitrile as a solvent in the presence of a buffer to neutralize trifluoroacetic acid formed in the reaction. This is a simple and convenient method of obtaining nitro aliphatic and alicyclic compounds. Thus, nitrocyclohexane and 1-nitroheptane were obtained with yields of 62 and 72\% respectively. See also [33].

Another method of oxidation of ketoximes to nitro compounds consists in the bromination of ketoximes with N-bromosuccinimide to obtain bromonitrosobenzene compounds which were oxidized with nitric acid and hydrogen peroxide to bromonitro compounds. The latter were debronnimatized by sodium borohydride to yield secondary nitro compounds [34] (1).

$$\begin{align*}
\text{RN}3 \rightarrow \text{NO}3 + \text{H2O} & \quad (1)
\end{align*}$$

The method has found an application to the preparation of nitro steroids [35].

Oximes can be oxidized to nitro compounds with ozone [227], and recently an excellent yield was obtained by oxidation of ketoximes with hypohypochlorous acid to form chloronitrosobenzene compounds which on further oxidation with tetro- 
butylammonium hypochlorite yielded secondary nitroalkanes [228].

**Oxidation of Amines**

The reaction of the oxidation of aromatic amines to nitro compounds examined by Ermont and co-workers (Vol. 1, p. 122) gave a high yield of nitro derivatives. Ermont [36] tried to use peracetic acid to obtain tertiary nitroalkanes. The reaction gave a low yield (e.g. nitrocyclohexane was obtained with a yield as high as 57\%). The use of peroxynitrophenetoleic acid, successful in the oxidation of oximes, did not give favorable results with amines. To obtain nitroalkanes from the amines, 2-chloroperbenzene oxide was successfully used (the yield was 70\%) [37].

Potassium permanganate can also be used to oxidize tertiary amines otherwise resistant to oxidation [38].

**Reaction of Alkyl Halides with Sodium Nitrite**

The method of Kornblum (Vol. 1, p. 125) received a wide application. For example, for the synthesis of nitro esters [39] and \(\beta\)-nitroketones [40]. However, this method has some limitations. Thus \(\alpha\)-butyl halide does not furnish the expected nitro compounds. Also cyclohexyl bromide does not react with sodium nitrite. On the contrary, cyclohexyl iodide reacts with sodium nitrite but the product is cyclohexane in 57\% yield.

Similar to the reaction of V. Meyer, nitrous esters are also formed during the

Kornblum reaction, for example, bromocyclopentane is converted to both nitrocyclopentane and nitrous ester [41]. For more information see [31].

**Nitromercuration of Alkenes**

An interesting reaction of nitromercuration was found by Bachman and Whitehouse [107]. It consists in acting with sodium nitrite and mercuric chloride on alkenes, for example, on cyclohexene (2).

$$\begin{align*}
\text{Cyclohexene} + \text{HNO}_2 + \text{HgCl}_2 & \rightarrow \text{Cyclohexyl nitrite} + \text{HgCl}_2 + \text{HCl} \quad (2)
\end{align*}$$

\(\beta\)-Nitromercuration chloride results with the yield of 80\%. The products were used to obtain nitroalkanes (2Na).

**Formation of Nitroalkanes from Nitrate Ethers**

Thermal decomposition of nitrate ethers has been shown to result in the formation of small amounts of nitroalkanes [237]. Bachman and Connon [238] described the method of converting nitrate esters into nitroalkanes by reacting nitrate esters with metal nitrites in suitable solvents. More detailed information is given in Chapter X on nitrate esters.

**CHEMICAL PROPERTIES OF NITROALKANES**

**Nitric Acids**

One of the most important properties of primary and secondary nitroalkanes is their ability to form aci-nitro compounds, also referred to as nitronic acids.

$$\begin{align*}
\text{R}^1\text{C} = \text{NO}_2 + \text{H} & \rightarrow \text{R}^1\text{C} = \text{NO}_2 \quad (3)
\end{align*}$$

**Polar Solvents Favor the Acid Form**

Nitronic acids are relatively weak (pK\(_a\) ≈ 2 – 4) resembling carboxylic acids with regard to their strength. The nitronic acids can form esters. They can be prepared in three ways:

1. by the alkylation of sodium or potassium nitronate salts, for example.

$$\begin{align*}
\text{R}^1\text{C} = \text{NO}_2 + \text{Na} & + \text{CH}_2\text{R} & \rightarrow \text{R}^1\text{C} = \text{NO}_2 \quad (4)
\end{align*}$$

2. by the formation of sodium or potassium nitro compounds, for example.
(2) by the alkylation of silver nitrate salts,
(3) by the reaction of nitro alkenes and nitronic acids with diazomethane.

Method (1) has considerable limitations, as the nitronic ester decomposes readily to yield oximes and aldehydes and ketones.

Nitronic esters are able to enter the 1,3-addition reaction (Chapter IV, formula 30).

Salts of nitronic acid can decompose readily in a dangerous manner. Particularly dangerous are salts of nitromethane (Vol. I, p. 586; Vol. III, p. 136). Dry sodium salt of nitromethane can explode when touched with a spatula.

The chemistry of nitronic acid and derivatives is a very wide field and the reader should consult an excellent monographic review by Nielsen [42].

Activating Influence of the Nitro Group

The nitro group activates aliphatic systems and makes possible a number of addition reactions such as: aldolic addition of aldehydes (Henry reaction), Mannich reaction, Michael addition, Diels–Alder reaction, for example [155].

The reader should be advised to consult an excellent monographic review given by Baer and Urbas [43].

Here are a few data based on more recent publications.

1. Aldolic addition and the Mannich reaction (Vol. I, p. 186). The aldolic addition reaction of nitroalkanes with carbohydrates (specifically aldoses) continues to be an important reaction in sugar chemistry which according to Baer [43] in some respects surpasses in versatility Emil Fischer's classical cyanohydrid synthesis. Particularly noteworthy are publications by Baer and Koval [44, 45], Funubashi, Yoshimura and co-workers [46–51] and other Japanese workers [52], Russian workers [53, 54] and Bilik [55].

A different method of preparing glucosinolates through nitroalkanes was given by MacLeod and Gil [56].

With regard to the Mannich reaction the monographs, for example, that of Reichter [57] should be consulted.

2. Michael addition. Ostaszewski and Wielgat [58] used potassium fluoride as a catalyst for the Michael addition of nitromethane to a double bond. (Alkali fluorides were originally suggested by Yasuda et al. [59] as catalysts for the Michael addition reactions) The work of addition of nitroalkanes was continued [60]. Various acceptors, for example, methy lacrylate and acrylonitrile, were used. Among nitroalkanes gem-dinitroalkanes were applied as donors. Nitroalkanes readily formed double salts with KHF₂, RbHF₂ and CsHF₂. The yield of the adducts of such salts with compounds containing a double bond varied between 60 and 90%, viz. (3).

3. Reaction of nitromethane with pyrimid salts. Dimroth [62] in a number of papers since 1956 [63] has described an interesting reaction in the formation of aromatic nitrocompounds by reacting nitromethane with pyrimid salts (e.g. perchlorate) substituted in positions 2,4,6 in basic medium (7) with a yield varying from 25 to 60%.

By-products of the reaction are cyclohexylinden derivatives.

4. Nitroalkanes as alkylation agents in Friedel-Crafts reactions. An interesting reaction was recently reported by Casini and co-workers [64]. They found that Friedel-Crafts reaction of benzylc or tertiary nitro compounds with benzene gave normal alkylation products (8) and (9) respectively. 2-Nitropropane gave cumene (10) subject to further transformations.

\[
\begin{align*}
CH_3C(CH_2NO_2)_2 + CH_2\equiv CHCOOCH_3 & \xrightarrow{60-65^\circ} CH_2C(CH_2COOCH_3)_2 \\
\text{Aliphatic Nitro Compounds} & \quad 79\% \\
\end{align*}
\]

Alternatively, nitroalkanes can be added to an activated double bond, (6) [61]:

\[
\begin{align*}
\text{NO}_2 + & \xrightarrow{\text{COOCH}_3} \text{COOCH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{NO}_2 + \text{C}_6\text{H}_5 & \xrightarrow{\text{K-2-Butyrate (bubbling)}} \text{R}^1\text{NO}_2 \quad + \text{H}_2\text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_3\text{NO}_2 + \text{C}_6\text{H}_5 & \xrightarrow{\text{AlCl}_3 \text{room temp.} \quad 24 \text{h}} \text{C}_6\text{H}_5\text{CH}_3\text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5\text{NO}_2 + & \xrightarrow{\text{AlCl}_3 \text{room temp.} \quad 2 \text{h}} \text{C}_6\text{H}_5\text{CH} = \text{CH}_2 \\
\text{CH}_3\text{NO}_2 + \text{C}_6\text{H}_5 & \xrightarrow{\text{AlCl}_3 \quad 55^\circ \text{C/2 h}} \text{C}_6\text{H}_5\text{CH} = \text{CH}_2 \\
\end{align*}
\]
5. Oxidation of nitroalkanes to aldehydes and ketones (Vol. I, p. 186). The Nef reaction (Vol. I, p. 186) for the formation of aldehydes and ketones from primary and secondary aliphatic nitro compounds was modified by Nametkin and Pozdnyakowa [90] and Grundman [91] who improved the yield of ketones (from secondary nitroalkanes) by using an oxidizing medium of potassium permanganate and hydrogen peroxide respectively. The reaction with permanganate was extensively used by Asinger et al. [20b, 22], Slezdowski, T. Urban and K. Kornblum [24] in the analysis of the products of nitration of long chain alkanes.

McMurray and co-workers modified the reaction by carrying it out in a reducing medium of TiCl₄ followed by hydrolysis and an oxidizing medium of O₃ [92a] and [92b] respectively. See also Bartlett et al. [93]. They used 1-butyl hydroperoxide in the presence of pentavalent vanadium salt as a catalyst. Kornblum and Wade [94a] gave an unusual method of oxidation of secondary nitroalkanes to ketones with nitrous esters and sodium nitrite at room temperature:

\[ R_2CHNO_2 + NaNO_2 + n - C_2H_5ONO \rightarrow R_2CO + n - C_2H_5OH + NaNO_3 + N_2O \]  

The yield was up to 88% depending on nitroalkane.

6. Nucleophilic displacement of the nitro group from nitroalkanes. Such reactions were described by Kornblum [95], Benn and Meesters [95]. The reactions consist in the substitution of the nitro group with aryls. The reaction of Kornblum will be described in the paragraph dedicated to aryl nitroalkanes.

NITROMETHANE (Vol. I, p. 579)

Shaw [65] presented new data referring to the physico-chemical properties of nitromethane (as compared with those of methyl nitrite).

Shaw's data are as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15°C</td>
<td>1.140</td>
</tr>
<tr>
<td>Boiling point</td>
<td>101.4°C</td>
</tr>
<tr>
<td>Melting point</td>
<td>-29°C</td>
</tr>
<tr>
<td>Heat of formation</td>
<td>-27 kcal/mol</td>
</tr>
<tr>
<td>Heat of vaporization</td>
<td>9.1 kcal/mol</td>
</tr>
<tr>
<td>Specific heat Cₚ</td>
<td>13.7 cal/mol deg</td>
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<tr>
<td>Activation energy of thermal decomposition</td>
<td>59.0 kcal/mol</td>
</tr>
<tr>
<td>Detonation velocity</td>
<td>6300 m/s</td>
</tr>
<tr>
<td>experimental</td>
<td>6300 m/s</td>
</tr>
<tr>
<td>calculated</td>
<td>6890 m/s</td>
</tr>
</tbody>
</table>

Some figures given by Meyer [66] are slightly different:

A considerable amount of work has been dedicated to the problem of decomposition of nitromethane in gas phase. They were reported in Vol. I (p. 579) and in the review article by Makovský and Lenji [67].

A few papers referring to flash photolysis should be mentioned: those by Norrish and co-workers [68], Pinet et al. [69], Nicholson [70], McGarvey and McGrath [71].

Crawforth and Waddington [72] examined pyrolysis of nitromethane between 305°C and 440°C. They found the reaction to be pressure dependent. Above 150 mm it is approximately of the first order

\[ k = 10^{14.1} \text{ exp.} (-55 \text{ kcal/RT}) \text{ sec}^{-1}. \]

The main products are: methane, CO, N₂, NO, HCN and water. The authors suggested the mechanism through the initially formed methyl radical:

\[ \cdot \text{CH}_3 + \cdot \text{CH}_3 \text{NO}_2 \rightarrow \: \cdot \text{CH}_3 + \cdot \text{CH}_2 \text{NO}_2 \]

\[ \cdot \text{CH}_3 + \text{NO}_1 \rightarrow \cdot \text{CH}_3 \text{NO}_2 \]

\[ \cdot \text{CH}_3 + \text{NO}_1 \rightarrow \cdot \text{CH}_2 \text{O} + \text{NO} \]

\[ \cdot \text{CH}_3 + \text{NO} \rightarrow \cdot \text{CH}_2 \text{NO} \]

A few papers were dedicated to the decomposition of nitromethane in shock-tubes: Bradley [73], Hiraoka and Hardwick [74], Borisov and co-workers [75]. Glänzer and Tree [76] examined the decomposition of nitromethane highly diluted with argon in shock waves between 900 and 1500 k, and concentration of argon 1.5 x 10⁻⁶ and 3.5 x 10⁻⁴ mol/cm³. A unimolecular reaction occurred:

\[ \text{CH}_3 \text{NO}_2 \rightarrow \cdot \text{CH}_3 + \cdot \text{NO}_2 \]

The rate constant k is expressed by the equation:

\[ K = 10^{17.3} \text{ exp.} (-42 \text{ kcal/RT}) \text{ sec}^{-1}. \]

A subsequent reaction occurred between free radicals:

\[ \cdot \text{CH}_3 + \cdot \text{NO}_2 \rightarrow \cdot \text{CH}_2 \text{O} + \text{NO} + \cdot \text{OH} \]
**CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES**

Shock initiation of liquid nitromethane (as compared with that of methyl nitrate) was given by Shaw [65].

**Practical use of nitromethane as an explosive.** The use of nitromethane is limited owing to its high volatility. According to Meyer [66] nitromethane was used in the U.S.A. for underground model explosion ('Pre-Gondola') in preparation for the nuclear charge technique, and for stimulation blasting in oil and gas wells.

Nitromethane can also be used as monergolic liquid fuel for rockets.

**NITROETHANE, 1-NITROPROPANE AND 2-NITROPROPANE**

Gänzer and Troe studied a shock wave thermal decomposition in argon of nitroethane [77], 1- and 2-nitropropanes [78].

The following are data obtained (Table 42).

**TABLE 42. Characteristics of shock wave thermal decomposition of nitroalkanes**

<table>
<thead>
<tr>
<th>Nitroethane</th>
<th>1-Nitropropane</th>
<th>2-Nitropropane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperatures (K)</td>
<td>905-1350</td>
<td>910-1350</td>
</tr>
<tr>
<td>Rate constant &amp; kcal/(RT)</td>
<td>$10^{14.5} exp^{(-57)}$</td>
<td>$2.3 \times 10^{15} exp^{(-55)}$</td>
</tr>
<tr>
<td>Primary reaction step of C=N bond fission</td>
<td>$C_2H_5^+ + NO_2$</td>
<td>$C_3H_7^+ + NO_2$</td>
</tr>
</tbody>
</table>

2-Nitropropane can be subjected to dimerization under the action of alkali metals in carbon tetrachloride, DMSO in the atmosphere of nitrogen (15) [79]:

\[
\begin{align*}
&\text{NO}_2^+ \\
&\text{CCl}_4, \text{DMSO}, \text{N}_2, \text{Li or K salt } & \rightarrow & \text{O}_3\text{N}^- + \text{NO}_2 \\
&\text{(15)} & & \\
\end{align*}
\]

2-Nitropropane is widely used in the U.S.A. as a solvent, however its carcinogenic action has been reported [80].

**ARYLNITROALKANES**

Arylnitroalkanes form an interesting group of compounds: they combine the properties of the aromatic ring with those of nitroalkanes. The simplest of course phenylnitromethane (Vol. I, pp. 96, 123, 275, 598). The chemistry of aryl nitromethane was reviewed by Novikov and Khmelnitskii [81].

As has already been pointed out (Vol. I, p. 275) phenyl nitromethane can be formed during the nitration of toluene, while using nitrogen dioxide as a nitrating agent.

**ALIPHATIC NITRO COMPOUNDS**

Higher nitrated derivatives of phenyl nitromethane, among them those of dinitro- and trinitromethane (Vol. I, p. 399) are important. The reaction of Ponzo [82] consists of acting with $N_2O_4$ on benzaldoxime: phenyl-dinitromethane results (16):

\[
\begin{align*}
&\text{CH}==\text{NOH} \\
&\text{N}_2\text{O}_4 & \rightarrow & \text{CH(NO}_2\text{)}_2 \\
&\text{(16)} & & \\
\end{align*}
\]

According to Fieser and Doering [83] the reaction should be carried out by gradually mixing solutions of benzaldoxime and $N_2O_4$ in dry ether at the temperature of boiling ether. The yield of the reaction produced in such a way was 38% lower than in the Ponzo original method (50%), but violent reaction is avoided.

Derivatives of phenylnitromethane nitrated in the aromatic ring have again received (Vol. I, p. 598) attention, particularly in relation to the properties of TNT. Sitzmann, L. A. Kaplan and Angres [84] acted on 2,4,6-trinitrotoluene in alkaline medium with fluorotritinomethane which is an alkaline nitrating agent and was prepared by Kamlet and Adolph [85]. The reaction (17) brought about the formation of 2,4,6-trinitrophenyl-nitromethane through the intermediate 2,4,6-trinitrotoluene anion (Chapter VI, reaction 5, and [86]):

\[
\begin{align*}
&\text{O}_1 \quad \text{CH}==\text{CH}_2 \quad \text{NO}_2 \\
&\text{+ NO}_2\text{CNO}(\text{NO}_2)_2 \quad \text{NaOH (C147)} \quad \text{NaO} \quad \text{CH}_3\text{CO}(\text{NO}_2)_2 \quad \text{O}_2\text{N} \quad \text{CH}_3\text{NO}_2 \quad \text{NO}_2 \\
&\text{2H} \quad \text{2H} \quad \text{2H} \quad \text{2H} \quad \text{2H} \quad \text{2H} \quad \text{2H} \quad \text{2H} \\
&\text{m.p. 116.5 - 118°C} \quad \text{[80]} \\
&\text{(17)} & & \\
\end{align*}
\]

The same compound was obtained earlier by Russian workers [87] through the action of chloranil (as an oxidizing agent) on the $\sigma$-complex (I) of 2,4,6-trinitrotoluene with potassium salt of nitromethane.

\[
\begin{align*}
&\text{O}_1 \quad \text{CH}==\text{CH}_2 \quad \text{NO}_2 \\
&\text{+ NO}_2\text{CNO}(\text{NO}_2)_2 \quad \text{NaOH (C147)} \quad \text{NaO} \quad \text{CH}_3\text{CO}(\text{NO}_2)_2 \quad \text{O}_2\text{N} \quad \text{CH}_3\text{NO}_2 \quad \text{NO}_2 \\
&\text{2H} \quad \text{2H} \quad \text{2H} \quad \text{2H} \quad \text{2H} \quad \text{2H} \quad \text{2H} \quad \text{2H} \\
&\text{m.p. 116.5 - 118°C} \quad \text{[80]} \\
&\text{(17)} & & \\
\end{align*}
\]

A considerable amount of work was done by Kornblum and co-workers on the chemistry of aryl nitroalkanes, particularly the $p$-nitrocumyl system with a
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

side chain of branched nitroalkane in the para position to the nitro group [17, 88]. Two interesting reactions are given here as examples:

\[
\begin{align*}
O_2N- & -CH_2-Cl + (CH_2)_2CNO_2Li' \rightarrow O_2N- & -CH_2-CH_2-C-\text{NO}_2 \\
\text{O}_2N- & -CH_2-CH_2-C-\text{NO}_2 \rightarrow O_2N- & -CH_2-CH_2-C-\text{NO}_2 \\
& \quad \text{[N}_2] \rightarrow \text{CH}_3 \\
& \quad \text{CH}_3 \\
(18) \\
& \quad \text{CH}_3 \\
& \text{CH}_3 \\
(19)
\end{align*}
\]

In both types of reaction lithium salts of nitroalkane were used and the reactions appeared to proceed via a chain mechanism in which radical anions and free radicals are intermediates.

A remarkable feature of reaction (19) is the substitution of the nitro group attached at tertiary carbon of the p-nitrocumene system. The reaction of the displacement of a nitro group from a saturated carbon atom through an anion has been described for the first time [88c].

In the same system of cumene a replacement of the nitro group by hydrogen was described by Kornblum and co-workers [88d]. The agent replacing the nitro group was sodium salt of methanethiol in an aprotic solvent:

\[
R_1CNO_2 + CH_2S^- \xrightarrow{\text{room temp.}} R_1CH
\]

(20)

Kytko-Krasuska, Piotrowska and T. Urbanski [89] reported the reaction of replacement of a secondary aliphatic nitro group by hydrogen while treating the nitro compound with potassium hydroxide in ethylene glycol at 120–140°C. The reaction proceeded by a radical anion mechanism. Ono and co-workers [121] described new methods of replacing the nitro group in aliphatic compounds by hydrogen. One of the methods consists in acting with N-benzyl-1,4-dihydropicolinamide [121a], and another [121b] by acting on tertiary and secondary nitro compounds with tin hydrides (or deuterides) of the type Bu3SnH (or Bu3SnD). The treatment of nitro compounds with tin hydrides occurred by refluxing in benzene in the presence of azobisisobutyronitrile. Bu3SnH was converted to the nitrite Bu3SnONO in an atmosphere of nitrogen. Only 2-methyl-2,2-nitropropyl ester gave a hard resin, whereas the other nitroalkanes gave viscous resins. The presence of the nitro group in the molecule seems to inhibit the polymerization in agreement with the findings described in Chapter IV.

ESTERS OF NITROALCOHOLS AND UNSATURATED ACIDS

Nitroalkohols composed of nitroalkanes and formaldehyde have been esterified with acryllic and methacrylic acids in order to obtain products which could be subjected to polymerization. This is a part of the big programme on searching for solid propellants. The work on the above line was initiated by British Thornson-Houston Co. [235] described in a number of patents reviewed by Marans and Zellinski [236] who also gave an account of their own experiments. Nitroalkohols from nitromethane, nitroethane, nitropropane and formaldehyde reacted with methyl esters of acryllic and methacrylic acids in the presence of concentrated sulphuric acid and cuprous chloride or toluene sulphonic acid and hydroquinone. Acrylic and methacrylic acid esters of nitroalkyls were formed through transesterification. They were polymerized at 100°C with benzoyl peroxide in an atmosphere of nitrogen. Only 2-methyl-2,2-dinitropropyl ester gave a hard resin, whereas the other nitroalkohols gave viscous resins. The presence of the nitro group in the molecule seems to inhibit the polymerization in agreement with the findings described in Chapter IV.

INDUSTRIAL METHODS OF NITRATING ALKANES

Commercial Solvents Corporation, Inc., Terre Haute, Indiana, U.S.A. has a factory producing nitroalkanes by the method of Hess and co-workers (Vol. I, p. 86). In 1956 the annual production was in the order of 4400 tons. Also in Germany during World War II Badische Anilin- und Soda-Fabrik A.G., Ludwigshafen had a pilot plant for the daily production of 300 kg of nitroalkanes. It was working for three years (1939–1942) and in 1942 a larger plant capable of producing 1 ton daily was under construction, but was destroyed by bombing (according to Doležel [4]).

The industrial method for the nitration of propane is based mainly on the description by Doležel [4] in the German edition of the book by the author of the present monograph. Some details can also be found in the review article by Shechter and R. B. Kaplan [6b].
German Method of Nitrification of Lower Alkanes

The method used in Germany at BASF (Ludwigshafen) was established by Schickh. It consisted of a stainless steel (V2A) nitrator in the form of a coil (1) (Fig. 29) submerged in a heating bath of molten sodium and potassium nitrate keeping the temperature at 400–450°C. A higher temperature was used for the nitration of methane and lower for higher hydrocarbons. Vapours of nitric acid (concentration 48% HNO₃) together with the hydrocarbon entered the coil from container (2). Molar ratio hydrocarbon : HNO₃ 8–10 was maintained. The reaction products entered the cooling coil (3) and condenser (4). Liquid products were collected in the separator (5). Lower acid layer entered (6) and the upper layer was distilled off and collected in a condenser (7). The cyclon (8) retained the liquefied product and the gaseous hydrocarbons entered scrubbers (9) and (10) where they were washed with water, and then with sodium hydroxide solution in (11) to free them of traces of acids. The residual higher boiling products were retained in (12) and gaseous hydrocarbons returned to the nitrator. The gaseous oxidation and decomposition products were released through a valve (13).

The conversion of methane, ethane and higher hydrocarbons were 13%, 30% and 40–50% respectively. Methane was also nitrated under pressure of 10 atm., which increased the conversion to 20%.

FIG. 29. Nitration scheme of Schickh used in Germany at BASF to nitrate alkanes according to Doležel [4].

Method of Commercial Solvents Corporation, Inc.

The nitration of hydrocarbons is carried out in a Stengel–Eagli [99] multisegment reactor (Fig. 30). It is usually composed of five segments.

The warmed alkane enters through (1) to the upper part of the nitrator. Nitric acid is injected through (2) and (3) to various segments of the nitrator. Electric heaters (4) maintain the correct temperature inside the apparatus. The constant temperature in the nitrator is maintained owing to the balance between the endothermic vaporization of nitric acid and exothermic heat of the reaction. Any deviations from the correct temperature are immediately avoided by valves (5) introducing air (or water). The products are evacuated through (6).

FIG. 30. Stengel–Eagli nitrator of alkanes used by Commercial Solvents Corp., Inc. according to Doležel [4].
gases leaving the last scrubber are rich with unreacted alkanes and return (through 19) to the nitrator. The gaseous by-products (e.g., N₂, CO, CO₂) leave the system through valve (18).

The conversion of propane to nitro compounds is in the order of 30–38%. The nitrated product is composed of 25% nitromethane, 10% nitroethane, 40% 2-nitropropane and 25% 1-nitropropane.

Distillation

The fractionation of nitro compounds is not a complicated problem, provided sufficiently efficient distillation columns are used. More difficult is the removal of acids (nitric acid, nitrogen oxides, organic acids), aldehydes and ketones, with water. The insoluble nitro compounds are subjected to azeotropic distillation. Water is separated as an upper layer and nitro compounds (with a small proportion of water on the bottom) are sent to distillation in order to separate the nitroalkanes. The flow sheet is given in Fig. 32. The mixture of nitro compounds from an intermediate container (1) enters through a rotameter (2), pre-heater (3) into the upper part of column (4). The azeotropic mixtures go through condenser (5) to separator (6). The separated water returns to column (4) and nitroalkanes through rotameter (7) enter column (8) where washing by a counter-current method with sodium bisulphite to free them from traces of nitric and nitrous acid. Nitroalkanes having a lower density pass through the column upwards to enter column (9) where the products are washed with water. Water is pumped back to column (4) to recover the dissolved nitroalkanes. The separated oil passes to the intermediate vessel (10). From here it goes through rotameter (11) and pre-heater (12) into the distillation column (13). An azeotrope which is composed of nitroalkanes and water distils. From the bottom part of column (13) and sent to an intermediate vessel (14), rotameter (15) and eventually to column (16) where nitromethane distils out. The bottom part of column (16) contains nitromethane, and nitropropanes. The mixture of nitroalkanes enters through intermediate (17) and rotameter (18) to column (19). Nitroethane distils out from the latter. In the bottom of column (19) both nitropropanes remain. They are sent through a pump to the intermediate vessel (20) and from there to rotameter (21) into column (22) where 2-nitropropane distils out. The lower part of column (22) passes through (23) and rotameter (24) to column (25) where 1-nitropropane distils out.

Hazards of the Nitration of Alkanes

Matasă [100] discussed the problem of the hazards of the nitration of alkanes. In his remarkably important paper he considered:

1. Explosibility of gaseous mixtures,
2. Exothermic reactions of nitration and oxidation,
3. Reactivity of the liquefied product,
4. Explosive properties of nitro compounds.

Oxidation can be suppressed by adding molten salts to the reacting compounds, according to Albright [101]. Sodium nitrate is the most suitable salt probably breaking the reaction chain. Matasă summarized his work in a diagram – Fig. 33 based on the nitration of cyclohexane with nitric acid in a vapour phase. It gives the zone of nitration against the time of contact, molar ratio and reaction temperature.

The dangerous zone is divided into two parts: upper (1) in which pyrolysis mainly occurs and is manifested by rapid variations of pressure and explosions, and lower (2) where the reaction proceeds quietly, but the products are liable to react further. He also indicated a practical criterion of the reaction: the colour of the products. Yellow colour characterized the normal course of the reaction,

FIG. 32. Fractional distillation of nitroalkanes by Commercial Solvents Corp., Inc. according to Doda [41].

FIG. 33. Variation of the zone of nitration of cyclohexane according to Matasă [98].
whereas green and brown indicate a reaction between liquid products and too high temperature of the reaction or a too long contact time.

The molar ratio hydrocarbon-nitric acid was of the order of 10:1 and if oxygen was added it was up to 4 moles in quantity.

To reduce the cost of nitration (and probably to increase safety) hydrocarbon and nitrogen were used instead of pure hydrocarbon [6]. The addition of oxygen to the system may offer the advantage of increasing the amount of heat evolved during nitration and thus helping to keep the reaction in adiabatic conditions. The oxygen helps in obtaining valuable oxidation products such as alcohols, aldehydes, ketones and carboxylic acid [6].

According to the same source, at 395°C conversion of propane increased from 20% to 76% based on nitric acid used while the ratios of oxygen, propane and nitric acid changes from 0:1:1 to 3:8:11:4:1.

1,2-DINITROETHANE (Vol. 1, p. 594)

Very little attention has been paid to this compound owing to its low stability. However, one paper can be mentioned which deals with the problem of conformation through the measurement of dipole moment [230]. The conclusion was that free rotation of NO₂ is most probable around the C-C axis. 1,2-Dinitroethane can be used as a source of hydroxylamine [231] and capro lactam from cyclohexanone [232].

2,2-DINITROPROPANE

This compound created a certain interest due to the presence of geminal nitro groups. The symmetry of the compound was examined by Huczukowski and Urbanski [248] by infra-red and Raman spectra. The authors came to the conclusion that the compound belongs to C₂ᵥ symmetry (according to Herzberg classification).

NITROALKENES (Vol. i, pp. 81, 95, 99, 107)

Nitroalkenes form an interesting group of compounds; they contain a strongly activating nitro group and a double bond which, under the influence of the nitro group, shows a particular activity.

The increasing interest in nitroalkenes is manifested by two monographs: those of Perekalin [8] and Novakov [9]. Some review papers dealing with the properties of nitroalkenes have also appeared [102].

Methods of Preparation of Nitroalkenes

The methods of preparation of nitroalkenes can be divided into several groups [6, 8, 9].

1. Action of nitrogen oxides and nitric acid on unsaturated hydrocarbons viz. NO (in the presence of catalytic amounts of NO₃), N₂O₅, N₂O₄, N₂O₃, HNO₃. Nitroalkenes are accompanied here by vicinal dinitro compounds, nitronitrates, nitronitrates, nitro nitroso compounds, nitronitrates, dinitriles and nitronitrates [6, 8, 9] (also Vol. 1, pp. 96, 594). Some mononitro alkenes can also be formed. Here are a few examples taken from the above monographs and [12]:

\[
\begin{align*}
\text{CH}_3\text{C} &= \text{CH}_3 \quad \text{NO} \\
&\text{CH}_3\text{C} \quad \text{C} &= \text{CH}_3 \quad \text{NO}_2
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{C} &= \text{CH}_2\text{Cl} \quad \text{NO}_2 \\
&\text{CH}_3\text{C} \quad \text{C} &= \text{CH}_2 \quad \text{NO}_2
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{C} &= \text{CH}_2\text{Cl} \quad \text{NO}_2 \\
&\text{CH}_3\text{C} \quad \text{C} &= \text{CH}_2\text{Cl} \quad \text{NO}_2
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{C} &= \text{CH}_2\text {NO}_2 \quad \text{NO}_2 \\
&\text{CH}_3\text{C} \quad \text{C} &= \text{CH}_2\text{Cl} \quad \text{NO}_2
\end{align*}
\]

Reaction (21a) needs some explanation as regards its mechanism. Nitrogen oxide is disproportionated into nitrogen and nitrogen dioxide and the latter acts as the nitrating agent.

Acetyl nitrate and nitronium chloride can also produce nitroalkenes while acting on alkenes:

\[
\begin{align*}
\text{CH}_3\text{C} &= \text{CH}_2\text{C} \quad \text{ClNO}_2 \\
&\text{CH}_3\text{C} \quad \text{C} &= \text{CH}_2\text {Cl} \quad \text{NO}_2
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{C} &= \text{CH}_2\text{Cl} \quad \text{NO}_2 \\
&\text{CH}_3\text{C} \quad \text{C} &= \text{CH}_2\text{Cl} \quad \text{NO}_2
\end{align*}
\]

The reaction of V. Meyer can also be used: for example, allyl bromide reacts with silver nitrite to yield 3-nitropropenal: \( \text{CH}_2 = \text{CH} - \text{CH}_2\text{NO}_2 \).

In some instances it has been found that esters can give purer substances [103]. According to Gold [104a] nitroalkanes can be obtained in good yield (up to 85%) by vapour phase catalytic cleavage of esters of nitroalcohols, for example:

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{CH}_3\text{NO}_2 \xrightarrow{\Delta (300-400^\circ \text{C})} \text{CH}_2=\text{CH(NO}_2) + \text{CH}_3\text{COOH} \quad (24)$$

As a catalyst calcium–magnesium phosphate appeared to be the best.

Dehydrohalogenation of halogenonitro alkanes, for example (25):

$$\text{Cl} \quad (\text{CH}_3)_2\text{C} = \text{CH}_{\text{NO}_2} \xrightarrow{\text{KOH} (202^\circ \text{C})} (\text{CH}_3)_2\text{C} = \text{CH}_{\text{NO}_2} + (\text{CH}_3)_2\text{C} = \text{N} = \text{NO}_2 \quad (25)$$

Vinyl product (I) was mainly formed.

Denitration of polynitroalkanes with potassium hydroxide can also produce nitroalkenes (Vol. I, p. 98, IX X).

Deamination of Mannich bases hydrochlorides can also furnish nitroalkenes [9] through pyrolysis (26):

$$\text{RC} = \text{CH}_{3} + \text{R}_2\text{N} = \text{HCl} \quad \text{NO}_2$$

For more information about the variety of reactions leading to nitroalkenes see [8, 9].

Recent Reactions of Formation of Nitroalkenes

Dehydrogenation of nitroalkanes was recently reported by Japanese workers: Sakakibara et al. [105]. The reaction consists in acting with phenylselenenyl bromide on nitroalkanes in the presence of butyl lithium. Nitrophenylenemalanes are formed in the first instance, and decompose under the action of hydrogen peroxide (27):

$$\text{R}^1\text{CH}_{2}\text{CHR}^2 \xrightarrow{\text{CuCl}, \text{SeBr}_{2}, \text{THF}} \text{CuCl} + \text{SeBr}_{2} \xrightarrow{\text{H}_2\text{O}} \text{RC} = \text{CH}_{3} + \text{NO}_2$$

Chemical Properties of Nitroalkenes

Nitroalkanes are pale yellow coloured liquids with boiling points slightly lower than those of corresponding nitroalkanes. They are lacrimatory substances with a pungent odour. They produce irritation of the mucous membranes, respiratory tract and skin.

They are susceptible to many addition reactions and anionic polymerization.
Addition Reactions

Addition of water and hydrogen sulphide yield alcohols and mercaptans respectively. Addition of alcohols and mercaptans yields nitroethers and nitrothioethers respectively. Halonitroalkanes are formed by the addition of halogens or hydrohalogenides. Nitrogen oxides yield dinitroalkanes. Nitronium chloride and nitrosochloride furnish nitrochloroalkanes. The addition of cyanohydrin yields nitroacyronitroalkanes. Amino nitroalkanes were obtained by adding ammonia or amines. Grignard reagent with a subsequent hydrolysis yielded dialkylhydroxylamine or nitroalkanes. Michael addition to nitroalkanes was also recorded. Nitroalkanes are important intermediates in the Diels-Alder reaction [104b].

A more detailed description of these reactions is outside the scope of this book but can be found in [1], in monographs [8, 9] and they are mentioned in a review article by Jagur-Grodzinski [109].

Among the recent papers an addition of allinesilane to α-nitroalkenes [110] was described.

A particular kind of addition is the polymerization of nitroalkenes – this will be discussed in a separate paragraph.

Isomerization

The isomerization of nitroalkenes is one of the most interesting properties of these compounds. The isomerization can be depicted by a diagram [102a]:

\[
\begin{align*}
R^1 & \xrightarrow{\text{R}^2} \text{CH} & \text{NO}_2 & \xrightarrow{\text{R}^1} \text{CH} & \text{NO}_2 \\
\text{NO}_2 & \xrightarrow{\text{R}^2} & \text{NO}_2 & \text{NO}_2
\end{align*}
\]

X can be H, halogen, COOH, CN etc.

Isomerization occurs under the action of catalytic amounts of bases (KOH, (C₂H₅)₂N).

Such isomerizations were described by Shechter and Shephard [111]. Bordwell and Gerbich [112]. Witanowski, T. Urbanski and co-workers [113] examined the isomerization of 3-nitropropene by catalytic amounts of sodium methoxide. By using the NMR technique, they established the existence of the equilibrium (31):

\[
\begin{align*}
\text{CH}_2=\text{CH} & \xrightarrow{\text{H}, \text{NO}_2} \text{CH} & \text{NO}_2 & \xrightarrow{\text{H}} \text{CH} & \text{NO}_2
\end{align*}
\]
So far poly-nitroethylene (and propylene) do not seem to have a practical application [119].

Characteristics of the main nitroalkenes are given in Table 43.

**TABLE 43. Physical constants of some nitroalkenes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Boiling point (°C)</th>
<th>Specific gravity</th>
<th>UV absorption nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Nitroethylene</td>
<td>CH₂⁺CH⁻-NO₂</td>
<td>98.5°</td>
<td>1.073</td>
<td>227</td>
</tr>
<tr>
<td>2-Nitro-1-propene</td>
<td>CH₂⁻C⁻-NO₂</td>
<td>57° (100 m kg)</td>
<td>1.0643</td>
<td>225</td>
</tr>
<tr>
<td>1-Nitro-1-propene</td>
<td>CH₃⁻-CH⁻CH⁻NO₂</td>
<td>54° (28 mmHg)</td>
<td>1.0661</td>
<td>229</td>
</tr>
</tbody>
</table>

**NITROACETYLENES**

A few representatives of this group of compounds were recently obtained by Russell _et al._ [122] by acting with lithium acetyldes on 2-chloro-2-nitropropane or 2,2-dinitropropane in tetrahydrofuran:

\[
RC = Cl + X⁻ · (CH₃)₂N₂O₂ \rightarrow RC = C · (CH₃)₂N₂O₂ + LiX \\
X = Cl, NO₂
\]

(32)

**POLYNITRO ALIPHATIC COMPOUNDS** (Vol. 1, p. 587)

Over the last three decades considerable attention has been given to the search for energy rich propellants and explosives among polynitro aliphatic compounds. An excellent review has been given by Noble, Borgardt and Reed [5] on such compounds.

However, most of the polynitro aliphatic compounds show relatively low stability and high sensitivity and these facts have limited their practical usefulness [119]. The author of the present book will describe only:

1. general methods of formation of polynitro compounds,
2. physico-chemical, chemical and explosive properties of the most important compounds for which a practical application can be found or have already become commercial products.

**NITRATION OF HYDROCARBONS**

The problem of whether the nitration of hydrocarbons can yield dinitro compounds became controversial. According to T. Urbanski and Słowiński (Vol. 1, p. 95) the nitration of hydrocarbons from propane to _n_-heptane at 220–230°C with a great excess of NO₂ can yield viscous oil containing dinitro products (10–22% of the total quantity of products). Grundman and Haldenwanger (Vol. 1, p. 84) obtained gem-dinitrocyclohexane when cyclohexane was nitrated at 122°C under pressure of 4 atm. Asinger and Oltay [123] nitrated 1-nitrooctane and obtained a mixture of dinitro products with various positions of the nitro groups. Statistical distribution equal to all positions from C(2) to C(7) (ca. 15%) was found.

It seems that the high temperature of nitration applied by Hess and co-workers (Vol. 1, p. 86) 410–430°C was too high for dinitro compounds and they decomposed.

The nitration of olefins can sometimes give polynitro compounds [124] (33)

\[
CH₃CH=CH(NO₂)₂CH₄ \xrightarrow{HNO₃} CH₃CH(NO₂)₂(CNO₂)CH₄
\]

(33)

Nitration through the addition of nitric acid or nitrogen oxides to alkenes forms a special chapter. This was described in Vol. 1, pp. 96–99 and reviewed [5–9].

Only a few typical reactions will be given here to leading to a higher number of nitro groups. Such is the reaction of Novikov and co-workers [124] (34)

\[
\begin{align*}
\text{NO}_2^- (1) \rightarrow & \text{NO}_2^- (2) \\
\text{NO}_2^- (1) \rightarrow & \text{NO}_2^- (2)
\end{align*}
\]

(34)

Parker, Emmons and co-workers [125] described the method of preparation of trinitroacetetanitride

\[
\text{NC} \rightarrow \text{CH₃COOH} + 3\text{HNO₃} \xrightarrow{\text{CCl}_4} \text{NC} \rightarrow \text{NC} \rightarrow \text{NC} + \text{CO}_2 + 3\text{H}_2\text{SO}_4
\]

(35)

The oxidation of oximes and other hydroxylamine derivatives followed by the action of nitric acid has also been described [126] (36)

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH} \rightarrow \text{HNO}_3 & \rightarrow \text{C}_6\text{H}_5\text{CH} \rightarrow \text{HNO}_3 \\
\text{NO}_2 & \rightarrow \text{C}_6\text{H}_5\text{CH} \rightarrow \text{HNO}_3 \\
\text{NO} & \rightarrow \text{C}_6\text{H}_5\text{CH} \rightarrow \text{HNO}_3
\end{align*}
\]

(36)

**Substitution of Halogen**

A modification of the Victor Meyer reaction for long chain hydrocarbons (over C₆) was given by Kornblum (Vol. 1, p. 127) [127] and reviewed by the same author. Another modification of the V. Meyer reaction was given as early as 1870 by ter Meer [128]. It applies to 1-nitro-1-haloalkanes. By acting with
sodium nitrite on the sodium salt of 1-nitro-1-haloalkanes \textit{gem}-dinitroalkanes are formed. The reaction was reviewed and studied by Hawthorne [129]. The reaction has a number of limitations, more universal is the ingenious method by R. B. Kaplan and Shechter [130] for preparing \textit{gem}-dinitro alkanes from nitroalkanes. It gives positive results where the method of ter Meer fails.

The reaction consists of an oxidation-reduction process of 1-nitroalkanes and can be depicted by scheme (37)

\[ R_2\text{C}(-\text{NO}_2) + \text{AgNO}_3 + \text{NaNO}_2 \xrightarrow{\text{H}_2\text{O}} R_2\text{C(NO}_2)\text{O} + 2 \text{Ag} \]  

(37)

The reaction proceeds smoothly in alkaline aqueous media with silver nitrate and inorganic nitrates. Because of this method, Feurer and colleagues [131] were able to obtain \(\alpha, \alpha, \omega, \omega\)-tetranitro alkanes. With four carbon atoms of chain of the nitroalkane, the yield of tetranitro compound could reach 84%.

\textit{Electrolytic Methods}

The electrolytic coupling of primary and secondary nitroalkanes in basic medium has been reported by Bahrmei [132]. Another reaction yielding \textit{gem}-dinitroalkanes was carried out with silver anode [133]. There is a similarity between this reaction and the Kaplan Shechter method as silver is generated at the anode.

\textbf{ADDITION REACTIONS}

Two addition reactions were applied to produce polynitro aliphatic compounds:

1. Michael addition.
2. Diels–Alder addition.

\textit{Michael Addition}:

One of the first papers was by Lambert and Piggott [134] who studied the reaction of \(\alpha\)-nitroalkanes (i.e., conjugated nitro compounds) with nitroalkanes:

\[ R'^1R'^2\text{HNO}_2 + CH=\text{C}(-\text{NO}_2) \xrightarrow{} R'^1R'^2\text{C}(-\text{NO}_2)\text{C}(-\text{NO}_2) \]  

(38)

Shechter and Cates [135] studied the addition of nitroform to \(\alpha, \beta\)-unsaturated ethers to produce \(\alpha\)-trinitromethyl ethers in good yield. Hamel [136] tried Michael addition and Mannich reaction and obtained a number of polynitro compounds.

\textit{Diels–Alder Addition}

Relatively less attention has been paid to the Diels–Alder reaction producing polynitro compounds. Gold and co-workers [137] successfully used 2,2-dinitromethanol which in the course of refluxing last water to produce 1,1-dinitroethylene, a very strong dienophile:

\[ \text{CH}_2\text{NO}_2\text{CH}_2\text{OH} \xrightarrow{\Delta} \text{CH}_2\text{C}(-\text{NO}_2)\text{C}(-\text{NO}_2)\text{H}_2 \]  

(39)

\textbf{OXIDATIVE DIMERIZATION}

Shechter and R. B. Kaplan [138] obtained \textit{gem}-dinitroalkanes by the oxidation of primary and secondary alkanes (in alkaline medium) with sodium persulphate (40):

\[ R_2\text{C}(-\text{NO}_2) \xrightarrow{\text{Na}_2\text{S}_2\text{O}_8} R_2\text{C}(-\text{NO}_2) \]  

(40)

\(\alpha, \omega\)-\textit{DINITROALKANES}

\(\alpha, \omega\)-Dinitroalkanes were prepared in a classical way by the V. Meyer method of reacting dinitro derivatives with silver nitrate [5]. The modification of the method by Kornblum (Vol. 1, p. 127) [127] using sodium nitrate in dimethylformamide made the compounds more accessible. Feurer, Nielsen and Colwell [139] used \(\alpha, \omega\)-dinitroalkanes for the Henry reaction with formaldehyde to obtain diols which can be nitrated to obtain compounds with two \(O\)-nitro groups.

\textit{gem-Dinitroalkanes (1,1-Dinitroalkanes)}

A considerable number of papers have been published on the properties of \textit{gem}-dinitroalkanes and their fluorine derivatives by Nazin, Maness and Dubovitskii [252] and kinetics of their thermal decomposition. The energy of dissociation of the bond \(C\text{—N}\) was found to be 47–48 kcal/mol.

\textbf{TRINITROMETHANE (NITROFORM) DERIVATIVES} (Vol. 1, p. 587)

The last two decades of searching for high energy compounds were dedicated to products with the trinitromethyl group. The growing interest in these compounds is reflected in two symposia [1] and [2] and in an excellent review by I. A. Kaplan [140].
The method of manufacture of nitroform from acetylene found as early as 1900 by Baschieri (Vol. 1, p. 587) was described by Orton and McRae [141]. It became possible to convert one of the carbons of acetylene to nitroform through a mercury catalysed oxidation—nitration process with nitric acid. Nitroform is an intermediate product of nitration and yields tetrylitromethane under the action of excess nitric acid (Vol. 1, p. 594). The method was developed during World War II by Schultheiss [142] and Schimmelshmidt [143] on a large laboratory scale with the aim of producing tetrylitromethane. Later the industrial scale method for the manufacture of nitroform was created by Wetterholm [144] (and is described below).

Properties of Nitroform

Trinitroalkanes derived from nitroform have a low intensity absorption band at ca. 280 nm and with hydrazine give a strong absorption at 350 nm. This fact can serve to spectrophotometric analysis [145, 146].

Three electron accepting groups in nitroform produce very strong acid properties. Its pKₐ₂ is 0.1 [146].

Nitroform is a nucleophile and can be added to nitroalkenes at low temperature (ca. 0°C) in methanol with a good yield. This was done by the pioneering work of Novikov and co-workers [246, 247] and L. A. Kaplan and Hine [147], for example (41):

\[
\text{H}(\text{NO}_2) + \text{C}_3\text{H}_5\text{CHNH} = \text{CH} \rightarrow \text{C}_3\text{H}_5\text{CHNH}_2 \quad (41)
\]

Addition to carbonyl compounds is an important reaction, for example, nitroform with formaldehyde yields 2,2,2-trinitroethanol (Vol. 1, p. 588) [148]. As previously mentioned (Vol. 1, p. 588) the reaction is strongly exothermic. According to Wetterholm [153] it evolves 8.56 kcal/mol. The next step is the Mannich reaction which offers synthetically valuable trinitromethyl amines and their derivatives. The simplest Mannich base is made of nitroform, formaldehyde and ammonia:

\[
\text{(NO}_2) \text{C}_2\text{H}_5\text{NHCH}_2\text{C}(\text{NO}_2)_2 \quad \text{II}
\]

\[
\text{(NO}_2) \text{C}_2\text{H}_5\text{NCH}_2\text{C}(\text{NO}_2)_2 \quad \text{III}
\]

Product II is unstable and can decompose on standing but after nitration, III shows a much better stability [149]. This observation is in agreement with that of Feuer and Swarts [150] and in the work of Feuer, Bachman and co-workers [151] who described reactions of nitroform with formaldehyde and amino acid esters to form N-trinitroethylamino acid esters.

The products were unstable, but after nitration stable N-nitro compounds resulted (42):

\[
\text{(NO}_2) \text{C}_2\text{H}_5\text{NHCH}_2\text{COOC}_2\text{H}_5 + \text{HNO}_3 \rightarrow \text{(NO}_2) \text{C}_2\text{H}_5\text{NCH}_2\text{COOC}_2\text{H}_5 \quad (42)
\]

Wetterholm [153] reacted 2,2,2-trinitroethanol with urea to obtain N,N'-bis (trinitroethyl) urea ("DTEU") (IV) a new strong explosive, near to Cyclonite with regard to its power.

\[
\text{(NO}_2) \text{C}_2\text{H}_5\text{NHCONHCH}_2\text{C}(\text{NO}_2)_2 \quad \text{m.p. 191°C}
\]

IV

It is described on p. 259, reaction (56) [250].

Another interesting and new approach to using 2,2,2-trinitroethanol as an explosive was given by Japanese authors: Shiino, Fujii and Kusakabe [214].

Frankel [152] described a number of Michael type additions of nitroform to unsaturated compounds. The most interesting was that of addition to nitroethylene.

Ville [234] also described some Mannich bases, their N-nitro derivatives and acrylic ester of trinitroethanol. He also obtained the product of addition of nitroform to acrylic esters.

The interesting properties of mercuric salt of nitroform were extensively studied by Novikov and co-workers [9a]. They described (among other reactions) the use of it for the mercuration of aromatic and heterocyclic compounds and the addition of mercuric salt to alkenes and their derivatives.

The thermal decomposition of nitroform and some of its fluorine derivatives were extensively studied by Mazin, Maneli and Dubovitskii [252, 253]. They obtained ortho-esters of 2,2,2-trinitroethanol: such as the orthoformate (TNEOF) (V) and orthocarbonate (TNEOC) (VI) by reacting 2,2,2-trinitroethanol with chloroform and carbon tetrachloride respectively in the presence of anhydrous ferric chloride. The yields were 74% and 89% respectively.

\[
\text{HC}[\text{OC} \text{H}_2\text{C}(\text{NO}_2)_2] \quad \text{m.p. 128°C}
\]

\[
\text{C}[\text{OC} \text{H}_2\text{C}(\text{NO}_2)_2] \quad \text{m.p. 161°C}
\]
The substances appear to be of good stability. They are soluble in polar solvents. The saturated solutions of V and VI in nitromethane are 1.53 and 1.48 respectively. Their oxygen balance is +0.10% and +0.13% respectively.

The substances show very low sensitivity to impact (they do not explode when 5 kg weight was dropped from 50 cm).

Data on the explosive properties of solutions of both substances in nitromethane and nitroethane are given in Table 44.

**Table 44. Explosive properties of TNEOF and TNEOC with nitroalkanes**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Density g/cm³</th>
<th>Detonation velocity m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNEOF</td>
<td>50</td>
<td>1.356</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>50</td>
<td>1.533</td>
</tr>
<tr>
<td>TNEOF</td>
<td>77.1</td>
<td>1.480</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>22.9</td>
<td></td>
</tr>
<tr>
<td>TNEOC</td>
<td>69.7</td>
<td>1.480</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>30.3</td>
<td></td>
</tr>
<tr>
<td>TNEOF</td>
<td>77.0</td>
<td>1.496</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>23.0</td>
<td></td>
</tr>
</tbody>
</table>

*Manufacture of Nitroform*

The manufacture of nitroform from acetylene was described by Wetterholm [144]. The flow-sheets of the process are given in Figs 34 and 35.

Figure 34 depicts a nitrator where the oxidation-nitrification takes place combined with a recovery system for the large amount of nitrogen oxides evolved.

Figure 35 presents a distillation system consisting of fractionating towers and an evaporator.

The equipment includes a concentration of dilute nitric acid formed in the course of the reaction. This is a standard procedure and is not included in the figures.

The reaction of nitrification is carried out at 45–48°C. From the overflow the products of the reaction go to a stripper where they are freed from nitrogen oxides with air in a countercurrent with cold nitric acid at −15°C. The scrubbing acid is used as part of the acid feed. The gases generated during nitrification consist of CO₂, CO, nitrogen oxides and some nitroform. The gases pass through a hot scrubber which retains nitroform. Next is a packed tower where pure N₂O₅ is condensed in a cooler. The waste gases are composed of 76% CO₂, 12% CO, 6% N₂, 6% HNO₃.

The extraction of nitroform from a strong nitric acid consists of two steps:

**FIG. 34. Production of nitroform. Nitration system according to Wetterholm [138].**
(1) Distillation of the acid until the composition reaches the minimum azeotropic. Nitroform does not distil during this period.
(2) Addition of water and distillation of nitroform with water.

The overall yield of transformation of acetylene to nitroform is ca. 74%.

TETRANITROMETHANE (TNM) (Vol. 1, p. 588)

There is an increasing interest in tetrinitromethane as a source of energy rich explosives and this is manifested by a number of papers related to the physical and chemical properties of the compounds. An excellent review on TNM was given by Altukhov and Perekalin [156].

Physical and Physico-chemical Properties of TNM

The setting point is +13.75 [157a], +14.2 [157b] (an incorrect figure was given in Vol. I, p. 588), boiling point 126°C [157]; specific gravity d<sub>20</sub> = 1.6484, d<sub>25</sub> = 1.5218, mol. refraction MR<sub>P</sub> = 31.39 (calculated 29.30) [158].

The ultraviolet spectrum is manifested by the main band at 280 nm, the infrared spectrum has two strong bands 1618 and 1266 cm<sup>-1</sup> corresponding to asymmetric and symmetric vibrations respectively, and a number of less prominent bands at 1645, 1439, 1370, 990 and 973 cm<sup>-1</sup> [159]. Examination of the infrared spectra of TNM at different temperatures (−40° to −126°C) [160] indicated that TNM exists in two crystalline forms with their transition point at −99.8°C.

The mobility of one nitro group of TNM suggested originally that one nitro group possesses a different structure from the others, for example, the nitrite or peroxy structure. This proved to be wrong and it has now been firmly established by X-ray analysis that TNM possesses a perfectly symmetrical structure [161] — Fig. 34. This was substantiated by dipole moment measurement which has been found to be equal to 0 within the experimental error. Electron diffraction also confirmed the symmetrical structure of TNM [162].

Quantum chemical calculation was carried out by Shlyapochkinov and Gagarin [163]. It was shown that the electron increased at the oxygen atoms of the nitro groups of TNM and was reduced at the nitrogen and carbon atoms. This is marked in Fig. 36.

The energy of formation of TNM is according to different authors 4.7–8.9 kcal/mol and enthalpy of formation −18.5 kcal/mol. [156]. Heat of decomposition — equation (43)

$$\text{C(NO}_2\text{)}_4 \rightarrow \text{CO}_2 + 3\text{O}_2 + 2\text{N}_2 \text{.} \ (43)$$

is according to various sources 89.6–102.9 kcal/mol [156]. The energy of the C–N bond was calculated: 38.2–39.3 kcal/mol [164, 165].
Chemical Properties (Vol. I, p. 589)

The most important and unique property of TNM is the perfect symmetry of the compound, absence of polarity and identical properties of all four nitro groups. In spite of it, TNM can yield the nitronium cation NO₂⁺ and trinitromethyl anion C(NO₂)₃⁻ under certain conditions. Also the existence of corresponding ionic pairs is possible as well as the formation of radicals NO₂⁺ and C(NO₂)₃⁻.

As a rich compound of NO₂ groups, TNM shows strong electron accepting properties and several complexes of charge transfer character are known which can further react to yield nitroaryl, arylnitroalkenes, α-nitroketones, tetrinitroalkanes and diminooxazolidines.

Perekalin and co-workers [156, 166, 167] subjected a number of charge transfer complexes formed by TNM to a systematic study using electronic spectroscopy.

Charge-transfer complexes of TNM with unsaturated compounds are particularly characteristic: an intense colour (from yellow to dark red) can detect the presence of double bonds, for example in tautomeric forms (reaction of Ostro-mysienkii [168] and Werner [169]). The reaction however, has a limited application, for example, no colour is given by maleic and fumaric acids. Also some compounds without double bonds give the colour. Such are compounds with divalent sulphur. TNM can be applied successfully to detect components in chromatograms.

Most complexes of TNM with unsaturated compounds are weak [170], their enthalpy of formation is of the order of 1.0 kcal/mol.

Nucleophilic Substitution

Hantzsch and Rinkenberger [171] established that TNM can quantitatively be hydrolysed to trinitromethane by potassium hydroxide or potassium ethoxide. However, aqueous concentrated KOH can produce a deeper hydrolysis with the formation of KNO₃, KNO₂ and K₂CO₃ [172]. The reaction of the formation of trinitromethane ('nitroform') from TNM became a standard method of making nitroform used for synthesis of polynitro aliphatic compounds.

TNM reacts with 3-5% aqueous Na₂SO₃ solution [173] (Vol. I, p. 589) and the reaction became the standard method of removing TNM from TNT.

An important reaction is that of halogenides of potassium, rubidium and caesium in dimethyl formamide yielding halogenotrintrinitromethane [174, 175]:

\[
\text{C(NO}_2\text{)}_3 \xrightarrow{\text{X}} \text{KNO}_3 \xrightarrow{\text{X}} \text{X(C(NO}_2\text{))}_3
\]

A similar chlorination can be carried out by chloramines [176].

Nitrosation of Tertiary Amines

Schmidt and co-workers [172, 177] obtained N-nitroso derivatives of tertiary amines by acting with TNM on the amines in pyridine or in acetic acid.

gem-Dinitromethylation

TNM in the presence of oxidizing agents can introduce gem-dinitromethylene group, for example, triphenylhydrazine and diphenylhydrazine can react according to scheme (46) [178] and (47) [179]:

\[
\text{(C}_6\text{H}_5\text{)}_3\text{N} = \text{HNO}_2 \xrightarrow{\text{TNM}} \text{(C}_6\text{H}_5\text{)}_3\text{N} = \text{C(NO}_2\text{)}_2
\]

\[
\text{(C}_6\text{H}_5\text{)}_2\text{N} = \text{HNO}_2 \xrightarrow{\text{TNM}} \text{(C}_6\text{H}_5\text{)}_2\text{N} = \text{C(NO}_2\text{)}_2
\]
An interesting reaction was reported on the action of TNM on tetramethyltetrazene [180] (48):

\[
\begin{align*}
(CH_2)_2 N\equiv N\equiv N\equiv N(CH_2)_2 & \xrightarrow{TNM} (CH_2)_2 N\equiv N\equiv N\equiv NCH\equiv(C(NO_2)_2) \\
\text{CH}_{3} & \text{CH}_{3}
\end{align*}
\] (48)

**Nitration**

TNM is a nitrating agent in alkaline medium. Schmidt and co-workers [181] succeeded in nitrating compounds such as arylalkanes with the double bond conjugated with those of the aromatic ring (49).

\[
\begin{align*}
\text{CH}_3 & \text{-O} \xrightarrow{\text{TNM}} \text{CH}_3\text{-O} \xrightarrow{\text{CH}_3\text{-CH}} \text{CH}_3\text{-CHNO}_2
\end{align*}
\] (49)

In the presence of methanol and ethanol the reaction leads to the formation of 
\[\text{OR} \xrightarrow{\text{NO}_2} \text{-CH-CH-CH}_3\] (R = CH$_3$ and C$_2$H$_5$ respectively).

It is important to note that non-conjugated aralkenes are not nitrated with TNM.

An important contribution to the reaction of TNM with alkenes, aralkenes and dienes was given by Altukhov and Perekalin [156]. An example of the reaction of 1,1-diphenylethylene with TNM is given.

Here originally a CT complex was formed, TNM being an acceptor and the alkene a donor, next an ionic pair and the cation can react forming nitroalkene or nitroalcohol. The anion yielded nitroform (50).

\[
\begin{align*}
\text{CT complex} & \xrightarrow{\text{CH}_3} \text{C(CH}_3)\text{H}_2\text{C}^-\text{CH}_2\text{NO}_2 + \text{C}^-\text{NO}_2_3 \\
\text{H}_3\text{O} & \xrightarrow{\text{H}^+} \text{C}_4\text{H}_1\text{CHNO}_2
\end{align*}
\] (50)

Nitroalkenes react in a different way owing to the presence of a strong acceptor:

\[
\begin{align*}
\text{CH}_3\text{H}_5 & \xrightarrow{\text{C(NO}_2)_3} \text{C}^-\text{CH}_3\text{NO}_2 \quad \xrightarrow{\text{H}_2\text{O}} \text{C}_4\text{H}_1\text{C}^-\text{CHNO}_2
\end{align*}
\]

Recently the bain was nitrated with TNM in methanol [182].

**Radical Reactions**

A number of papers have been dedicated to homolytic degradation of TNM under the action of ultraviolet or $\gamma$-rays. The reaction of TNM with bases (e.g., benzidine) brings the formation of CT complexes [183] yielding radical anions which in turn are split into radicals (NO$_2$) and anions (e.g., nitroform). Irradiation with $\gamma$-rays at 77K yielded radicals: $\cdot$NO$_2$ and $\cdot$(NO$_2$)$_3$ [184].

As most nitro compounds, TNM inhibits polymerization induced by radiation [185, 186] and free radical polymerization [180-191]. This is rationalized by the fact that TNM is a radicals acceptor. The higher the number of nitro group in nitroalkanes the stronger the inhibition of polymerization [189].

**Ionic Polymerization**

TNM is a strong acceptor of electrons and subsequently can initiate ion polymerization. As an example it can serve the polymerization of vinylcarbaz in the presence of methyl methacrylate [192].

**Metalorganic Compounds**

The reaction of TNM with aryl mercury or tin compounds yielded hydrid carbons [193], for example (52):

\[
\begin{align*}
\text{Ar}_2\text{HgAr} + \text{C(NO}_2)_3 & \xrightarrow{\text{Ar}^+} \text{Ar}_2\text{HgC(NO}_2)_3 + \text{NO}_2 \\
\text{Ar}_2\text{HgC(NO}_2)_3 & \xrightarrow{\text{ArH}} \text{ArH} + \text{N}_2\text{O}_4
\end{align*}
\] (5)

TNM reacts with copper to yield free radicals $\cdot$C(NO$_2$)$_3$ and $\cdot$NO$_2$ [194].

**Explosive Properties**

According to Roth (Vol. I, p. 590) TNM can be detonated [195] by using a strong booster of 10.5 g PETN. In a steel tube 21/27 mm diameter it gave 64 m/s. The heat of detonation was found to be 540 kcal/kg [157]. As in m-
explosives with a high positive oxygen balance the addition of a small amount of organic substances to TNM considerably increases the ease of detonation.

Thermal decomposition of TNM was studied by Nazin and co-workers [196], and is depicted by scheme (53):

\[
\begin{align*}
\text{C(NO}_2\text{)}_4 & \rightarrow \text{C}^+ (\text{NO}_2)_3 + \text{NO}_2 \\
\text{C(NO}_2\text{)}_3 & \rightarrow \text{C}^+ (\text{NO}_2)_2 + 2 \text{NO}_2 \\
\text{C(NO}_2\text{)}_2 & \rightarrow \text{C}^+ (\text{NO}_2)_1 + \text{N}_2\text{O}_4 \\
\text{C(NO}_2\text{)}_1 & \rightarrow \text{C}^+ = \text{O} + \text{NO} + \text{NO}_2
\end{align*}
\]  

(53)

Toxicity (Vol. 1, p. 593)

TNM is highly toxic affecting respiratory organs and the nervous system. According to the American Industrial Hygiene Association [197] the permitted concentration in air is 0.001 mg/l. A considerable number of papers have been published on the toxicity and pharmacology of TNM [198-203].

In connection with the health problem a number of physico-chemical methods for the determination of TNM in air and in solutions have been described, such as spectrophotometry, colorimetry of solutions and polarography. They are reviewed by Altukhov and Perekhin [156].

Preparation of TNM (Vol. 1, p. 594)

Nitration of acetylene in the presence of mercuric nitrate seems to be the most common method of preparation of TNM. It means that the reaction is not stopped at the stage of the formation of nitroform [144] but the latter is further nitrated under the action of the excess of nitric acid.

According to Meyer [157] the best method of making TNM consists of the nitration of ketene by introducing a stream of it into cold 100% nitric acid. After the reaction is completed the resulting solution is poured into water and ice, and TNM is separated. This method was described by Darzens and G. Levy [204].

HEXANITROETHANE (HNE) (Vol. 1, p. 596)

Interest has recently been revived in hexanitroethane and some data on the properties of the substance have been collected by Meyer [66], viz.:

- m.p. 147°C
- density 1.85 g/cm³, ignition point 175°C

Heat of explosion 743 kcal/kg
Volume of detonation gases 672 l/kg
Vapour pressure: at 20°C 0.5 millibar
50°C 2.5 millibar
70°C 5.0 millibar
85°C 28.0 millibar

Physico-chemical properties were given by P. Noble and co-workers [239], the oxidizer properties by Frankel and co-workers [240], and heat of formation by Apin, Pepekin and co-workers [241]. The standard enthalpy of formation was found to be 20.0 ± 1.0 kcal/mol, in the gas phase 36.9 ± 1.4 kcal/mol. The enthalpy of sublimation is 16.9 ± 0.4 kcal/mol.

An important finding has been described by Kriem, Licht and Trimborn [242], who discovered that HNE changes its crystalline structure at around 16-19°C. The low temperature modification is stable in the range from −8°C to +16°C. The low temperature form is rhombic and has density 2.21 g/cm³ whereas that of ambient temperature is cubic and possesses the density given above (1.85). The transition is reversible and the heat of transition ΔH is 9.87 cal/kg. Specific heat at 16°C is 0.26 kcal/kg.

It was found [242] on a differential scanning calorimeter that the endothermic crystal change begins at +17°C, sublimation at +15°C followed by exothermic decomposition (140°C) and endothermic melting at 147°C.

The substance has a waxy appearance and can be readily pressed at 0°C and below that temperature some cracks can appear due to the change of the crystal habit.

Thermal decomposition of HNE was studied by H. P. Marshall and co-workers [243], Nazin, Manulis and Dabrowskij [244]. They gave the following values for the energy of activation: E = 37.8 kcal/mol and log B = 18.5 [243] and 35.8 kcal/mol and log B = 17.3 (for the interval of temperatures 90-135°C) [244].

NITROCARBOXYLIC ACIDS

Nitrocarboxylic acids were reviewed by Novikov and co-workers in their rich monograph [9]. Although not possessing explosive properties they may be valuable for the synthesis of amino acids, surface active agents and ingredients of rocket propellants.

Only a brief outline will be given here, the reader should otherwise consult the monograph [9].

Nitration of fatty acids was first effected by Bous in 1855 [205] who nitrated caprylic acid with nitric acid. Claus and Pfeiffer [206] nitrated stearic acid with nitric acid (d 1.48) in glacial acetic at the solutions boiling temperature. In search for an industrial application for the nitrated saponifiable oils, Radchenko
and Polychronis [207] nitrated stearic, hydroxystearic, oleic and ricinoleic acids. They found that cold nitric acid had no effect on stearic acid, whereas oleic acid (as should be expected from its unsaturated character) yields nitrooleic acid along with oleic acid nitrate. Ricinoleic acid in turn gave on nitrilation nitro-nitrate and nitrate derivatives.

T. Urbanski and Biernacki [208] nitrated ethyl n-valerate with nitric acid in glacial acetic acid-acetic anhydride at 23 ± 2°C and found that a mixture of 2-, 3- and 4-nitrovalerates was formed in the ratio 0.6:0.7:1. At 63 ± 2°C a certain amount of 1-nitrobutane was formed due to the decarboxylation of the 2-nitrovalerate.

Valeric acid was not nitrated at 23°C and required a minimum temperature of 33 ± 2°C.

The nitrilation of propionic acid with nitric acid in the vapour phase gave a small yield (5%) of 3-nitropropionic acid according to Hass and Hudgin [209].

**NITRODIAZOMETHANES**

Interesting nitro derivatives of diazomethane were obtained by Schöllkopf and co-workers. Thus Schöllkopf and Markusch [210] described nitrodiazomethane which was obtained from tert-butyl diazoacetic ester by nitrilation with N₂O₃ followed by hydrolysis (54) see also Chapter I, p. 30:

\[ 2\text{N}_2 := \text{CH}_2\text{COO}^-\text{Bu} + \text{N}_2\text{O}_3 \rightarrow \text{N}_2 := \text{CH}_2\text{COO}^-\text{Bu} + \text{O}_2\text{NO}_2\text{COO}^-\text{Bu} + \text{N}_2 \]  

\[ \text{m.p. 55°C} \]

Nitrodiazomethane decomposes with HCl in moist ether yielding ClCH₂NO₂.

Dinitrodiazomethane was prepared by the action of nitric anhydride on mononitrodiazomethane [211] (55):

\[ \text{N} \quad \overset{\text{N}_2\text{O}_3}{\rightarrow} \quad \overset{\text{O}}{\text{NO}_2} \]

\[ \text{H} = \text{C} = \text{NO}_2 \quad \text{N} \quad \overset{-30°C}{\rightarrow} \quad \overset{-\text{NO}_2}{\text{N}} \]

\[ \text{m.p. 65°C c. d., 42°C} \]

No data on explosive properties are available. It appears that the low decomposition temperature renders the compounds of no practical use, but they are certainly of great theoretical interest.

**ALIPHATIC NITRO COMPOUNDS**

**NITRO DERIVATIVES OF UREA**

\[ \text{N,N-bis(β,β,β)-Trinitroethyl Urea (IV), p. 247} \]

This interesting substance was obtained by Wetterholm [250] in 1951 by reaction (56):

\[ 2\text{NO}_3\text{CH}_2\text{OH} + \text{NH}_2\text{CONH}_2 \rightarrow (\text{NO}_2\text{H})_3\text{CH}_2\text{NHCONHCH}_2\text{C(NO}_2\text{H)}_3 \]

DiTeU separated as a white precipitate sparingly soluble in water. Another method consists in reacting dimethylurea with nitroform [251]. The product is not a single compound: it contains less soluble fractions of di- and trimer, which can be removed by crystallization:

\[ \text{The pure DiTeU has a favourable oxygen balance:} \]

\[ \text{C}_4\text{H}_4\text{O}_3\text{N}_4 \rightarrow 5\text{CO}_2 + 3\text{H}_2\text{O} + 4\text{N}_2 \]

The explosion enthalpy is 1645 kcal/kg.

The deflagration point is 210°C, the rate of detonation 8000 m/s at density 1.62, lead block 465 cm³. It is less sensitive to impact than RDX.

A pilot plant for DiTeU, producing 30 kg/hr DiTeU, exists in Sweden at Nitro-Nobel A.G. A great advantage of the production is that no spent acid is formed.

**NITROSO COMPOUNDS** (Vol. 1, p. 602)

**Nitro-nitroso Alkanes ('Pseudonitroles')**

As is known, pseudonitroles are formed by nitrosation of secondary nitro-
alkanes. Very little interest has been shown to this class of compounds which have been known since the classical work of Victor Meyer in 1873. For early work see [7].

More recently the mechanism for the formation of pseudonitroles and their stereo chemistry has been examined by Noland and Libers [212]. The pseudonitroles can be oxidized to gem-dinitro compounds with air or hydrogen peroxide.

Recently de Boer and Bolsman [213] examined photolysis of 1-nitro-1-nitroso cyclohexane with red light in the absence of oxygen and came to the conclusion that a homolytic fission of C—NO bond occurred at 40°C and generated a radical pair: NO and α-nitroso cyclohexyl. Solvolysis occurred in different solvents. In benzene, cyclohexanone was formed as a major product and small amounts of 1,1-dinitrocyclohexane, as well as 1-nitrocyclohexene and nitrocyclohexane.

"Hexanitrosobenzene"

As mentioned in Vol. I, p. 603, hexanitrosobenzene now has the accepted structure of "Benzotriisfuraneoxygenet." This was confirmed by several physico-chemical methods, such as:

- X-ray diffraction [215], X-ray photoelectron spectroscopy [216], Vibrational spectroscopy [217], Laser-Raman study [218], Nitrogen NMR [219], Carbon-13 NMR [220].

It should also be pointed out that the substances with a furane structure (VII):

possess explosive properties [221–225].

An excellent review has been given by Kaufman and Picard [226].

Nitroenamines

Enamines are an interesting group of compounds, for example VIII.

\[(\text{CH}_3)_2\text{NCH} = \text{CHNO}_2\]

VIII

An excellent review has recently been given by Rajappa [229]. The substances and their properties are outside the scope of the present book.

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APPENDIX

Nitromethane - Aluminum Chloride Complex

Z. Zavada, Pankova, and Z. Arnold [1] described a complex of nitromethane with aluminum chloride which is a convenient form of the Friedel-Crafts catalyst [2].

Substituted Nitro Alkanes

Thermal decomposition. A considerable number of substituted nitroalkanes were prepared by Soviet chemists and their thermal decomposition was examined by Nazin and co-workers [3, 4] in view of determining their activation energy and frequency factor. Some of the results are collected in Table A1 and in a summarizing review of Nazin and Munell [5].

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Enthalpy of formation in gas-phase kcal/mol</th>
<th>Energy of the bond C-C between phenyl or benzyl and C(NO₂)₂ or (NO₂)₃ kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅CH(NO₂)₂</td>
<td>8.5</td>
<td>100.2</td>
</tr>
<tr>
<td>C₆H₅CH₂CH(NO₂)₃</td>
<td>15.7</td>
<td>79.1</td>
</tr>
<tr>
<td>C₆H₅C(CH₃)₂(NO₂)₂</td>
<td>44.2</td>
<td>105.1</td>
</tr>
<tr>
<td>CH₃(NO₂)₂</td>
<td>56.1</td>
<td></td>
</tr>
</tbody>
</table>

Steric Effects in Nitroalkanes

Novikov and co-workers [8] studied steric effects in mono- and polynitroalkanes. They calculated the equilibrium of configuration, energy of strain and enthalpy of atomization. Steric effects from the nitro groups increase with the increase of their number and the increase of the length of the alkyl chain.

REFERENCES

CHAPTER 9

DIFLUOROAMINO COMPOUNDS

As a result of searching for new explosives and in particular rocket propellants, a new group of explosives was found - that of organic compounds containing difluoroamino group, e.g., NF₂. The group can also be regarded as a modification of the nitro group, where two atoms of oxygen were replaced by atoms of fluorine.

There is now extensive patent literature covering the preparation of difluoroamino compounds and describing their potential use as high-energy propellant ingredients. However, some of the compounds possess properties which cast doubt on the safety of their preparation and handling. A striking example is the simplest member of the family with difluoroamino group, i.e., difluoramine (NHF₂). This is a particularly dangerous compound, unexpected detonations have been reported.

It appears that interest in difluoroamino compounds is now diminishing, as far as their application as explosives is concerned. Nevertheless, the chemistry of difluoroamino compounds remains very interesting.

Two routes for the preparation of difluoroamino compounds are known:

(1) through the direct fluorination of amines,

(2) through the reactions with tetrafluorohydrazine, accompanied by thermal or photochemical dissociation of this compound.

A review of the work on derivatives of nitrogen fluoride compounds including those with difluoroamino group was given by J. K. Ruff [1]. Larkin and Kozyrev [30] published an extensive review dedicated to difluoroamino compounds.

Reviews on difluoroamino compounds appeared also in Advances in Chemistry Series of American Chemical Society [34]. They were reviewed mainly for their application as rocket propellants.

DIRECT FLUORINATION OF NONAROMATIC COMPOUNDS

Although the first compounds with NF₂ group were obtained as early as 1936 by O. Ruff and Gliese [35] the most important work started relatively recently in the early sixties. These were the indications of the possible transformation of NH₂ into NF₂ given by Lawton and co-workers [2] and Graukauskas [3].

DIIFLUOROAMINO COMPOUNDS

Direct Fluorination of NH₂ and NH Groups in Aliphatic Compounds

Lawton acted on solid urea with fluorine diluted with nitrogen at 0°C and among a variety of compounds isolated a solid substance which proved to be identical with that prepared by Graukauskas [3] through the action on urea in aqueous solution with fluorine diluted with nitrogen at 0–5°C. It proved to be N,N-difluorourea (I). It was extracted with ether as a hygroscopic, lacrimatory solid, m.p. 43°C.

Additional examples of fluorination of compounds containing NH₂, NHC₃H₅ or NHC₂H₅ groups in an aqueous medium were later also reported [4]. They described the formation of such compounds as II–IV.

A compound analogous to I with SO₂ group instead of CO was prepared by fluorination of sulphonamide: NH₂SO₂NF₂ [5].

Difluoramine (Difluorimide) NHF₂

Difluoramine NHF₂ was prepared by decomposition of I or III.

Difluoramine is a gaseous substance [6] with m.p. −116.4 to −117.1°C, b.p. −23.6°C density d = 1.344 ± 0.00202 [d measured at −42.5°C was 1.513]. It possesses extraordinary explosive properties, being extremely sensitive to impact, detonating spontaneously when cooled to −196°C in liquid nitrogen. The N⋯F bond strength in NHF is estimated to be 72 kcal/mol [7b]. According to Lawton and Weber [6] it was formed as one of the products of the action of fluorine diluted with nitrogen (in proportion 1.4:1 to 1:1) on solid urea at 0°C. The resulting liquid mixture was distilled under reduced pressure and condensation at −142°C gave NHF₂ with a yield of 30% (calculated on the fluorine used). The non-distilling residue was composed of difluorourea (I).

Difluoramine was formed from N,N-difluorourea through acid hydrolysis:

\[
\text{NF}_2 + \text{CONH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_2\text{O} + \text{H}_2\text{NF}_2 - 1
\]

Kennedy and Colburn [7a] obtained a small quantity of difluoramine by acting on nitrogen trifluoride with arsenic at 250–300°C. The best method of making the compound consists in hydrolysis of trityldifluoramine with sul
phoric acid. A quantitative yield was obtained [8]. Trityldifluoroamine in turn was obtained by acting with tetrafluorohydrazine on trityl cation [9]:

\[
\text{N}_2\text{F}_4 + (\text{C}_6\text{H}_5)_3\text{C}^+ \rightarrow (\text{C}_6\text{H}_5)_3\text{CF}_2 \quad \text{H}_2\text{SO}_4 \rightarrow \text{NF}_2
\]

m.p. 75-77°C

(2)

Difluoroamine hydrolysed under the action of bases and fluorine anion was evolved [16].

Difluoroamine forms complexes with ethers and Lewis acids, and decomposes on contact with copper, stainless steel and some organic compounds, such as urea [6].

It reacts with carbonium ions to yield \(N,N\)-difluoroamines [11].

Difluoroamine reacts with carbonyl compounds in acid medium to yield difluoroamino derivatives [12a], for example:

\[
\begin{align*}
\text{CH}_3\text{COCH}_3 + 2\text{NF}_2 & \rightarrow \text{CH}_3\text{C}(-\text{CH}_3)\text{NF}_2 \quad \text{(85%)} \\
& \text{b.p. 73°C}
\end{align*}
\]

(3)

and with acetylenes to yield \(\text{NF}_2\) substituted olefins [12b].

No explosive properties of such substances were reported.

Other Non-aromatic Difluoroamines

Sharts [13] fluorinated a number of aliphatic amines. He fluorinated hexamethylenediamine with a fluorine-nitrogen mixture (1:2) in aqueous medium in the presence of sodium bicarbonate, trichlorofluoro-methane and methylene dichloride at temperatures below 25°C. \(N,N,N^1,N^2\)-Tetrafluorohexamethylenediamine or 1,6-bis(difluoroamino)hexane (b.p. 70-75°C at 0.1 mmHg) resulted with a yield of 23%.

In a similar manner cyclohexylamine was converted into \(N,N\)-Difluorocyclohexylamine (the yield was 66%, based on cyclohexylamine and 23% on fluorine). It is a liquid boiling over the range 69-81°C under 80-90 mmHg.

Davis and Graves [14] fluorinated guanidine and obtained an explosive product: perfluoroguanidine \(=\text{C(NF}_2\text{)}_3\). Rosenthal and co-workers [15] fluorinated cyanoguanidine and obtained three major products V – VII:

\[
\begin{align*}
\text{V} & \quad \text{F}_1\text{SCNCF}_2\text{NF}_2 \\
\text{VI} & \quad \text{NF} \\
\text{VII} & \quad (\text{F}_2\text{N})\text{SCNCF}_2\text{NF}_2
\end{align*}
\]

FLUORINATION OF NITROAROMATIC AMINES

Coon and co-workers [16] have found a general synthetic procedure for the preparation of nitroaromatic difluoroamines. Nitroaromatic monoamines, such as picramide and its analogues have been converted in high yield into the corresponding difluoroamines in liquid hydrogen fluoride and in some cases in organic solvents, such as acetonitrile, by using fluorine diluted with nitrogen, at temperatures below 60°C.

Nitroaromatic diamines and triamines undergo similar fluorination reactions. Dinitroanilines were fluorinated in good yield, but fluorination of non-nitro amines (such as aniline) is accompanied by ring fluorination ortho to the \(\text{NF}_2\) group.

According to the same authors the reaction of fluorination occurs through a radical mechanism.

All substances described below possess marked explosive characteristics [16].

\[
\begin{align*}
\text{VIII} & \quad \text{O}_2\text{N} \quad \text{N} \quad \text{NO}_2 \\
\end{align*}
\]

\(1\)-Difluoroamino-2,6-dinitrobenzene (VIII)

This substance forms light yellow coloured needles (from 50/50 chloroform/hexane), m.p. 91-93°C.

It was obtained by fluorination of 2,6-dinitroaniline in acetonitrile at \(-10\) to \(-5°C\) with a stream of 15% fluorine in nitrogen. The yield was ca. 60%.

\(1\)-Difluoroamino-2,4-dinitrobenzene

This substance was not isolated in a pure form. The liquid product of fluorination of 2,4-dinitroaniline contained 1-difluoroamino-6-fluoro-2,4-dinitrobenzene.
1-Difluoroamino-2,4,6-trinitrobenzene (IX)

The substance forms light yellow coloured crystals, m.p. 69°C.
As mentioned already it was obtained by fluorinating 2,4,6-trinitroaniline dissolved in anhydrous hydrogen fluoride at −5°C to 0°C with a stream of 60% fluorine in nitrogen. The yield was 75%.

![Chemical Structure of IX](image)

1-Difluoroamino-2,3,4,6-tetranitrobenzene (X)

The substance forms yellow coloured crystalline solids, m.p. 84°C.
It was obtained [16] from tetranitroaniline (Vol. I, p. 560) in the same way as 1-difluoroamino-2,4,6-trinitrobenzene, the only difference being that no external cooling was used and the temperature in the course of fluorination was that of the b.p. of anhydrous hydrogen fluoride (+19°C). The yield was 75%.
Difluoroaminopentanitrobenzene was obtained by fluorinating pentanitroaniline (Vol. I, p. 562) in the same way as fluorination of picramide, the only difference was that no external cooling was applied. The product was stable only in solution and could be detected by NMR spectrum. In the solid state the orange coloured crystals decomposed quickly and formed viscous oil.

![Chemical Structure of X](image)

Hexanitrodiphenylfluoramine (XI)

This is a crystalline, orange coloured solid, m.p. 102−105°C.
It was made from hexanitrodiphenylamine in acetonitrile solution by fluorinating with 15% fluorine at temperatures of −10 to −5°C (54% yield). It decomposed at room temperature within a few days and is stable only below −18°C.

![Chemical Structure of XI](image)

3-Difluoroamine-2,4,6-trinitrotoluene (XII)

This substance forms yellow coloured crystalline solids, m.p. 111°C.
It was obtained in the same way as (IX) at −16 to −4°C with 46% fluorine−nitrogen. The yield was 78%.

Other Difluoroamino Nitroaromatics

The following difluoroamino nitroaromatics were also prepared [16]:

a. 3-Difluoroamin-2,4,6-trinitroanisol, a yellow coloured liquid,
b. 3,5-bis(difluoroamino)-2,4,6-trinitrotoluene, yellow coloured crystals m.p. 143–145°C,
c. 3-difluoroamino-5-chloro-2,4,6-trinitrotoluene, yellow coloured crystals,
   m.p. 149–153°C,
d. 1,5-bis(difluoroamino)-2,4-dinitrobenzene,
e. 1,5-bis(difluoroamino)-2,4-dinitro-6-fluorobenzene. Compounds (d) and (e)
   were obtained in a mixture by fluorinating 1,5-diamino-2,4-dinitrobenzene,
f. 1,3,5-tris(difluoroamino)-2,4-dinitrobenzene, light yellow coloured crystals,
   m.p. 54–56°C.

The latter was obtained in the course of fluorination of 1,3,5-triamino-2,4-
dinitrobenzene along with 1,3,5-tris(difluoroamino)-2,4-dinitro-1,2,3,4,5,6-hexa-
fluorocyclohexane—a liquid product which was formed from the saturation of the
benzene ring of the product (I) with fluorine.

No reference to their explosive properties was given, but private information is that they do not differ from the mother nitro compounds.

FLUORINATION THROUGH THE ADDITION OF TETRAFLUOROHYDRAZINE

Tetrafluorohydrazine $NF_2-NF_2$

Tetrafluorohydrazine is a gaseous substance with b.p. −73°C.
The preparation of tetrafluorohydrazine was in a way a turning point in the chemistry of difluoroamino compounds by offering a stable reactive substance which could also yield NF$_2$ free radicals. The enthalpy of dissociation (4)

$$N_2F_4 \rightarrow 2NF_2$$

(4)
is very low 20 ± 1 kcal/mol [1].

Tetrafluorohydrazine was obtained by Colburn and Kennedy [17] by passing nitrogen trifluoride over copper at 375°C:

$$2NF_3 + Cu \rightarrow N_2F_4 + CuF_2.$$
The reaction can also be carried out with other metals, such as Fe, As, Sb and Bi. The conversion was 42–62% and the yield 62–71%.

(Nitrogen trifluoride was obtained by O. Ruff and co-workers [18] through electrolysis at 125°C of molten ammonium hydrogen fluoride: NH₄F. HF. It is a stable, gaseous, b.p. −119°C, substance which can be hydrolysed by hot water vapour.)

It was also reported that nitrogen trifluoride could be obtained by reacting N₂O with fluorine at 700°C [19].

On other methods of preparation of tetrafluorohydrazine – see [1].

**Reactivity of Tetrafluorohydrazine**

Frazer [20] has shown that tetrafluorohydrazine can react with methyl and ethyl iodide in a light initiated reaction to give N,N-difluoroaminomethane and ethane respectively.

A number of authors reported the formation of bis(difluoroamino) compounds by the addition of tetrafluorohydrazine to unsaturated aliphatic and aromatic compounds [21–26].

According to Cerfontain [24] tetrafluorohydrazine can react with polycyclic aromatic hydrocarbons in iso-octane as a solvent at 40°C. Thus anthracene yielded 9,10-bis(difluoroamino)-9,10-dihydroanthracene. The product does not show good stability, it decomposed above 130°C with a gas evolution and at 220°C yielded mainly the parent hydrocarbon. Similarly the product of the reaction of stilbene with tetrafluorohydrazine (which was 1,2-bis(difluoroamino)-1,2-diphenylethane) decomposed above 80°C.

The reaction of tetrafluorohydrazine with diallil ether was studied by Reed [26]. The main product of the reaction (48%) was di[2,3-bis(difluoroamino) propyl] ether (6)

\[
\text{CH}_2=\text{CH}-\text{CH}_2\text{O} + \text{N}_2\text{F}_4 \rightarrow \begin{array}{c} \text{CH}_2=\text{CH}-\text{CH}_2 \text{NF}_2 \text{NF}_2 \end{array}
\]

The other products were tetrahydrofurane derivatives.

Fokin and co-workers [32] described interesting reactions of nitroalkenes with tetrafluorohydrazine. Such was the reaction of 2,2-dinitropentene-4 with tetrafluorohydrazine yielding 2,2-dinitro-4,5-bis(difluoroamino)-pentane (7) with a yield of ca. 36%:

\[
\begin{array}{c}
\text{CH}_2=\text{CH}-\text{CH}_2
\end{array} + \text{N}_2\text{F}_4 \rightarrow \begin{array}{c} \text{CH}_2=\text{CH}-\text{CH}_2 \text{NF}_2 \text{NF}_2 \end{array}
\]

**DIFLUOROAMINO COMPOUNDS**

The reaction is very solvent dependent. Decomposition occurred in most solvents but the best proved to be acetonitrile.

Fokin and co-workers [33] studied reactions of oximes with tetrafluoro-hydrazine, for example (8)

\[
\text{CH}_2\text{CH}=\text{NOH} + \text{N}_2\text{F}_4 \rightarrow \text{CH}_3\text{C} = \text{NF} \quad \text{CN}
\]

Most of the latter products are unstable. The only stable compounds were obtained from aromatic oximes.

The addition of N₂F₄ to acetylenes was studied by a number of authors [27, 28]. The reactions give ethylene derivatives unstable and readily isomerizing on further heating or under the influence of irradiation (9)

\[
\text{RC} = \text{CR} + \text{N}_2\text{F}_4 \rightarrow \begin{array}{c} \text{RC} \text{CN} \text{NF}_2 \text{NF}_2 \end{array}
\]

The fact that NF₃ radical formed through the equilibrium N₂F₄ = 2·NF absorbs at 260 nm suggests that it possesses photochemical properties. Indeed it was found that the irradiation of methane with N₂F₄ produced difluoroamino-methane (10)

\[
\text{CH}_4 + \text{N}_2\text{F}_4 \rightarrow \text{CH}_3\text{NF}_2 + \text{HF}
\]

Similarly ethane yielded difluoroaminoethane C₂H₄NF₂ and CH₃CN.

Olefins also reacted with N₂F₄ under irradiation, for example propylene yielded 50% of a mixture of substituted propylene and propane (XIII–XIV) [29]

\[
\begin{array}{c}
\text{CH}_2=\text{CH}_2
\end{array} \rightarrow \begin{array}{c} \text{CH}_2=\text{CH}_2 \text{NF}_2 \text{NF}_2 \end{array}
\]

**EXPLOSIVE PROPERTIES OF DIFLUOROAMINOALKANES AND ALKENES**

A few experimental data of explosive properties of difluoroaminoalkanes and alkenes were collected and theoretical calculation of their properties was given by Pepekin [31].
According to Berke and associates [43] bis-difluoroaminopropane and -butane give the rates of detonation:

\[ \begin{align*}
C_3H_6N_2F_4, & \quad \rho = 1.26, \quad D = 6300 \text{ m/s}, \\
C_6H_8N_2F_4, & \quad \rho = 1.20, \quad D = 6000 \text{ m/s}.
\end{align*} \]

Voskoboyinov and co-workers [44] have found similar figures for bis-difluoroaminobutane and -pentene. They also described an interesting compound: tetra-difluoroamino-pentane:

\[ CH_2 - \left[ \begin{array}{c}
\text{CH}_3
\
\text{NF}_2
\end{array} \right] - \text{CH}_3, \quad \rho = 1.51, D = 7000 \text{ m/s}. \]

The general conclusion is that compounds with NF₂ group show similar explosive properties as those with the same number of NO₂ groups.

Theoretical Aspects of Properties of NF₂ Compounds

A series of theoretical papers on the difluoroamino group and compounds have appeared. Their aim was to find a theoretical background for the use of difluoroamino compounds in propellants.

1. Isotopic exchange reaction of difluoroamine (NF₂H) with D₂O and trifuloro deutero acetic acid (CF₃COOD) was examined by Becker and Impastato [36].

2. The reaction of difluoroamine with Lewis Acids [37].

3. A paper on the chemistry of difluoroamines by Craig et al. [38] was also published. It was dedicated to understanding the nature of N–F and N–N bonds and to obtain a picture of the relative electron distribution in X NF₂ compounds, where X = F, Cl, H, NF₂, CH₃, V₂F₂, and CH₃. The electron affinity of cation NF₂⁺ was found to be very high and by adding an electron, a relatively stable radical NF₂⁻ was favored. The electron distribution is more symmetrical than in anion NF₂⁻ and cation NF₂⁺ which do not seem to be sufficiently stable.

4. In searching for high energy explosives the reactions were examined between difluoroamino compounds and

(a) organometallic compounds,
(b) nitric acid [39]. A variety of compounds were obtained in both instances, such as:

(a) azo-compounds, dialkyl difluoro-hydrazine, tertiary amine and hydrocarbon.
(b) alkyl nitrates and nitrates.

5. Reactivity of nitrogen fluorides NF₃, N₂F₂ and cis- and trans-N₂F₂ was examined by Hurst and Khayat [40]. Nitrogen trifluoride (NF₃) is inert to pure water but reacted with aqueous bases at 100°C to give nitrite and fluoride. N₂F₂ was hydrolyzed slowly with water at 60–100°C. Cis- and trans-N₂F₂ were hydrolyzed with water at 74°C and 89°C respectively. The reactions were of the first order with respect to N₂F₂ and the major products are N₂ and O₂ [41].

Thermochimistry

Pepeklin and Apin [42] calculated enthalpy of formation of 1,1-bis(difluoroamino)cyklohexane and the energy of the bond N–F. The enthalpy of formation was found to be 52.5 kcal/mol and the thermochemical energy of the bond N–F was 68.4 cal.

REFERENCES

CHAPTER 10

ESTERS

NITRATE ESTERS

(O-NITRO COMPOUNDS)

Although nitrate esters continue to be widely used and are important explosives, their chemical properties are described to a much lesser extent than those of C-nitro compounds. This is understandable when considering the wide use of C-nitro compounds, particularly aromatic ones, not only as explosives but in a great variety of uses as intermediates and finished products. For this reason the excellent monograph of Patay, series edited by H. Feuer [1], does not contain a chapter on O-nitro compounds and the only review papers dedicated solely to O-nitro compounds were by Boschan, Merrow, Van Dolah [2] and Connin [3].

STRUCTURE (Vol. II, p. 1)

Three kinds of nitrate esters are distinguished: primary, secondary and tertiary deriving from primary, secondary and tertiary alcohols respectively:

1. primary \( \text{CH}_3\text{ONO}_2 \)
2. secondary \( \text{CH}_2\text{ONO}_2 \)
3. tertiary \( \text{CONO}_2 \)

This was pointed out by T. Urbaniski and Witanowski (Vol. I, p. 6) who found the spectroscopic (infrared) method of distinguishing the above species which is described later in the paragraph on spectroscopy of nitrate esters.

DIPOLE MOMENTS (Vol. II, p. 3)

Recent measurements of dipole moments carried out by Lemanceau and Caire-Maurisset [4] brought some new and important conclusions to the problem of the conformation of nitroglycerine and other nitrate esters with three or four atoms of carbon in the chain. They concluded that there is less need for admitting various conformations produced by the rotation around C-C bonds of the chain \( \text{CH}_2\text{CH} \). Instead they rationalized their results in terms of the rotation in groups \( \text{CNO}_2 \) around the bonds C-O, viz. Formulae 1a and 1b:

\[
\begin{align*}
1a: & \quad \text{CIMO}_2, \\
1b: & \quad \text{CH}_2\text{ONO}_2
\end{align*}
\]
The same applies to propane-1,2-diol dinitrate (II) and butane-1,2,4-triol trinitrate (III). They also examined NMR spectra of nitrate esters — their conclusions are reported in the paragraph on NMR of nitrate esters (p. 284).

\[
\begin{array}{c|c}
\text{CH}_3\text{ONO}_2 & \text{CH}_3\text{ONO}_2 \\
\text{CH}_2\text{ONO}_2 & \text{CH}_2\text{ONO}_2 \\
\text{CH}_3 & \text{CH}_2 \\
\text{II} & \text{III} \\
\end{array}
\]

SPECTROSCOPY (Vol. II, p. 4).

T. Urbaniński and Witanowski [5] found that a stepwise substitution of hydrogen atoms with methyl groups in methyl nitrate lowers the frequency of asymmetric vibrations by about 5 cm\(^{-1}\) for each methyl introduced. Subsequently it is possible to distinguish between primary, secondary and tertiary simple alkyl nitrates by their \(\nu_{as}\) as frequencies, viz.:

\[1632 - 1630,\]
\[1626,\]
\[1621 \text{ cm}^{-1}\] respectively.

On the contrary, \(\nu_{asym}\) vibrations of simple nitrate esters (1283 - 1280 cm\(^{-1}\)) is unaffected by the substitution as above.

The fact observed by Pristera (Vol. II, p. 6) that the infra red asymmetric vibration band of az 1639 cm\(^{-1}\) of nitroglycerine has a shoulder was rationalized by Rossmy [6], T. Urbaniński and Witanowski (Vol. II, pp. 4, 6) as the result of rotational isomerism around the bond C-C \(\text{ONO}_2\).

Nevertheless the shoulder can also be partly produced by the fact that the nitroglycerine molecule contains both the primary groups and the secondary O-nitro group. This refers also to all nitrate esters with longer chains, such as esters of erythritol and hexitols (e.g. mannitol, sorbitol), but not in esters of ethylene glycol and pentaerythritol which show a splitting of the absorption bands. [7] and (Vol. II, p. 6).

The data for infra red spectra obtained by T. Urbaniński and Witanowski [5, 7] were used by Czuchajowski and Kucharski [8] in the series of papers on calculation force constants. Such a theoretical approach for methyl nitrate was first given by Shlyapochkin, Novikov and Zavilovich [9].

Czuchajowski and Kucharski examined a full range of derivatives of ethyl nitrate of the general formula \(Y-\text{CH}_2-\text{CH}_2-\text{ONO}_2\). Table 45 gives comparative results of experimental values [5, 7] and their calculation [8]. Table 46 gives stretching force constants and the influence of +I inductive effect of the substituents \(Y\).

<table>
<thead>
<tr>
<th>Y</th>
<th>(\nu_{as}(\text{NO}_2)) cm(^{-1})</th>
<th>(\nu_{as}(\text{NO}_2)) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>1631</td>
<td>1632</td>
</tr>
<tr>
<td>Cl</td>
<td>1652</td>
<td>1651</td>
</tr>
<tr>
<td>Br</td>
<td>1640</td>
<td>1650</td>
</tr>
<tr>
<td>I</td>
<td>1662</td>
<td>1660</td>
</tr>
<tr>
<td>ONO_2</td>
<td>1656</td>
<td>1656</td>
</tr>
</tbody>
</table>

**Table 46.** Stretching force constants in \(Y-\text{CH}_2-\text{CH}_2-\text{ONO}_2\). Influence of +I inductive effect (according to Czuchajowski and Kucharski [7]).

<table>
<thead>
<tr>
<th>Y</th>
<th>(N_O-N) m dyn A</th>
<th>(N_O-N) m dyn A</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>4.4</td>
<td>9.04</td>
</tr>
<tr>
<td>Cl</td>
<td>4.10</td>
<td>9.25</td>
</tr>
<tr>
<td>Br</td>
<td>4.07</td>
<td>9.29</td>
</tr>
<tr>
<td>I</td>
<td>3.99</td>
<td>9.35</td>
</tr>
<tr>
<td>ONO_2</td>
<td>4.07</td>
<td>9.29</td>
</tr>
</tbody>
</table>

In the next paper [10] Czuchajowski and Kucharski extended their calculations of valence force field (VFF) to compounds of the general formula \(Y-\text{CH}_2-\text{CH}_2-\text{ONO}_2\), where \(Y\) was \(\text{NO}_2\), \(\text{CN}\), \(\text{ONO}_2\). Their calculated results included the difference between gauche and trans conformers, the values of which were 1655-1652 and 1644-1641 cm\(^{-1}\) respectively and are also in agreement with the experimental data [7].
NUCLEAR MAGNETIC RESONANCE

Lemanceau and Caire-Maurisier [4] examined NMR spectrum of nitroglycerine with a view to determining the conformation of the compound. The spectrum is of the type A B C A' B' and appears to favour the eclipsed conformation of C-ONO₂ groups.


ELECTRON ATTRACTING PROPERTIES OF NITRATE ESTERS AND CHARGE-TRANSFER COMPLEXES

T. Urbaniński (Vol. II, pp. 167, 169) and later Witanowski [12] have shown by way of thermal analysis that some O-nitro compounds such as D-mannitol hexanitrate and erythritol tetranitrate can form additional complexes with aromatic nitro compounds.

In a series of papers [13–15, 22] T. Urbaniński, Hetnarski and Paluchnikiewicz described charge-transfer complexes with nitrate esters as electron acceptors. Tetramethyl-p-phenylenediamine (TMPD) was used as an electron donor. The visible stage of the reaction between nitrate esters and TMPD in 1,2-dichloroethane as the solvent was the formation of the blue-violet coloured radical known as Wurster cation (IV) [16, 17] formed from TMPD through the loss of one electron. The presence of Wurster cation is manifested by two absorption bands in the electronic spectrum: 570 and 620 nm [17]. The authors established that at least three O-ONO₂ groups are needed to form one mole of IV, for example:

\[
\text{IV} \quad \text{III}
\]

The comparison of the enthalpy of the formation of Wurster cation of primary, secondary and tertiary butyl nitrate has shown that the primary O-ONO₂ group is the weakest electron acceptor and the strongest is the tertiary O-ONO₂ group the enthalpy of formation (ΔH f) being 0.47 and 0.61 kcal/mol respectively. Nitroglycerine, pentaerythritol tri- and tetranitrate reacted with TMPD at the molar ratio 1:1. The same ratio was observed with erythritol tetranitrate but comparison with pentaerythritol tetranitrate (PETN) shows a stronger electron accepting property of the former probably due to the presence of secondary nitrate groups.

Hexanitrate of hexitols show strong accepting properties: 1 mole of hexanitrate with 2 moles of TMPD, in agreement with the rule 3 O-ONO₂ groups for 1 mole of TMPD.

More detailed examination of the electronic spectra of TMPD with pentanitrites of D-xylitol, D-mannitol and hexanitrate of D-mannitol, D-sorbitol, D-lyeitol and myo-inositol has shown three stages of the reaction in 1,2-dichloroethane as a solvent. At first all of them showed a rapid formation of low intensity transient bands between 909 and 1030 nm, which corresponds to an unstable (I-III) complex. Within 15 min (as in the case of all other nitrate esters) two bands of Wurster cation appeared. While these bands of nitrate esters persisted for a few days, both bands of pentanitrites and hexanitrates disappeared within 2 hours and were transformed into one band of 450 nm characterizing the yellow coloured relatively stable complex of the ratio 1:1 of hexanitrate to TMPD. The enthalpy of the formation of the new complex was ΔH f = 5.12 kcal/mol, a value of the same magnitude as in many π-π complexes. Following the overlap and orientation principle of Mulliken [18] the structure of the I-III complex was rationalized [15] being as shown on formula V. (Fig. 40, p. 308).

The structure of TMPD is represented here as TMPD being transformed into a quinoid compound: tetramethyl-p-phenylenediamine dication formed by disproportions of Wurster cation. Its structure was confirmed by infra red spectroscopy.
A hypothetical structure of complexes of nitrate esters with one to four nitrate groups was also advanced [19]. It was suggested that TMPD be used for analytical detection (including TLC) of nitrate esters [20].

In the light of the above work the finding of Parihar, Sharma and Varma [21] on the colour reaction of O-nitro compounds with potassium sulphanilate and α-naphthylamine in acetic acid should also be attributed to the oxidation of amines. The reaction produced the coloured cations and possibly charge—transfer complexes between the O-nitro compounds and the amine.

Further experiments were carried out on CT complexes between D-mannitol hexanitrate and pyrimidine and purine bases important in biochemical processes [22]. A summarized report has also been given on nitrate esters as electron acceptors [23].

Fraser and Paul [159] examined nitrate esters by mass spectrometry. Both mononitrates and polynitrates were examined. The main conclusions of this important work are given below.

n-Alkyl mononitrates are subject to cleavage as:

\[
\text{RCH}_2\text{ONO}_2^+ (m/e 76)
\]

\[
\text{RCH}_2\text{ONO}_2^+ \rightarrow \text{RCH}_2\text{O}^+ (m/e 30) \rightarrow \text{NO}_2^- (m/e 30)
\]

\[
\text{R}^+ \rightarrow \text{CHO}^+ (m/e 29) \rightarrow \text{CO}^+ (m/e 28)
\]

Diol dinitrates:

\[
\text{O}_2\text{NOCH}_2^+ \rightarrow \text{O}_2\text{NO}^{\cdot} \rightarrow \text{CH}_2\text{ONO}_2^+ (m/e 15)
\]

\[
\text{CH}_2\text{ONO}_2^+ \rightarrow \text{CH}_2\text{O}^+ (m/e 43) \rightarrow \text{NO}_2^- (m/e 44)
\]

\[
\text{CH}_2\text{CHO}^+ (m/e 44) \rightarrow \text{NO}^+ (m/e 43)
\]

\[
\text{NO}_2^- \rightarrow \text{NO}^+ \rightarrow \text{NO}_2^-
\]

Branched-chain nitrates, for example isopropyl nitrate:

\[
\text{CH}_3\text{CHO}^+ (m/e 44) \rightarrow \text{NO}_2^- (m/e 43)
\]

Nitroglycerine shows a low intensity peak of 76 m/e.

Kriemler and Buttrill [161] studied the formation of positive and negative ion-molecules from ethyl nitrate by ion cyclotron resonance technique. They found three kinds of reactions of positive ions:

(a) transfer of \(\text{NO}_2^+\) from \(\text{CH}_2\text{ONO}_2^+\) and \(\text{H}_2\text{NO}_3^+\) to ethyl nitrate to form \(\text{C}_2\text{H}_5\text{N}_2\text{O}_7^+\).

(b) protonation of \(\text{C}_2\text{H}_5\text{ONO}_2\) by \(\text{C}_2\text{H}_5^+\), \(\text{C}_2\text{H}_4^+\) and \(\text{CHO}^+\).

(c) fragmentation of protonated ethyl nitrate into \(\text{H}_2\text{N}_2\text{O}_7^+\) and ethylene.

Negative ions have been found \(\text{C}_2\text{H}_5\text{O}^-\), \(\text{C}_2\text{H}_5^-\) and \(\text{OH}^-\) to produce \(\text{NO}_3^-\).

**HYDROLYSIS OF NITRATE ESTERS** (Vol. II, p. 7)

Baker and co-workers (Vol. II, p. 8; [23–25]) have undertaken extensive research on alkaline hydrolysis of nitrate esters. Their results, as those of the other authors [27], were reviewed [2, 3]. They can be summarized as follows:

Nucleophilic attack on carbon (\(S_N 1\) and \(S_N 2\)):

\[
\text{HO}^- + \text{RCH}_2\text{O}^- \rightarrow \text{RCH}_2\text{OH} + \text{NO}_3^-.
\]

Nucleophilic attack on nitrogen (\(S_N 2\)):

\[
\text{HO}^- + \text{RCH}_2\text{O}^- \rightarrow \text{RCH}_2\text{O}^- \rightarrow \text{RCH}_2\text{OH} + \text{NO}_3^-.
\]

Nucleophilic attack on \(\alpha\)-hydrogen (E2):

\[
\text{HO}^- + \text{RCH}_2\text{O}^- \rightarrow \text{RCH}^- + \text{H}_2\text{O}.
\]

Nucleophilic attack on \(\beta\)-hydrogen (E1 and E2):

\[
\text{HO}^- + \text{RCH}_2\text{O}^- \rightarrow \text{RCH}^- + \text{H}_2\text{O} + \text{NO}_3^-.
\]

Thus both cleavage of bonds \(\text{C}^-\text{O}\) and \(\text{O}^-\text{N}\) can occur.
The reaction of primary and secondary mononitrate esters are slow, for example slower than alkaline hydrolysis of carboxylic esters.

Primary nitrate esters can undergo alkaline hydrolysis mainly by two pathways (4a and 4b) and the yield of elimination reactions (4c and 4d) are, generally speaking, negligible.

Secondary nitrate esters give a more complicated picture. The dominating reaction is SN2 but reactions (4c) and (4d) are of importance. Reaction (4c) can yield (depending on R) 8–45% of the carbonyl compound in addition to a certain amount of alkenes. A striking example was given by Baker and Easty [23] on hydrolysis of isopropyl nitrate (Vol. II, p. 13). An important contribution to the mechanism of the reaction of hydrolysis was given by Cystol and co-workers (Vol. II, p. 14) while reacting optically active 2-octyl nitrate.

Reaction (4c) E2 [24] has been used to introduce a carbonyl group into steroids [28].

Neutral hydrolysis of primary and secondary nitrates is very slow [23]. On the contrary, simple tertiary nitrate esters are readily hydrolysed [23, 27, Lucas and Hammett (Vol. II, p. 8)] to yield either alcohol (SN1) or olefin (E1). Both go through the tertiary carbamion ion.

The four modes of hydrolysis can explain the reaction of nitrate esters with other nucleophiles such as ammonia and amines, hydrazine (Vol. II, p. 12), hydroxide and alkoxide ions (SN1 and SN2). Here the esters can act as alkylating agents.

Alkaline hydrolysis at 25°C of glycerol trinitrate, 1,2-glycerol and 1,3-glycerol dinitrates, 1-glyceryl and 2-glyceryl mononitrates with CO2 free aqueous calcium hydroxide was studied by Capellos and co-workers [103]. They found that 2-glyceryl mononitrates isomerized on hydrolysis to 1-glyceryl mononitrates and 1,2-glycerol dinitrate isomerized to the 1,3-dinitrate before the hydrolysis was accomplished. 1,3-Glycerol dinitrate furnished on hydrolysis glyceryl nitrate in agreement with the reactions described in Vol. II, p. 128.

Nitrile ester hydrolysis is not catalysed by mineral acids to an appreciable extent [29, 26]. This is in contrast to nitrile esters which readily hydrolyse in an acid medium. According to Dewar [30] nitrile esters are protonated preferentially at the alkoxy oxygen according to equation (5a):

\[ R \cdot ONO_2 + H^+ \xrightarrow{\text{fast}} R \cdot O^+ \cdot NO_2 \xrightarrow{\text{slow}} ROH + NO_2^+ \]  

(5a)

The last stage of the reaction is inhibited by the large positive heat of the dissociation [3].

In concentrated sulphuric acid nitrate esters are almost completely dissociated according to equation (5b):

\[ RONO_2 + 3H_2SO_4 \rightarrow ROSO_4^+ + NO_2^- + 3H_2O + 2H_2SO_4^- \]  

(5b)

Such a system can be used as a strong nitrating agent (Vol. I, pp. 15, 122). The nitration of an active methylene group with nitrate esters was basically described in Chapter I.

An interesting method of hydrolysis of nitrate esters to alcohols was given by Pews [158]. It consists in refluxing nitrate esters with formic acid followed by refluxing with methanol. Pentenyltrinitrate yielded pentenylthanol.

REDUCTION OF NITRATE ESTERS (Vol. II, p. 18)

The review on nitrate esters [2] should be mentioned here. The following are agents which can be used to recover the original alcohols: LiAlH₄, sulphides, H₂ on Pd-charcoal, Raney Ni, Pt. The reduction on platinum can go as far as to the formation of ammmony from ONO₂. Grignard reagent can be also used to reduce nitrate esters [31]. Reduction has been used to remove the O-nitro group which serves for protection of OH during the synthesis of some steroids [32, 33].

Polarography can be used as an analytical method of quantitative determination of O-nitro groups. It was applied to simple esters [34] and to nitroglycerine [35].

CONVERSION OF NITRATE ESTERS INTO NITROALKANES

Bachman and Common [37] described an interesting reaction of conversion of nitrate esters into nitroalkanes according to (6):

\[ RONO_2 + NaNO_2 + \text{solvent} \rightarrow RNO_2 + ROH \text{ (from RONO)} \]  

(6)

The reaction of nitrate esters with metal nitrates (e.g. sodium nitrite) was carried out in a suitable solvent at temperatures below 100°C. The nature of solvent is decisive to the yield. In the instance of n-propyl nitrate the best result (42% of 1-nitropropane) was obtained by keeping the reagents for one hour at 45°C in hexamethylphosphamide. The rest of the nitrate ester was converted to the original alcohol (54% of n-propyl alcohol in the described example).

The reaction has little value for the preparation of nitroalkanes, but it is of theoretical importance as it indicates the reactivity of nitrate esters. It should be added that J. B. Levy [59] has found that thermal decomposition of nitrate esters resulted in the formation of small amounts of nitroalkanes. Thus the formation of nitroalkanes from nitrate esters seems to merit a more detailed examination of the mechanism of the conversion and decomposition.

FORMATION OF NITRATE ESTERS (Vol. II, p. 20)

The review by Van Dolah and co-workers [2] should be mentioned. Owing to the fact that sulphuric acid in a nitrating mixture promotes hydrolysis of nitrate
ESTERS, it is often desirable to nitrate alcohol with nitric acid alone in the presence of urea. The method was used on a large scale to make iso-propyl nitrate [36]. Urea obviously is a scavenger of nitric oxides and nitrous acid—compounds which can lead to oxidation and often dangerous decomposition.

Other nitrating agents which are the source of NO$_3^-$ ion can also be used (Chapter I).

An interesting method of making nitrate esters consists in reacting dinitrogen pentoxide with alcohols in a vapour phase as developed by Bachman and Connon [3, 37]. A continuously working laboratory nitrator was described by Connon [3]. Here N$_2$O$_5$ is produced as a dilute mixture with oxygen by reacting NO$_2$(N$_2$O$_5$) with ozonized oxygen and has a composition according to the diagram (7).

\[
\text{NO}_2 + \text{O}_2 \rightarrow \text{NO}_3 + \text{O}_2 \rightarrow \text{N}_2\text{O}_5
\] (7)

The addition of N$_2$O$_5$ to an alkene oxide can also produce nitrate esters. E. White and Feldman [38] reacted with a solution of N$_2$O$_5$ on sodium butoxide—butanol at -75°C and received butyl nitrate with a yield of 89%. The reaction is also an example of N$_2$O$_5$ acting according to equation (16). Chapter I, on pair nitronium nitrite (NO$_2^+$ + NO$_3^-$). The order of adding reagents is critical: the reversed nitrations can occur in due to the action of N$_2$O$_5$ in the capacity of nitrosyl nitrate (NO$_2^+$ + NO$_3^-$) — equation (17). Chapter I. This was substantiated by Bachman and Connon [3, 37]. They also found that sodium hydroxide can be used instead of sodium butoxide.

A convenient laboratory method for the preparation of nitrate esters consists in acting with silver nitrate on alkyl bromide or iodide in nitromethane or nitrobenzene [2] or acetonitrile [3]. Kornblum and co-workers [39] made an extensive study of the stereochemistry and mechanism in the reaction of silver nitrate (and nitrite) with alkyl halides. Their conclusion can be summarized: the optically active nitrate esters (as well as nitrite esters) are produced with an inversion. Thus optically active 2-bromo-octane when treated with silver nitrate gives 2-ethyl nitrate of the inverted configuration regardless of the solvent. With α-phenylethyl chloride however, the stereocourse of the reaction is solvent dependent: in ethyl ether and in benzene α-phenylethyl nitrate is produced with retention of configuration but in acetonitrile or petroleum ether the nitrate ester is produced with the inversion. The authors came to the conclusion that the reaction of silver salts with alkyl halides is rationalized as concerted S$_{N}$1 S$_{N}$2 processes.

Nitrate esters are formed as by-products in the reaction of alkyl bromide or iodide with silver nitrate [40]. By using a temperature below 0°C the formation of nitrate ester can be prevented [41].

Olah and co-workers [42] suggested a convenient and safe method for the preparation of alkyl nitrates (particularly polynitrates) via transfer nitrification of alcohols (polyols) with N-nitrosoctydium tetrafluoroborate according to scheme (8)

\[
\begin{align*}
\text{R} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{N} & \quad \text{OH} \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{Cl} & \quad \text{Cl} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

The yield is 41-100% thus ethyl nitrate, glycol dinitrate and nitroglycerine can be obtained in theoretical yield.

Among the other methods of formation of nitrate esters the reaction discovered by Blanchard [43] of the action of nitric acid on nitramines is of importance:

\[
\text{CH}_3\text{NCl} + \text{HNO}_3 \rightarrow \text{CH}_2\text{ONO}_2 + \text{N}_2\text{O}
\] (9)

The reaction should be taken into consideration when examining the formation of nitramines including cyclonite.

Interesting reactions of the formation of nitrate esters consist in the action of some nitratating agents on alkanes and alkyl groups. Titov and Shchitov [44] established that cyclohexane, α-decane and γ-octane react with dinitrogen pentoxide to yield cyclohexyl, 2-heptyl and 2-ethyl nitrates respectively. Suzuki and co-workers [45] described the action of an excess of nitric acid or cerium ammonium nitrate on 2,4,5-trimethylhexcenzen and found that compounds were formed with one of the methyl groups subjected to nitro-oxidation according to abridged scheme (10).
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

In another series of experiments Suzuki and associates [46] found a similar reaction of nitration \( \text{CH}_3 \rightarrow \text{CH}_2\text{ONO}_2 \) by acting with nitrous acid on pentamethyl derivatives of acetophenon.

Nitrates esters can also be made by the oxidation of nitrite esters (Vol. I, p. 2). This reaction can also be carried out through a photolysis of nitrate esters. Such is, for example, the photolysis of octyl nitrite in heptane saturated with oxygen of the probable mechanism as below [47, 48]:

\[
\begin{align*}
\text{C}_8\text{H}_{17}\text{ONO} + \text{hv} & \rightarrow \text{C}_8\text{H}_{17}\text{O} + \text{NO}_2 \quad (a) \\
2\text{NO} + \text{O}_2 & \rightarrow 2\text{NO}_2 \quad (b) \\
\text{C}_8\text{H}_{17}\text{O} + \text{NO}_2 & \rightarrow \text{C}_8\text{H}_{17}\text{ONO}_2 \quad (c)
\end{align*}
\]

The yield was 50%.

Bachman and Connan [49] have shown that simple nitrate esters can be partly oxidized to corresponding nitrate esters by mixtures of \( \text{N}_2\text{O}_4 \) and oxygen which probably react as \( \text{N}_2\text{O}_4 \) or free radical \( \text{NO}_2 \). The same authors [37] obtained nitrate esters by reacting nitrate esters with a mixture of \( \text{N}_2\text{O}_4 \) with ozonized oxygen according to (7). Octyl nitrite gave a 70% yield of the nitrate as well as 30% octanoic acid. When octyl nitrite reacted with dilute ozonized \( \text{N}_2\text{O}_4 \) (which reacted as \( \text{N}_2\text{O}_4 \)) in a counter current reactor [3] the yield of octyl nitrate could be as high as 97%.

GAS-CROMATOGRAPHY OF ALKYL NITRATES

Although analytical problems are not discussed in the present book, it is important that some information should be given, as the problem of the presence of nitrate esters, for example in air, is connected with problems of safety.

Alkyl nitrates can be separated and identified by gas-liquid chromatography. Ethylene glycol succinate was used as the partition liquid and Celite C224K was used as support [155]. Gas-liquid chromatography was used to determine nitrate esters in the presence of aromatic nitro compounds [156]. An improvement was made in the gas-chromatography by using an electron capture detector with tritium source [157].

ALKENES AS A SOURCE OF NITRATE ESTERS

As pointed out in Vol. I, p. 146 nitrate ester of \( \beta \)-nitroethanol can be formed by passing ethylene into a nitric-sulphuric acid mixture, and a side reaction is the formation of ethylene glycol dinitrate. However in most experiments nitrate ester is the minor product of the reaction. The reactions of alkene with \( \text{N}_2\text{O}_4 \) were described in the excellent review paper by Shechter [50]. The classic work of N. Levy, Scaife et al. (Vol. I, pp. 594-5); [51-53] should be mentioned here, as well as those of Lachowicz and Kreuz [54], Bonetti and co-workers [55], Stevens [56].

Connan [3] summarized their results in two schemes. The simple version is (12).

\[
\begin{align*}
\text{C}_n\text{H}_{2n+1}\text{ONO} + \text{hv} & \rightarrow \text{C}_n\text{H}_{2n+1}\text{O} + \text{NO}_2 \quad (a) \\
\text{NO} + \text{O}_2 & \rightarrow 2\text{NO}_2 \quad (b) \\
\text{C}_n\text{H}_{2n+1}\text{O} + \text{NO}_2 & \rightarrow \text{C}_n\text{H}_{2n+1}\text{ONO}_2 \quad (c)
\end{align*}
\]

Here the oxidizing agent can be \( \text{N}_2\text{O}_4 \) or \( \cdot \text{NO}_3 \) which can be formed by the action of oxygen on \( \text{NO} + \text{NO}_2 \) [57].

An interesting method for the formation of an iodo nitrate ester consists in acting with \( \text{Hg(NO}_3\text{)}_2 \) and iodine on alkene [58].

NITRATE ESTERS AS EXPLOSIVES (Vol. II, p. 2)

Relatively little work has been dedicated to the examination of such problems as the rate of detonation of nitrate esters, except in the instance of new compounds or those which are not yet sufficiently known. They are now reported in a description of the salt compounds. On the contrary, considerable work has been done on thermal decomposition of nitrate esters. Particularly numerous are papers by Soviet authors mainly those of Andreev and his School collected in three monographs [60-62]. The data on the energy of activation of thermal decomposition of nitrate esters and the frequency factors are collected in Table 47 [63-65]. The calculated figures are remarkably similar for all nitrate esters and also are in agreement with those formerly found for nitroglycerine – Vol. II, p. 50. It should also be pointed out that the energy of activation is greatly influenced by the temperature of experiments – see [76, 77].

Determination of stability remains largely unchanged and is much the same as described in Vol. II, p. 23. The ‘Heat test’ (Aibel test) is frequently used to determine the purity of nitrate esters such as nitroglycerine, glycol dinitrate, DGN and nitrotoluenes because of its simplicity [66]. Fraser [67] examined the stability of nitrate esters by determining the hydrolysis rates of the esters using sodium hydroxide in 90% ethanol at 30° and 60°C. The reactions are all second order in both nitrate ester and hydroxide ions. As the measure of the stability of an ester Fraser took the initial specific rate of hydrolysis. His results are summarized in Table 48.

He concluded that stability increases as the length of the carbon chain increases and is further enhanced by the introduction of an \( \alpha \)-methyl group. Alkyl substitution in \( \beta \)-position has a smaller but similar effect. The replacement of a hydrogen by methyl or substituted methyl group decreases the rate of hydro-
TABLE 47. Energy of activation of nitrate esters

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energy of Activation kcal/mol</th>
<th>log B</th>
<th>Temperature ranges °C</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Nitrate</td>
<td>39.0</td>
<td>15.5</td>
<td>100 170</td>
<td>64b</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>39.0</td>
<td>15.4</td>
<td>80 140</td>
<td>64c</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>39.0</td>
<td>14.5</td>
<td>80 140</td>
<td>64c</td>
</tr>
<tr>
<td>Dimethyl Nitrate (Nitroglycerol)</td>
<td>42.0</td>
<td>16.5</td>
<td>80 140</td>
<td>64c</td>
</tr>
<tr>
<td>Diethylene Glycol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dinitrate</td>
<td>40.3</td>
<td>15.8</td>
<td>72 140</td>
<td>65</td>
</tr>
<tr>
<td>1,2-Propylene Glycol Dinitrate</td>
<td>39.1</td>
<td>14.9</td>
<td>72 140</td>
<td>65</td>
</tr>
<tr>
<td>1,3-Propylene Glycol Dinitrate</td>
<td>39.1</td>
<td>14.9</td>
<td>72 140</td>
<td>65</td>
</tr>
<tr>
<td>1,4-Butylene Glycol Dinitrate</td>
<td>41.6</td>
<td>16.7</td>
<td>72 140</td>
<td>65</td>
</tr>
<tr>
<td>Methyl Hexaminate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3-Butylene Glycol Dinitrate</td>
<td>39.2</td>
<td>15.0</td>
<td>100 170</td>
<td>63</td>
</tr>
<tr>
<td>Nutrocellulose (13.35% N)</td>
<td>38.0</td>
<td>15.0</td>
<td>80 140</td>
<td>64a</td>
</tr>
<tr>
<td>Collodium Cotton</td>
<td></td>
<td></td>
<td>70 140</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 48. Initial second order rates of hydrolysis of nitrate esters [67]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$k_{2}$</th>
<th>$k_{1}$ ^1</th>
<th>$k_{2}$ ^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl nitrate</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
<td>10 ^-3</td>
</tr>
<tr>
<td>Nitroethyl nitrate</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
<td>10 ^-3</td>
</tr>
<tr>
<td>n-propyl nitrate</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
<td>10 ^-3</td>
</tr>
<tr>
<td>n-butyl nitrate</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
<td>10 ^-3</td>
</tr>
<tr>
<td>iso-butyl nitrate</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
<td>10 ^-3</td>
</tr>
<tr>
<td>Ethylene glycol mono-nitrate</td>
<td>10 ^-8</td>
<td>10 ^-7</td>
<td>10 ^-6</td>
</tr>
<tr>
<td>Ethylene glycol dinitrate</td>
<td>10 ^-8</td>
<td>10 ^-7</td>
<td>10 ^-6</td>
</tr>
<tr>
<td>1,3-Propane dinitrate</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>1,4-Butane dinitrate</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>DGN</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>Triethylene glycol diminate (TGGDN)</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>1,2-Propane dinitrate</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>1,3-Butane dinitrate</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>2,3-Butane dinitrate</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>Methyl (nitrate (trimethyl)methylmethane trinitrate)</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>1,3-Glycerol dinitrate</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>1,2-Glycerol mono-metate</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>2,3-Glycerol mono-metate</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>Nitro-n-butyl glycerol trinitrate</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
<tr>
<td>PFTN</td>
<td>10 ^-6</td>
<td>10 ^-5</td>
<td>10 ^-4</td>
</tr>
</tbody>
</table>

Lysis (compare the rate of n-propyl and iso-butyl nitrates, nitroglycerine and metriol trinitrate).

The recent novel use of nitrate esters (in addition to their primary role as constituents of high explosives and propellants) is also directed towards the improvement of high explosives and propellants, for example isopropyl nitrate (p. 306). Curne [68, 69] suggested the addition of polyethylene glycol nitrate and polypropylene nitrate as an addition to liquid fuel. Currently experiments are being carried out in Brazil on adding a small proportion (ca. 3%) of nitroglycerine to ethanol used as engine fuel (p. 299).

**BIOLICAL ACTION OF NITRATE ESTERS**

According to Von Detttingen [70] nitrate esters oxidize haemoglobin to methaemoglobin and, by depression of the muscles in the vascular walls, cause a peripheral vasodilatation resulting in lower systolic blood pressure, and increased pulse and respiratory rates. The maximum permitted concentration in working places differs for different nitrate esters: a typical example is nitroglycerine with a maximum permitted concentration of 1.5 mg/m^3.

**GLYCEROL TRINITRATE (NITROGLYCERINE) (Vol. II, p. 84))

### Setting Point

Some new data have appeared on the physical properties of nitroglycerine. Such is the determination of the setting point by Andreou and Bezpalov [71] on highly pure nitroglycerine. Nitroglycerine was purified by molecular distillation at 40-50°C under pressure of 10^-4 10^-5 Torr. After two or three distillations the setting point +13.1 was found. The authors considered this method for the purification of nitroglycerine to be the most efficient and the safest.

However Meyer [72, 73] gives slightly higher setting points for nitroglycerine:

- +13.2 [72] and +13.2-13.5 [73] for stable modification,
- +2.2 [72] and +1.9-2.2 [73] for labile modification.

### Vapour Pressure (Vol. II, p. 43)

The data on vapour pressure of nitroglycerine were collected by Meyer [72, 73] as being:

- 0.00033 millibar at 20°C
  - 0.0097
  - 0.13
  - 0.31
Absorption Spectra (Vol. II, p. 45)

The shoulder on the band of asymmetrical and symmetrical vibrations is due to the rotational isomerism [4–7]. Also it should be attributed to the fact that nitroglycerine contains both primary and secondary nitrate groups which according to T. Urbański and Witanowski [5] give different frequencies of asymmetric vibrations (p. 281).

Chemical Properties and Stability (Vol. II, pp. 46–47)

Thermal decomposition of nitroglycerine (and other similar nitrate esters) has been studied intensively by Soviet Union authors and their work has been described in collective volumes [61, 62] and the monograph by Andreev [60].

Here are the main conclusions of some of these important works as presented by Andreev and Bezaplov [71, 74]. They examined the action of water (at 80°, 100° and 120°C) and nitric acid (at 100°C).

Figure 37 shows the decomposition of nitroglycerine in the presence of 0.03% of either nitric acid or water or both, as compared with pure nitroglycerine. The decomposition was recorded by the pressure which developed inside the closed vessel. The strongest action was produced by nitric acid alone, less active was pure water and still less active nitric acid with water. The authors explain it in terms of different rates of hydrolysis and oxidation–reduction processes.

Larger quantities of nitric acid (0.13–1.5%) with water produce a characteristic shape for the curve of decomposition – Fig. 38. It comprises three stages:

(a) induction period under constant pressure,
(b) rapid fall of pressure, due to the reactions between the products of hydrolysis,
(c) increased pressure due to decomposition and oxidation.

The practical conclusion drawn by the authors was that moist nitroglycerine may become dangerous in storage if it contains traces of acid, for example, from insufficient washing.

Svetlov [75] examined the thermal decomposition of pure nitroglycerine in the range of 80–140°C. Two stages have been found. The first is not influenced by the products of the reaction. This is followed by the second stage when the products of the decomposition greatly influence the rate of the reaction. This is presented in Fig. 39. The value of log Δp/Δτ is greatly influenced by δ-density inside the container of the sample.
Gorbunov and Svetlov [76] confirmed these findings for the temperature range 80–140°C. The energy of activation depends on the range of temperatures: at 80–140°C and 100–140°C it was found to be 28 kcal/mol and 32 kcal/mol. As previously pointed out (p. 293) the energy of activation is greatly influenced by the temperature range of experiments. Thus Wenograd [77] found value $E = 21.8$ kcal/mol for nitroglycerine at temperatures 300–1000°C.

Gorbunov and Svetlov [76] also examined the role of water in the decomposition of nitroglycerine. Thus water has a very strong influence particularly at higher temperatures, whereas nitric acid increases the rate of decomposition at lower temperatures. As a consequence Gorbunov [78] determined the solubility of water in nitroglycerine at 20–90°C. It varies from 0.26% at 20°C to 0.97% (weight %) at 120°C. The solubility increases when nitroglycerine contains some (0.3–0.6%) nitric acid.

As already reported, Fraser and Paul examined nitrate esters, among them nitroglycerine, by mass spectrometry [159].

Recently Caire-Maurisier and Tranchant [160] examined thermal decomposition of nitroglycerine at 110°C using NMR, infra red and mass spectrometry and gas chromatography techniques. Mass spectrometry fragmentation suggested the formation of such fragments as: $\text{N}_2^+$, $\text{NO}_2^+$, $\text{NO}_3^-$, $\text{CO}^+$, $\text{CO}_2^+$, $\text{CH}_2\text{O}^+$, $\text{CH}_2\text{ONO}_2^+$, $\text{CH}_2\text{CHO}^+$, $\text{CHO}^-$, $\text{CH}_3\text{ONO}_2^+$ and fragments with a nitrite ester group, for example $\text{CHONO}^-$, $\text{CH}\text{NO}_2^+$, $\text{CHO}^-$, $\text{CH}_2\text{ONO}_2^+$, $\text{CHONO}^-$, $\text{CH}_2\text{ONO}_2^+$.

**Sensitivity to Impact**

Bowden and Yoffe [79, 80] pointed out the role of small trapped gas bubbles in the sensitivity of both liquid and solid explosives. The adiabatic compression of small trapped gas bubbles creates 'hot spots' manifested by high temperature. Also friction occurs at the surface of the containing walls, on grit particles or between the crystals of explosives and forms an additional factor governing the sensitivity of explosives to impact.

This was confirmed by a number of authors, their work has been collected in monographs by Afanasyev and Bobolev [81] and Dubovik and Bobolev [82] and in the paper by Coley and Field [83]. The collapse of air bubbles is shown to lead to an increase of sensitivity of liquid explosives by:

(a) local increase of the deflagration velocity and
(b) generating a pressure pulse which is capable of producing hot spots.

This explains the data on the high sensitivity to impact of liquid nitroglycerine and relatively low sensitivity of solid nitroglycerine (Vol. II, p. 53).

The air bubbles produce a type of micro-Munroe jet oriented in the direction of the shock.

**Burning of Nitroglycerine**

Nitroglycerine burns readily in open vessels under atmospheric pressure. When confined it burns more readily under reduced pressure, for example 0.5 atm. When confined in a tube nitroglycerine burns under atmospheric pressure if the diameter is larger than 0.5 mm. The rate of burning at the critical diameter of 0.5 cm is 0.14 cm/sec. [60]. Andreev and Bezpalov [84] indicated that the critical diameter of burning of nitroglycerine under pressure within the range 20–100 atm is still reduced. They pointed out that three diameters exist:

- $d_1$ – the smallest which allows normal burning,
- $d_2$ – the largest which allows normal burning, beyond which extinguishing can occur due to turbulent phenomena and heat losses,
- $d_3$ – the increase of that diameter gives normal burning.

Under atmospheric pressure the diameters $d_1$, $d_2$ and $d_3$ are 0.5, 2.6 and 7.5 mm respectively.

The increase of viscosity of nitroglycerine by dissolving nitrocellulose reduces the ability of nitroglycerine to burn under turbulent conditions and reduces the critical diameter. The same author gave critical diameters of:

<table>
<thead>
<tr>
<th>Ethylene glycol dinitrate</th>
<th>1.0 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGDN</td>
<td>5 mm</td>
</tr>
</tbody>
</table>

The ability of nitroglycerine to burn is now being utilized (on a large experimental scale) to improve the burning of ethanol being used as a fuel for car engines in Brasil. A small proportion (ca. 3%) is added to ethanol for this purpose, so far with a positive result [108].

**Explosion and Detonation of Nitroglycerine** (Vol. II, p. 51)

Andreiev [55] described his experiments on the thermal decomposition of nitroglycerine and the possible transformation into an explosion. The decomposition is speeded up by the reaction products. The rate of decomposition depends very much on the concentration of the products and much less on the temperature, in agreement with former findings of Roginskii (Vol. II, pp. 47–48).

Two different rates of detonation of nitroglycerine (explosion and detonation) (Vol. II, pp. 54–55) became the subject of experiments and discussion for example, Taylor [86], Häussler [87] and Soviet workers [88, 89]. It has also been shown that the reaction front in homogeneous liquid explosives becomes distorted under conditions close to failure [9, 91].

Coley and Field [83] discussed the LVD (low velocity detonation) in liquid explosives. According to the author of the present book the LVD should be called not the detonation, but the explosion (Vol. II, pp. 54–55). In order n
to create confusion the term LVD will be accepted. Coley and Fields [83] pointed out that LVD in liquid explosives systems is a stable reaction regime, readily initiated by shock pressures of a few kilobars with propagation velocity of the order of 2000 m/s. The thermodynamic theory of detonation is not applicable to this regime since the pressures involved are too small for direct shock heating of homogeneous explosive to be significant. According to Coley and Fields new experiments have shown that the presence of gas or vapour filled cavities within the explosive is an essential requirement for initiation and propagation of LVD [91–95].

In liquid explosives bubble size becomes an important factor – this was pointed out by Coley and Field [84]: small bubbles facilitate the transfer to LVD.

Zimmer [96] came to the conclusion that the LVD of nitroglycerine (1500–1600 m/s) could be manifested by a spiral mode of propagation. (It should be pointed out that T. Urbanski [97] expressed the view that non-homogeneous explosive mixtures can show a spiral way of detonation.) According to Zimmer the irregularities of the LVD are caused by the interaction of incident and reflection waves forming Mach waves under certain conditions. An analogy can be drawn between the spiral way of detonation of gas-mixtures [98–102] and spiral way of detonation of solid–liquid systems.

The critical diameter in a steel tube is 24 mm according to Meyer [72, 73].

Specifications for glycerine and nitroglycerine are given in Chapter XI on the manufacture of nitroglycerine.

GLYCEROL DINITRATES (‘DINITROGLYCERINE’) AND DERIVATIVES

‘Dinitroglycerine’ is a common impurity present in nitroglycerine. Most frequently it is glycerol 1,3-dinitrate. 1,2-Isomer is usually present in negligible quantity. Krasiejko [104] isolated the dinitrates by TLC and spectrometrically determined the nitrates obtained by hydrolysis of dinitrate. (The chromatography of nitroglycerine has been described in a few papers prior to the work of Krasiejko [105–107].)

Glycerol dinitrate does not currently have a practical application.

**Glycerol nitrolactate Dinitrate (VI) [72, 73]**

\[
\begin{align*}
\text{ONO}_2 & \quad \text{ONO}_2 \\
\text{CH}_3 & \quad \text{CH}_2\text{COOCH}_2 & \quad \text{CH}_2\text{CH}_2\text{ONO}_2
\end{align*}
\]

**VI**

This is an oily substance of density 1.47 and ignition temperature 190°C obtained by the nitration of glycerol mono lactate. It is a good gelatinizer of nitrocellulose.

**Glycerol 2,4-Dinitrophenylether (VII) and Trinitrophenylether (VIII) Dinitrates [72, 73]**

**VII**

\[
\begin{align*}
\text{NO}_2 & \quad \text{NO}_2 \\
\text{CH}_3 & \quad \text{O} & \quad \text{CH}_2\text{ONO}_2
\end{align*}
\]

**VIII**

\[
\begin{align*}
\text{NO}_2 & \quad \text{NO}_2 \\
\text{CH}_3 & \quad \text{O} & \quad \text{CH}_2\text{ONO}_2
\end{align*}
\]

Here are some pertinent data on the properties of the substances:

<table>
<thead>
<tr>
<th></th>
<th>VII</th>
<th>VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ignition temp.</td>
<td>205–210°C</td>
<td>200–205°C</td>
</tr>
<tr>
<td>Lead block</td>
<td>320 cm³</td>
<td>420 cm³</td>
</tr>
<tr>
<td>Sensitivity to impact</td>
<td>0.8 kpm</td>
<td>0.4 kpm</td>
</tr>
<tr>
<td>Gelatinization of nitrocellulose</td>
<td>poor</td>
<td>none</td>
</tr>
</tbody>
</table>

Both compounds VII and VIII can be obtained by the nitration of o-nitrophenylglycerol ether and phenyl glycerol ether respectively.

**Hexanitrodiphenylglycerol Mononitrate (IX) [72, 73]**

\[
\begin{align*}
\text{NO}_2 & \quad \text{NO}_2 \\
\text{CH}_3 & \quad \text{O} & \quad \text{CH}_2\text{ONO}_2
\end{align*}
\]

**IX**

\[
\begin{align*}
\text{NO}_2 & \quad \text{NO}_2 \\
\text{CH}_3 & \quad \text{O} & \quad \text{CH}_2\text{ONO}_2
\end{align*}
\]

m.p. 160–175°C

The wide range of melting temperatures indicates the decomposition of the substance during heating. The substance gives lead block test of 355 cm³. It is much less sensitive to impact than VII and VIII due to the presence of only one O-nitro group. It was obtained by dissolving glyceryl diphenyl in nitric acid followed by mixing the solution with nitric–sulphuric acid.
Mixed Esters of Glycerol

Among esters of glycerol with nitric and organic acids the most important appears to be Glycerol Acetate Dinitrate (X) described by Meyer [72, 73]

\[
\begin{align*}
\text{CH}_3\text{ONO}_2, \\
\mid \\
\text{CHOCOCH}.
\end{align*}
\]

\[
\text{CH}_2\text{ONO}_2, \\

X
\]

This is an oily substance of density 1.42 with ignition temperature 170–180°C. It yields lead block test 200 cm³. It was prepared by nitration of acetyl-glycerol with mixed acid rich with nitric acid.

GLYCOL NITRATES

Ethylene Glycerol Mononitrate (2-Nitroethanol) (Vol. II, p. 142)

Glycol mononitrate has aroused a certain amount of interest. Twist and Baughan [109] examined the vapour pressure of the solution of this substance, and a number of other nitrate esters, and found the deviations from Raoult laws to be of the same order as those observed by Chédin and Vandoni for nitrocellulose [110]. Prior to this work Marams and Zelinski [111] prepared a number of mixed esters of the type XI where R is unsaturated acyl apt to polymerize and thus to give combustible polymers.

\[
\begin{align*}
\text{CH}_3\text{ONO}_2, \\
\mid \\
\text{CH}_2\text{OR} \\
\text{CH}_3 \text{CH} \equiv \text{CHCO} \\
\text{CH}_2 \equiv \text{CCO} \\
\text{CH}_3 \text{CH} \equiv \text{CHCO} \\
\text{X}
\end{align*}
\]

They acted on 2-nitroethanol with chlorides of acrylic (a), methacrylic (b) and crotonic (c) acids in the presence of cuprous chloride as a polymerization inhibitor. The radical polymerization was initiated by benzoyl peroxide in nitrogen atmosphere. It lasted 20 min at 100°C. In the absence of a catalyst polymerization occurred at 20°C in the course of a few days. This observation is in agreement with the finding reported in Vol. II, p. 19 that nitrate esters can catalyse polymerization reaction, contrary to C-nitro compounds (Chapter IV).

Ethylene Glycerol Dinitrate (‘Nitroglycerol’) (Vol. II, p. 142)

Relatively less attention is now paid to ethylene glycol dinitrate. It is currently used in mixture with nitroglycerine for low freezing dynamites but some mining explosives, used in countries with harsh winters, contain nitroglycerol alone.

Kondrikov [112] rationalized thermal decomposition of ethylene glycol dinitrate by diagram (13):

\[
\begin{align*}
\text{CH}_3\text{ONO}_2 \overset{k_1}{\longrightarrow} \text{CH}_2\text{O} \overset{k_2}{\longrightarrow} 2\text{CH}_3\text{O} + \text{NO}_2 \\
\text{CH}_3\text{ONO}_2 \\
\text{CH}_3\text{O} \overset{k_2}{\longrightarrow} 2\text{CH}_3\text{O} + \text{NO}_2
\end{align*}
\]

Ethylene glycol dinitrate is more toxic than nitroglycerine because of its higher volatility. According to Meyer [72, 73] the maximum permitted concentration in a work place is 1.5–1.6 mg/m³.

Diethylene Glycerol Dinitrate (Vol. II, p. 149)

Diethylene glycol dinitrate – DGDN has currently become the most important (next to nitroglycerine and nitroglycol) C-nitro compound, much in use in ‘double base’ propellants. The great advantage of DGDN is its relatively low sensitivity to impact and subsequently safer handling than nitroglycerine and good solubility of nitrocellulose. The disadvantage is in the danger produced by spent acid (Vol. II, pp. 152–153).

Svetlov [113] examined thermal decomposition of DGDN in the liquid phase in the temperature range 60–150°C. He calculated the energy of activation — see Table 47 (p. 294).

Lurge and Svetlov [114] examined the decomposition of DGDN in the presence of oxygen, NO₂ and NO, H₂ NO₃ and oxalic acid at 80–120°C and found that nitric and oxalic acids can increase the rate of decomposition up to one hundred times. Oxygen also increases the rate of decomposition but to a much smaller extent. The first stage of the reaction consists in binding oxygen, probably due to the formation of peroxides. The latter decompose at a later stage.

The specification for diethylene glycol for nitration is given in Chapter XI.

Triethylene Glycerol Dinitrate (Vol. II, p. 154)

This substance was used (together with diethylene glycol dinitrate) in Germany during World War II for making double base propellants. It is less volatile than diglycol dinitrate but more soluble in spent acid (Vol. II, p. 155).
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

The specification for triethylene glycol for nitration is given in Chapter XI.

**Butine-2-diol-1,4 Dinitrate**

\[ \text{O}_2\text{NOCH}_2\text{C} \equiv \text{CCH}_4\text{ONO}_2 \]

XII

This substance was obtained by T. Urbaniński and Tarantowicz [115]. The aim was to produce an explosive of greater power considering that the acetylenic bond increases exothermic properties of the substance. In lead block it gave a better performance (385 cm³) than tetryl and ethylene glycol mononitrate.

It is an oily substance of density (at 20°C) 1.408. On a hot plate, temperature 245–380°C, it gave a violent explosion similar to that of nitroglycerine. Below 245°C it evaporated and above 380°C took on a spheroidal shape and burned quietly. It is more sensitive to impact than nitroglycerine, and is a good solvent for nitrocellulose.

The substance gives a negative heat test (Abel test): at 80°C potassium iodide-starch paper was coloured after 3 min.

The diol dinitrate (XII) was obtained in a standard way by nitrating the acid mixture composed of 40% nitric and 60% sulphuric acid at 18–22°C. The yield was 70–75% of the theoretical.

---

**NITRATE ESTERS OF MONOHYDROXYLIC ALCOHOLS**

(Vol. II, p. 160)

The main interest in nitrate esters of monohydroxylic alcohols lies in their application as rocket fuels. Subsequently a thermal decomposition of nitrate esters is examined. Kondrakov [112] gave the following diagram (14) of the thermal decomposition of nitrate esters of a general formula \( \text{RCH}_2\text{ONO}_2 \):

\[
\begin{align*}
\text{RCH}_2\text{ONO}_2 & \rightarrow \text{RCH}_2\text{O} + \text{NO}_2 \\
\text{RCH}_2\text{O} & \rightarrow \text{R} + \text{CH}_2\text{O} \\
\text{CH}_2\text{O} + \text{NO}_2 & \rightarrow \text{NO}, \text{CO}, \text{CO}_2, \text{H}_2\text{O} \\
\text{RCH}_2\text{O} + \text{NO} & \rightarrow \text{RCH}_2\text{ONO} \\
\text{RCH}_2\text{O} + \text{NO} & \rightarrow \text{RCHO} + \text{NOH} \\
2\text{NOH} & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}
\end{align*}
\]

(a) (b) (c) (d) (e) (f)

A few other schemes of thermal decomposition are given with the description of particular nitrate esters.

All the mono-nitrate esters give a colour reaction with tetramethylp-phenylene-diamine due to Wurster cation [13–15, 22a]. The colour remains for several days.

---

**NITRATE ESTERS (O-NITRO COMPOUNDS)**

With regard to the nitration of alcohols attention should be drawn to the work of Ermenko [140] who pointed out the role of undissociated nitric acid in the O-nitration mechanism.

**Methyl Nitrate** (Vol. II, p. 160)

Some properties of methyl nitrate, such as the thermal decomposition and explosive properties are given in Vol. II. Some additional data are given by Meyer [72, 73]:

- boiling point 65°C
- density 1.217
- heat of explosion 1462 kcal/kg
- volume of gases 873 l/kg
- critical diameter in a steel tube 18 mm

Methyl nitrate was found to be present in the products of the decomposition of azomethane \((\text{CH}_3\text{–N=N–CH}_3)\) when the latter substance was subjected to ultraviolet irradiation [116]. This was due to an intermediate formation of \(\text{CH}_3\text{O}_2\) radical which reacted with NO to yield the nitrate ester:

\[ \text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2. \] (15)

**Ethyl Nitrate** (C\(_2\)H\(_5\)ONO\(_2\)) (Vol. II, p. 163)

Ethyl nitrate is currently an important component of liquid rocket fuel. In that respect considerable work is being done to elucidate the mechanism of thermal decomposition by Pollard, H. S. Marshall and Pedier [151]. Some fragments of their mechanism are as follows (16):

\[
\begin{align*}
\text{C}_2\text{H}_6\text{NO}_2 & \rightarrow \text{C}_2\text{H}_4\text{O} + \text{NO}_2 \\
\text{C}_2\text{H}_6\text{O} & \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} \\
\text{C}_2\text{H}_4\text{O} & \rightarrow \text{HCHO} + \text{CH}_3, \text{etc.}
\end{align*}
\] (16)

Considering the formation of a number of simple molecules and free radicals, such as \(\text{CH}_3\), \(\text{CH}_3\text{O}^\cdot\), \(\text{NO}, \text{NO}_2, \text{CO}, \text{CO}_2\) several less defined reactions can take place, for example, the formation of nitrate esters [2]:

\[
\begin{align*}
\text{C}_2\text{H}_4\text{O}^\cdot + \text{NO} & \rightarrow \text{C}_2\text{H}_4\text{ONO}_2 \\
\text{CH}_3^+ + \text{O} & \rightarrow \text{CH}_3\text{O}^\cdot. \\
\text{CH}_3\text{O}^\cdot + \text{NO} & \rightarrow \text{CH}_3\text{ONO}_2, \text{etc.}
\end{align*}
\] (17)

Nitrate esters are marked by their relatively low stability (p. 318). Meyer [72, 73] gives some additional data on the properties of ethyl nitrate:

- melting point −102°C
Acetaldehyde, nitrogen dioxide and nitromethane are main products of the decomposition. In the presence of oxygen ethyl radicals yield formaldehyde. Acetaldehyde is very reactive and by abstraction of hydrogen yields acetylene which is the principal source of CO and CO₂:

\[
\text{CH}_3\text{CHO} \rightarrow \text{CH}_2=\text{CHO} + \text{CO} \\
\text{CH}_3\text{CO} + \text{NO}_2 \rightarrow \text{CH}_2=\text{CHO} + \text{CO}_2 + \text{NO}.
\]  

(19)

POLYHYDROXYLIC ALCOHOL ESTERS (Vol. II, p. 166)

Butane-1,2,4-triol Trinitrate (Vol. II, p. 166)

Meyer [72, 73] gave some data on the properties of the substance, such as:

- freezing point: \(-27^\circ\text{C}\)
- density: 1.52
- oxygen balance: \(-16.6\%\)
- heat of explosion: 1420–1470 kcal/kg.

1,2,4-Butanetriol is nitrated to trinitrate with a nitric–sulphuric acid mixture. The nitrated product shows good stability. It is less volatile than nitroglycerine and according to Meyer is in use for tropic-proof double base powder.

Erythritol Tetranitrate, Erythrol Tetranitrate (Vol. II, p. 100)

Meyer [72, 73] gives some data:

- melting point: 61.5°C
- deflagration point: 154–160°C with a violent explosion
- density: 1.6
- heat of explosion: 1443 kcal/kg
- volume of gases: 704 l/kg.

It has an intense magenta colour with tetramethyl-p-phenylene-diamine due to Wurster cation [13–17].

Pentitol Pentanitrate (Vol. II, p. 168)

D-Xylitol pentanitrate with tetramethyl-p-phenylene-diamine (TMPD) gives a blue colour due to the formation of Wurster cation after which another charge-transfer complex is formed by 2 moles of xylitol pentanitrate and 1 mole of TMPD dication formed from Wurster cation [13–17].

D-Mannitol Pentanitrate (Vol. II, p. 170)

D-Mannitol-1,2,3,5,6-pentanitrate (m.p. 81–82°C) is prepared by heating
hexanitrate of mannitol with pyridine [120]. Denitration occurs with the evolution of nitrogen dioxide. D-Mannitol pentanitrate reacts with TMPD in much the same way as D-Xylitol pentanitrate forming a charge-transfer complex of 2 moles of mannitol pentanitrate and 1 mole of the dication [15].

D-Mannitol Hexanitrate (Vol. II, p. 168)

According to Elias and Hayward [123] the nitrations of D-mannitol to hexanitrate can be carried out with N₂O₅ vapour at 0 ± 2°C under reduced pressure. After two hours the hexanitrate was formed with 100% yield.

The charge-transfer between D-mannitol hexanitrate and TMPD is best presented on Fig. 40 according to T. Urbański et al. [15]. Curve I shows a CT colourless complex at ca. 1030 nm which disappears after 5 min, and two maxima of Wurster cation (570 and 620 nm) appear. The intensity of the latter increased in the course of 15 minutes (curve II).

![Figure 40: General shape of electronic spectra of hexanitrate of D-mannitol and tetramethyl-4-phenylenediamine charge transfer phenomenon.](image)

After 2 hours both maxima vanished and a new maximum at 450 nm appeared (curve III). The yellow coloured complex is formed from 1 mole of mannitol hexanitrate and 1 mole of TMPD dication. The dication is formed as the result of the disproportionation between the Wurster cation and TMPD:

NITRATE ESTERS (3-NITRO COMPOUNDS) 309

The stereochemistry of the complex is rationalized by diagram V (p. 285). It was suggested that a six-member chain of mannitol hexanitrate was coined into a pseudo-ring. It is not surprising if one considers that long chain organic substances in solution have a tendency to be coiled. This is based on thermodynamical analysis, dipole measurements etc. [124].

Lurye and Svetlov [125] examined the thermal decomposition of mannitol hexanitrate in the temperature range 80–140°C. They came to the conclusion that the decomposition of molten hexanitrate occurred in two (at least) stages. The first stage is manifested by splitting off nitrogen dioxide. This stage follows the equation of Arrhenius (Table 47). After that secondary reactions occur – mainly of oxidation accompanied by hydrolysis with formed water.

Mass spectrometry showed the decomposition occurs according to XIV [159]

![Diagram V: Stereochemistry of the complex.](image)

Meyer [72, 73] gives some data on the explosive properties of D-mannitol hexanitrate:

- Heat of detonation: 1420 kcal/kg
- Volume of gases: 694 l/kg
- Deflagration point: 185°C

**Dulcitol (D- or L-galactitol) Hexanitrate and D-Sorbitol hexanitrate**

(Vol. II, pp. 171, 172)

Both substances can be obtained with 85 and 94% yield respectively by
nitrating dulcitol and D-sorbitol with N₂O₅ vapours under reduced pressure at 0 ± 2°C [123].

Both substances form charge-transfer complexes with tetramethyl-p-phenylenediamine in much the same way as D-mannitol hexanitrate [14, 15, 22a].

**PENTAERYTHRITOL TETRANITRATE (PETN) (Vol. II, p. 175)**

Some new data on the properties of PETN have been reported by Meyer [72, 73]:

| melting enthalpy | 36.4 kcal/kg |
| specific heat   | 0.26 kcal/kg |
| density         | 1.76         |

An important practical problem is how to obtain PETN in a crystalline shape which would allow an easy flow to a high bulk density, that is, greater than 1.1–1.2 g/cm³. The needle habit gives the lowest bulk density which can be used for certain purposes.

A fairly wide range of particle sizes can be obtained by adding water to an acetone solution of PETN and a bulk density of 1.1–1.2 can be reached. It is known that various sizes of crystals make the better filling of a container possible and can give a higher density.

Duncan [126] described experiments on crystal size and shape of PETN by its recrystallization.

To produce the substance having a high specific surface area S₀ = 10 to 20 x 10³ cm²/g suitable for detonators a 'shock crystallization' was used. Pure PETN was dissolved in acetone (1:5) and the solution dropped into aqueous ethanol at 0°C, then 30°C. The resulting crystals are much different in sizes (0.5–16 μ) and irregular shapes from spheres to needles. A modification of the method can be used by introducing a 10% solution of pure PETN in acetone–ethanol into ethanol–acetone (1:2) cooled to −20°C.

Crystallization from DMSO produces crystals which are too large. On the contrary, crystallization by spraying saturated acetone solution into an air tunnel gives very fine spherical particles when the tunnel walls are struck.

Duncan also gives a new table of the solubility of PETN in some solvents (Table 49).

The size of crystals increases by keeping them at 90–120°C for several hours (e.g. 20–30 hours).

Chromatography (TLC) showed very small spots of hexanitrate of dipentaerythritol (DPEHN), and in some cases octanitrate of tripentaerythritol (TPEON) and pentaerythritol trinitrate.

T. Urbański [127] suggested recrystallization to add a protective colloid such as an acetone solution of nitrocellulose (low viscosity grade colodium cotton).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>0</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.46</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.60</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0.096</td>
<td>0.108</td>
<td>0.118</td>
<td>0.121</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>1.5</td>
<td>4.1</td>
<td>11.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>0.18</td>
<td>0.27</td>
<td>0.40</td>
<td>0.58</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Methyl-1-propanol</td>
<td>0.07</td>
<td>0.195</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitromethane</td>
<td>3.34</td>
<td>8.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>13.0</td>
<td>17.0</td>
<td>22.0</td>
<td>31.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-Ethoxyethyl acetate</td>
<td>1.5</td>
<td>4.1</td>
<td>7.6</td>
<td>11.2</td>
<td>14.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PETN was examined by mass-spectroscopy [128]: electron impact gave two fragments: 76 and 46.

Field ionization fragments: 194, 76, 74 are depicted by scheme XIV.

**Thermodynamic Properties and Thermal Decomposition of PETN**

Dinegar and Stammler [129] determined enthalpies connected with the volatility of PETN. The enthalpies of sublimation and of vaporization were:

- 35 ± 3 kcal/mol and
- 19 ± 2 kcal/mol respectively.

A considerable number of papers have been dedicated to the thermal decomposition of PETN. They were reviewed by Andreev [71]. He quoted the work of Robertson [130] who examined the decomposition of PETN in the temperature range: 161–233°C, the energy of activation was

\[ E = 47 \text{ kcal/mol, } \log B = 19.8. \]

For a 5% solution of PETN in dicyclohexylphthalate at 171–238°C the values of E and B were:

\[ E = 39.5 \text{ kcal/mol, } \log B = 16.1. \]

Robertson analysed gaseous products while keeping PETN for 2 min at 210°C. He found (in mol %): 0.51 NO₂, 2.11 NO, 0.42 N₂O, 0.07 N₂, 0.09 H₂, 0.93 CO, 0.28 CO₂ and formaldehyde and water.

He suggests that the first stage of the decomposition of PETN consists in splitting off NO₂, after which –CH₂O is removed as formaldehyde.
A different approach to the thermal decomposition of PETN was given by T. Urbaniski [131-133]. The shape of the curve of the induction time against the temperature is given in Fig. 41, much the same as in Vol. I, Fig. 13, p. 50 for nitroglycerine.

\[ E = 22.4 \text{kcal/mol for the temperatures } 240-310^\circ C \]
\[ E = 4.5 \text{kcal/mol for the temperatures } 460-790^\circ C. \]

Wenograd [77] in the temperature range 400-1000°C established the energy of activation as \( E = 20.4 \text{kcal/mol}. \) Evidently the energy decreases with the increase in temperature.

Andreev and Kaidynov [134] published a review on the thermal decomposition of PETN and a description of their own results. Their data for activation energy are given in Table 47. They confirmed the results of T. Urbaniski and co-workers (Vol. II, pp. 181-183) and similarly of Tongutti [135] and Bourjol [136]. In all experiments it was shown that decomposition in the liquid phase, that is, the molten system, engenders faster decomposition than that of the solid phase.

According to the author of the present book lowering of the stability has the result that on melting the substance passes to a higher energy level with an increased entropy.

Differential Scanning Calorimeter (DSC) was used by Rogers and Dinegar [165] in combination with X-ray and microscopy to find the reason for anomalous behaviour in the heat of fusion of PETN crystallized by different methods. Microscopy revealed the existence of at least three crystal habits of PETN: (1) 'tetragonal', (2) needle, (3) irregular plates. Their heats of fusion \( \Delta H_f \) were:

- (1) 36.5-37.4 cal/g
- (2) 36.5-37.7 cal/g
- (3) 31.7-33.2 cal/g

\[ \text{FIG. 41. Behaviour of PETN at high temperatures according to T. Urbaniski [131-133]. Induction period } \tau \text{ is given against the temperature. Curve } \text{B corresponds to spheroidal shape of the molten substance.} \]

Differences in heat of fusion was attributed to the lattice energy changes resulting from random inclusions within the lattice.

### Explosive Properties

An interesting finding was made by Institut Franco-Allemagne de Recherches de St. Louis [166] that the rate of detonation of PETN takes different values along different crystal axis:

- (001) 8424 m/s
- (110) 8887 m/s.

T. Urbaniski and Galas [137, 138] examined the rate of detonation of PETN with various liquids. The results with two liquids which do not dissolve PETN: water and glycerol are given in Table 50. The general trend of the change of the observed rate of detonation with the addition of a liquid is given in Fig. 42.

#### Table 50. Detonation of PETN with water and glycerol [137-138] in tubes 20/26 mm diameter, detonator No. 8 with 10 g PETN

<table>
<thead>
<tr>
<th>Proportion of liquid</th>
<th>Density ( \rho_l )</th>
<th>Rate of detonation ( V_0 ) at density ( \rho_l )</th>
<th>Rate of detonation ( V_T )</th>
<th>Difference ( V_0 - V_T )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.45</td>
<td>7275</td>
<td>7275</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1.45</td>
<td>7275</td>
<td>7275</td>
<td>195</td>
</tr>
<tr>
<td>10</td>
<td>1.45</td>
<td>7145</td>
<td>7200</td>
<td>635</td>
</tr>
<tr>
<td>20</td>
<td>1.45</td>
<td>7125</td>
<td>7250</td>
<td>920</td>
</tr>
<tr>
<td>30</td>
<td>1.44</td>
<td>6645</td>
<td>5530</td>
<td>1115</td>
</tr>
<tr>
<td><strong>Glycerol</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.40</td>
<td>7350</td>
<td>6880</td>
<td>425</td>
</tr>
<tr>
<td>10</td>
<td>1.40</td>
<td>7350</td>
<td>6080</td>
<td>1745</td>
</tr>
<tr>
<td>30</td>
<td>1.45</td>
<td>7675</td>
<td>5620</td>
<td>3055</td>
</tr>
<tr>
<td>35</td>
<td>1.45</td>
<td>7280</td>
<td>5250</td>
<td>2050</td>
</tr>
</tbody>
</table>

The observed rate of detonation of the explosive with the liquid was \( V_0 \) and the total density 1.45. By adding a liquid and keeping the same total density (density of the mixture) the real density of the explosive was lowered to \( \rho_l \) which at this density gives the rate of detonation \( V_T \). Hence \( V_0 - V_T \) is the increase in the rate of detonation by adding the liquid. This is fully discussed in Chapter XIII (Table 60).

Dinegar, Rochester, Horton and Johnson [145] examined the shock sensitivity of PETN and came to the conclusion that the nature of the gas in a small scale 'gap-test' influences the sensitivity of PETN. Thus He, Ar, N₂ and CO₂ have a desensitizing effect, whereas oxygen sensitized the compressed charges.
Nitration of Pentaerythritol (Vol. II, p. 185)

It is known that the nitration of pentaerythritol on an industrial scale is carried out mostly with nitric acid alone, without sulphuric acid. Therefore, it was necessary to establish the solubility of PETN in nitric acid of different concentrations and at different temperatures. Such data were given by Camera and Mauro [139] and are collected in Table 51. The same authors established the solubility of dipentaerythritol hexanitrate (Vol. II, p. 195) – Table 52.

TABLE 51. Solubility of PETN in nitric acid [139] in g of the substance in 100 g of the solution

<table>
<thead>
<tr>
<th>% HNO₃</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.018</td>
<td>0.041</td>
<td>0.109</td>
<td>0.352</td>
<td>0.645</td>
<td>0.880</td>
</tr>
<tr>
<td>65</td>
<td>0.036</td>
<td>0.113</td>
<td>0.322</td>
<td>0.778</td>
<td>1.010</td>
<td>1.300</td>
</tr>
<tr>
<td>70</td>
<td>0.075</td>
<td>0.134</td>
<td>0.302</td>
<td>0.845</td>
<td>1.170</td>
<td>2.240</td>
</tr>
<tr>
<td>75</td>
<td>0.069</td>
<td>0.124</td>
<td>0.265</td>
<td>0.557</td>
<td>1.340</td>
<td>2.650</td>
</tr>
<tr>
<td>80</td>
<td>0.106</td>
<td>0.195</td>
<td>0.335</td>
<td>0.650</td>
<td>1.291</td>
<td>2.775</td>
</tr>
<tr>
<td>85</td>
<td>0.190</td>
<td>0.329</td>
<td>0.585</td>
<td>1.056</td>
<td>1.957</td>
<td>3.849</td>
</tr>
<tr>
<td>90</td>
<td>0.441</td>
<td>0.762</td>
<td>1.318</td>
<td>2.314</td>
<td>4.036</td>
<td>7.156</td>
</tr>
<tr>
<td>95</td>
<td>1.060</td>
<td>1.825</td>
<td>3.023</td>
<td>4.822</td>
<td>8.090</td>
<td>12.609</td>
</tr>
</tbody>
</table>

Eremenko questioned this trend of the reactions particularly in view of the facts described in Chapter I that nitric acid still possessed the nitrating ability at a concentration where the presence of NO₃⁻ ions are excluded. With regards to O-nitration this was described by T. Urbanski and Haake [143]. By nitrating pentaerythritol and some ¹⁸O labelled alcohols, Eremenko came to the conclusion that molecular, undissociated electrolytically nitric acid can be an agent for O-nitration of alcohols. He depicted this in diagram – Fig. 43 (in weight percents) referred to O-nitration of pentaerythritol.

A summary of his conclusions, based on the analysis of the curves, is given here: region I limits the composition of the nitrating mixtures which transform...
pentaerythritol into PETN with 94–98% yield without the formation of esters of sulphuric acid as intermediates. In region II the formation of PETN goes through the acid sulphates. In III tetranitrate is formed only in 10–50% yield with side reaction of oxidation accompanied by violent evolution of nitrogen oxides. In region IV O-nitration does not occur.

ALC curve shows the limit of the detection of NO$_2^-$ ions and the small region limited by curve CD shows the complete dissociation of nitric acid into NO$_3^-$ [144] and Vol. I, Fig. 9, p. 25 (in mol %). One can see that pure O-nitration can occur in region I which is beyond the detectable NO$_2^-$ concentration.

Eventually Eremenko suggested the scheme of O-nitration (22):

\[
\text{ROH}^+ + \text{HONO}_2 \rightleftharpoons \text{ROH}^+ + \text{NO}_2^-(\text{fast})
\]

\[
\text{ROH}^+ + \text{HONO}_2 \rightleftharpoons \text{ROH}^+ + \text{HONO}_2^-(\text{slow})
\]

\[
\text{ROH}^+ + \text{HONO}_2 \rightleftharpoons \text{ROH}^+ + \text{HONO}_2^-(\text{slow})
\]

\[
\text{ROH}^+ + \text{HONO}_2 \rightleftharpoons \text{ROH}_2^+ + \text{HONO}_2^-(\text{fast})
\]

\[
\text{ROH}_2^+ + \text{HONO}_2 \rightleftharpoons \text{ROH}_2^+ + \text{HONO}_2^-(\text{slow})
\]

\[
\text{HONO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O} \cdot \text{HONO}_2(\text{fast})
\]

Proof of the accuracy of the scheme is also in the observed fact that the oxygen of nitrated alcohol remains in the nitrate. This was substantiated by nitrating alcohols labelled with $^{18}$O.

**METHOD OF PREPARATION OF PETRINO AND PEDN**

(according to [148] and [149])

Pentaerythritol (60 g) was dissolved at 5°C in a ca. 6 times larger quantity of sulphuric acid (67%). CH$_2$Cl$_2$ (ca. 50 parts) was added followed by the addition of the nitrating mixture composed of sulphuric acid (98%) (72 g) and nitric acid (96%) (232 g) at 5°C. After mixing for 75 min, water (1000 cm$^3$) was added. The organic phase was neutralized with 10% NaHCO$_3$, evaporated to dryness and the solid was extracted with ether to eliminate PETN which was not dissolved.

The solution was cooled to -60°C to eliminate the precipitated impurity. On evaporation the trinitrate - PETRINO (40 g) resulted. It contained some PETN and PEDN and was purified while removing PEDN by dissolving it in water.

The part insoluble in water was crystallized from CH$_2$Cl$_2$. Finally pure PETRINO was obtained by distillation under reduced pressure. Under 1 mmHg a fraction of 155–160°C was collected. Precaution should be taken: it can explode at 175°C. It has m.p. 27–28°C (Vol. II, p. 194).

The aqueous solution was evaporated to dryness and furnished PEDN.

Camer [149] draws attention to the fact that PETN in spent acid is readily subjected to hydrolysis leading to the formation of tri- and dinitrate of pentaerythritol at different temperatures (20 and 40°C) and concentration of nitric acid (70–90%).

He calculated the constants of equilibria:

\[
\frac{[\text{PE-Tri N}]}{[\text{PETN}]} \cdot \frac{[\text{HNO}_2]}{[\text{H}_2\text{O}]} = K_1
\]

\[
\frac{[\text{PE-Di N}]}{[\text{PE-Tri N}]} \cdot \frac{[\text{HNO}_2]}{[\text{H}_2\text{O}]} = K_2
\]

The values of $K_1$ and $K_2$ are given in Table 53.
TABLE 53

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$K_1$ 20$^\circ$C</th>
<th>$K_2$ 40$^\circ$C</th>
<th>$K_1$ 20$^\circ$C</th>
<th>$K_2$ 40$^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>% HNO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70%</td>
<td>0.996</td>
<td>1.362</td>
<td>0.608</td>
<td>0.726</td>
</tr>
<tr>
<td>80%</td>
<td>0.873</td>
<td>1.395</td>
<td>0.606</td>
<td>0.721</td>
</tr>
<tr>
<td>90%</td>
<td>0.950</td>
<td>1.396</td>
<td>0.749</td>
<td>0.838</td>
</tr>
</tbody>
</table>

The solubility of PETriN and PEDN in nitric acid of different concentrations is given in Table 54.

TABLE 54. Solubility of tri and dinitrates of pentaerythritol according to Camera [149]

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Temperature $^\circ$C</th>
<th>PETri N</th>
<th>PEDN</th>
<th>PETri N</th>
<th>PEDN</th>
</tr>
</thead>
<tbody>
<tr>
<td>% HNO$_3$</td>
<td></td>
<td>20</td>
<td>40</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>60</td>
<td>0.032</td>
<td>0.040</td>
<td>0.179</td>
<td>0.265</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>0.099</td>
<td>0.102</td>
<td>0.209</td>
<td>0.307</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>0.094</td>
<td>0.079</td>
<td>0.511</td>
<td>0.486</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>0.085</td>
<td>0.054</td>
<td>0.456</td>
<td>0.337</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.103</td>
<td>0.049</td>
<td>0.441</td>
<td>0.245</td>
<td></td>
</tr>
<tr>
<td>85</td>
<td>0.160</td>
<td>0.054</td>
<td>0.629</td>
<td>0.246</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>0.283</td>
<td>0.060</td>
<td>1.081</td>
<td>0.267</td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>0.376</td>
<td>0.038</td>
<td>1.144</td>
<td>0.157</td>
<td></td>
</tr>
</tbody>
</table>

NITRITE ESTERS (O-NITROSO COMPOUNDS)

Nitrite esters (O-nitroso compounds) are usually not discussed as explosives. They are relatively unstable compounds but may possess some significance as products of the decomposition of O-nitro compounds according to Gray [150] and Pollard et al. [151].

Chemical and physico-chemical properties of O-nitroso compounds have been extensively studied by Steacie since 1934 [152] and described in a monograph [153].

An important work on the chemical stability and decomposition of ethylene dinitrite and glycerol trinitrate was done by Kondr frontline [154]. Their activation energies were found to be:

- at 170–190$^\circ$C, $E = 35.6$ kcal/mol, log $B = 13.8$
- and at 143–160$^\circ$C, $E = 41.6$ kcal/mol, log $B = 17.8$ respectively.

The decompositions of the former can be depicted by diagram:

\[
\begin{align*}
\text{CH}_2\text{ONO} & \quad \longrightarrow \quad 2\text{CH}_2\text{O} + 2\text{NO} \\
\text{CH}_2\text{ONO} & \quad \longrightarrow \quad \text{(24)}
\end{align*}
\]

ESTERS OF OXY-ACIDS OF CHLORINE (Vol. II, p. 447)

Esters of oxy-acids of chlorine have not received any practical application owing to their very high sensitivity to impact and friction, but they are interesting from a theoretical point of view.

A few papers have appeared on the use of alkyl perchlorates, especially methyl perchlorate as alkylating (particularly methylyating) agents [162]. Kevill et al. [163] established that methyl perchlorate in acetone-toluene is a much weaker methylaing agent than for example trifluoromethanesulphonate.

Geminal Diperchlorates

Baum [164] obtained geminal diperchlorates by reacting carbonyl compounds with perchloric acid in halogenated hydrocarbons: for example acetic and perchloric acid in chloroform yielded an oily product within a few minutes. This was 2,2-diperchloratopropene (CH$_3$)$_2$C(OClO$_2$)$_2$. It can be distilled: b.p. 52$^\circ$C/0.1 mmHg.

It is very hygroscopic. Differential thermal analysis shows one exotherm peak at 159$^\circ$C and second at 202$^\circ$C which ended in an explosion at 250$^\circ$C.

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CHAPTER 11

PRODUCTION OF NITRATE ESTERS
(Vol. II, pp. 62–125, 185)

NITROGLYCERINE (NG)

No fundamental progress on methods of the manufacture of NG can be re-
corded. The main efforts have been concentrated on the problem of increasing
the safety of the processes by using perfect automation with remote control
devices, avoiding immediate contact between personnel and dangerous parts of
the process and the reduction of the quantity of explosive in the working place.
All these requirements can be achieved with continuous methods, although
batch processes are still in use.

Continuous and semi-continuous methods are as described in Vol. II:

(1) Schmid (p. 99),
(2) Schmid-Meissner (p. 104),
(3) Raczyński (p. 106),
(4) Biazzi (p. 107),
(5) N.A.B. Injector Process (A.B. Gyttorp) (p. 114),
(6) Semi-continuous method of Jarek (p. 120).

Of the above methods 1, 2, 4 and 5 have been widely used in many countries.
A novel method (7) has been described and is known as:

(7) Hercules Tubular Nitrator described by McKinney [1] and in Encyclo-
pedia of Explosives [2].

Hercules Tubular Process

This description is based on that given in the Encyclopedia [2]. A continuous
stream of glycerine flows through a tubular path to a tubular reaction zone
where it meets a stream of precooled nitrating acid. The tubular reaction zone
is uncooled, the temperature is controlled by regulating the temperature of pre-
cooled nitric acid and also the proportion of nitric acid to glycerine. It is desir-
able to cool the mixture of nitrate ester and spent acid to facilitate the separa-
tion of the nitrated product.

The diagram of the system is presented in Fig. 44. Nitrating acid passes
through pump 1 to the cooler, and valves 2 to 6 and meets glycerine in the

counter current which enters through valve 3, pump 4 and valve 5 to the same
place 6.

Nitration starts in 6 and continues in the tubular nitrator before entering the
cooler and finally the separator. Valve 5 is a quick opening by-pass valve. In the
case of an emergency valve 5 is turned to stop the flow of glycerine to the
nitrator 6 switching through 7 to the glycerine container.

Figure 45 shows a diagram of the 'mixing tee' 6.

The nitrating acid in the Hercules Tubular Process is composed of 18–40% HNO₃, 45–70% H₂SO₄ and 11–17% H₂O. The preferred acid to glycerine ratio
is 10–12 parts of acid per one part of glycerine.
Stow [3] improved the method by introducing a centrifugal separator of nitroglycerine from the spent acid.

The method can be used to both: nitration of glycerine, glycerine—ethylene glycerol mixture, diethylene glycol or ethylene glycol.

_Biazzi Process (Vol. II, p. 107)_

The detailed description of the process given in Vol. II remains valid with a few additions described by Biasutti [4]. Figures 48 and 49 (Vol. II, pp. 108, 111) are still valid, and the main points which introduce some additional, novel information are given here.

Mixed acid and glycerine are stored externally in separate tanks and are transferred by means of centrifugal and gear pumps to small feed tanks. From the feed tanks the reactants are sent to the nitrator by means of two positive displacement pumps driven by the same electric motor. Two speed variators allow change in the total flow rate as well as the ratio between acid and glycerine. The glycerine feed pipe in the nitrator, fitted with a multi-nozzle distributing head is retractable and can only be extended if all safety conditions are fulfilled. The feed arrangements are such that the acid and glycerine are quickly submerged, emulsified and forced down the nitrator through the central space formed by the cooling coils. Part of the emulsion overflows into the separator and part returns to the vortex in the nitrator fluid. Cooling is achieved by sodium nitrate brine circulating through helical coils. The reaction temperature is kept constant by thermostatic control of the brine valve.

The intensity of mixing in the nitrator by the turbine is such that the emulsion of nitroglycerine in the acid cannot be initiated by a No. 8 blasting cap. The turbine is driven by V-belts of a motor mounted in a room separated from the nitrator unit by a partition wall.

The bottom of the nitrator is provided with a quick opening flap valve placed considerably off the axis which can be operated manually or pneumatically for quick draining of the contents into a large tank full of water.

**Control of the Nitration**

The emulsion overflowing from the nitrator enters the separator through a short section of pipe in which a special electrode is fitted for the measurement of the Redox-potential of the spent acid against a reference sample of mixed acid. The Redox-potential of the spent acid has a direct relation to the HNO₃ and HNO₂ content in this acid composed of HNO₃—HNO₂—H₂O and can serve as a control on the extent that nitration follows the normal course without too many oxidation reactions and deviations from the normal course. It was first introduced by Öhman in 1938 [5]. He applied the method for the control of the nitration of glycerine [6–9], glycol and similar compounds [9] and eventually to the nitration of aromatic hydrocarbons [10]. More recently the method was extended by Camera [11] to the control of the nitration of penterythritol. See also a general description by Biasutti [12].

The Redox-potential of the system (1)

\[
\text{HNO}_3 + 2\text{H}^+ \rightarrow \text{HNO}_2 + \text{H}_2\text{O}
\]

(1)

can be expressed by equation (at 20°C):

\[
\epsilon = \epsilon_0 + 0.0291 \log \frac{[\text{HNO}_3]}{[\text{HNO}_2]} \left(\frac{[\text{H}^+]}{[\text{H}_2\text{O}]}\right)^2
\]

(2)

where \(\epsilon_0\) is the potential of the standard electrode. Considering that HNO₂ is relatively small and HNO₃ is constant at 20°C a simplified equation (3) can be used [13]:

\[
\epsilon - \epsilon_0 = 0.0291 \log [\text{HNO}_3].
\]

(3)

The reference sample [11] is composed of

\[
\begin{array}{ll}
\text{H}_2\text{SO}_4 & 49.1\%
\end{array}
\]
Nitrous acid is introduced into this solution in the form of NaNO₂.

By recording the value of e in mV the operator can see whether the trend of the reaction is normal. If the value of e deviates too much from normal, the nitrating should be stopped by cutting the inflow of glycerine and, if necessary, the inflow of the mixed acid.

The following are some values of e in mV given by Camera [11]:

<table>
<thead>
<tr>
<th>% HNO₃</th>
<th>% HNO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>90</td>
<td>164</td>
</tr>
<tr>
<td>80</td>
<td>282</td>
</tr>
<tr>
<td>70</td>
<td>366</td>
</tr>
</tbody>
</table>

The permissible values of e should be established by experiments.

**Separation of NG from the Spent Acid**

From the tangential separator NG flows to the washing vessels and then to a storage tank. The spent acid flows from the base of the separator to its storage tank through a variable overflow valve by means of which the height of the nitroglycerine—spent acid interface may be controlled. This adjustment is effected automatically through a float on the spent acid layer in the separator. A small amount of water is added to the overflowing spent acid to avoid further separation of NG as in the system of Nathan et al. (Vol. II, p. 95).

**Alkaline Washing of NG**

Sodium carbonate solution is introduced to the first washing vessel by gravity. The automatic feed control is obtained by means of a pH-meter with its electrode placed at the outlet of the first washer. The soda water/NG emulsion passes through two additional washers for completion of the neutralization reaction. From the last washer the emulsion flows to a Biauzzi separator. The wash water flows to a catch tank for the recovery of the last portions of unseparated NG.


**Nitrator**

- Heat Transfer Coefficient: 700 kcal/m²·h·°C

**Production of Nitrate Esters**

<table>
<thead>
<tr>
<th>Ratio Coil Volume to Useful Volume</th>
<th>80/100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio Coil surface to Useful Volume</td>
<td>10 m²/100 l</td>
</tr>
<tr>
<td>Ratio Useful Volume to Production Capacity</td>
<td>110 l/1000 kg/h NG</td>
</tr>
<tr>
<td>Ratio NG content to Production Capacity</td>
<td>70 kg/1000 kg/h NG</td>
</tr>
<tr>
<td>Throughput of Emulsion through Turbine Wheel</td>
<td>10 m³/min</td>
</tr>
<tr>
<td>Average Retention Time Draining Time</td>
<td>4 min/8 sec</td>
</tr>
</tbody>
</table>

**Separator**

| Ratio total Volume to Production Capacity | 800 l/1000 kg/h NG |
| Ratio Separated NG to Production Capacity | 40 kg/1000 kg/h NG |
| Ratio total NG to Production Capacity | 170 kg/1000 kg/h NG |
| Average Retention Time (NG) | 10 min |
| Average Retention Time (Spent Acid) | 50 min |
| Draining Time | 20 sec |

**Washers**

| Ratio NG/Production Capacity | 50 kg/1000 kg/h NG |
| Retention Time (NG) | 3 min |

**Safety Measures**

When the Biauzzi unit has to be shut down, it is necessary to remove all the NG from the nitrator—separator system. This is done by introducing spent acid from an overhead storage tank into the bottom of the nitrator until all the NG has been displaced through the overflow of the separator. A level sensor automatically stops the displacement process as soon as all the NG leaves the separator.

In general layout and design the possibility of the retention of a minute quantity of NG is eliminated. All the vessels are highly polished internally to prevent the adherence of NG to rough surfaces.

There are two control rooms. One is near the nitrator house in a ‘control bunker’, another is further away in a remote control room at a safe distance. The latter is provided with instruments to start, supervise Redox, pH NG—water emulsion and a device to shut down the unit. Both control rooms are provided with TV sets. Signals between the two houses are both electric and pneumatic, although controls on the nitrator unit are only pneumatic. The remote control room is operated in case of emergency and necessity or breakdown of the automatic system.
The 'control bunker' is provided with a number of 'push buttons'. They are:

Preparation button. By pressing this button the nitratode separator are filled with water, the pumps are started, brine is circulated through the cooling coils etc. When all red lights on the alarm panel are out the unit is ready to start. The start button is then pressed, the glycerine pipe is extended to the nitratode, glycerine and mixed acids begin to flow at the selected production rate between the nominal rate (100%) and reduced to 50%.

The stop button causes the glycerine and acid flow to end and the glycerine pipe is retracted. One minute later the automatic shut-down sequence starts and continues until all the nitroglycerine has been evacuated from the building.

An alarm sounds in the case of irregularities.

The early history of the Biazzi invention was given by Biasutti [12].


Because of the high temperature of glycerine or glycerine + glycol mixture the viscosity is considerably reduced and helps the action of the injector. The temperature rise through nitration is 46 – 48°C. The influx of the alcohol is automatically regulated and registered. Only one second after the two components are mixed, cooling of the emulsion begins, first in a coil with cold water or brine and then in a tubular cooler with brine to reduce the temperature to +15°C.

The nitrate ester is separated in a centrifuge of 4 – 8 kg capacity. The spent acid contains 0.1% emulsified NG and by adding 4 – 5% water the nitroglycerine remains in the solution (Vol. II, p. 95).

The acid NG from the centrifuge runs to an injector where it is mixed with 8% aqueous solution of sodium carbonate. It is transported to a special degassing vessel, where CO₂ is evolved. After that the emulsion passes to two wash columns provided with perforated discs made of stainless steel. Mixing is achieved by air inlet to the column, from the second column the emulsion runs to a specially designed wash centrifuge. The stabilized nitrate ester runs to an injector and is transported as a non-explosive aqueous emulsion to a separate storage building.

From the point of view of safety, the main advantage of the injector method is the very small quantity of nitrate ester present in the reaction space and the very short reaction time (ca. 1 second). After the reaction has ended, the quantity of nitrate ester is too small to be able to detonate. If nitration is stopped, the emulsion flows downward, leaving the apparatus empty, cleaned by nitrating acid and subsequently there is no need for a safety tank for draining nitrate ester and acid in the case of emergency.

If the power fails or the reaction temperature becomes too high, a valve for the inlet of air to the injector opens automatically and prevents the alcohol being sucked into the injector. If the electric current returns, the nitration process cannot restart by itself.

Centrifugal separation of NG is safe on condition that lubrication is carried out according to instructions.

The injection nitration is supervised by remote control.

**Safety Problems (Vol. II, p. 122)**

Safety problems have already been tackled in the general description of processes. Biasutti [15] described over 20 accidents in nitroglycerine manufacture.

In the batch process two accidents were caused by faulty mixing. Thus in Granberg, Sweden in 1955, the supply of compressed air to stir the content of the nitratode was stopped. Glycerine started to decompose which produced a heat evolution and hot acid together with decomposing organic substances entered the separator and detonated the charge of nitroglycerine in the separator probably over 1000 kg.

Also in continuous methods of nitration faulty functioning of mixing in the nitratode has caused a few accidents. Another cause of accidents in continuous methods was the malfunctioning of the automation device which produced an inflow of the wrong proportions of glycerine and acid. Thus two accidents with the Schmid method (in Gyttorp, 1933 and in Bofors, 1953) and one with the Biazzi system (Kaohsiung, Taiwan, 1966) were caused by an insufficient proportion of acid in the unit. Insufficiently trained personnel can also be responsible for accidents where the production is fully automatic and requires skilled workers (e.g. wrong calibration and incorrect setting of control instruments).

A process for drying nitroglycerine with calcium chloride was probably the cause of an explosion of stored nitroglycerine in Schlebusch (1956). It is believed that drying with calcium chloride evolved enough heat to produce the decomposition of the substance.

Generally speaking storage of nitroglycerine should be avoided. The continuous methods were originally ended by batch processes of weighing and mixing nitroglycerine. By fully continuous methods no storage would be required. According to Biasutti [12] in Japan and Sweden for the manufacture of commercial explosives of ca. 500 kg/hr, only 40 kg of NG and 20 kg of dynamite can be present at any time.

A separate danger of handling nitroglycerine has recently been described. It consists in chisels combined with adiabatic compression of minute air bubbles. The first described accident of this kind took place at ASA in Japan (1962). Meticulous study revealed that in the suction tube the air bubbles were originally under 0.1 atm, later the pressure increased to 1 atm, which caused a rise in the temperature by 300°C. A similar accident took place with a 'water hammer' it suddenly opening a water pipe which produced an adiabatic compression of air
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

(Marions, Illinois, 1968). A few more accidents produced by compressing air bubbles have also been reported [15].

Biasutti [16a] reported statistics of accidents which [16b] are given in Table 56.

<table>
<thead>
<tr>
<th>Number of accidents</th>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>Nitrating—Separation</td>
</tr>
<tr>
<td>66</td>
<td>Washing and Storage</td>
</tr>
<tr>
<td>13</td>
<td>After-Separation and Handling</td>
</tr>
<tr>
<td>4</td>
<td>Wash Water Handling</td>
</tr>
<tr>
<td>2</td>
<td>Decontamination</td>
</tr>
<tr>
<td>15</td>
<td>Transportation</td>
</tr>
</tbody>
</table>

Accidents in the nitration—separation section were mostly due to self-decomposition of the NG—spent acid mixture following incorrect nitration ratio (9 cases), insufficient stirring (4 cases), leakage of cooling brine in the nitrator (2 cases), self-decomposition because of impure raw materials, instability of spent acid used for displacement. A high number of accidents during the washing and storage of NG have occurred mainly in older batch processes where the two sections were installed in the same building.

A great number of accidents have been caused by human error, for example the opening of closing valves on NG (9 cases), stumbling when carrying buckets full of NG (4 cases) shock of metal pieces (6 cases). Chemical decomposition was the cause of the explosion of nitroglycerine sludge accumulated at the bottom of settling tanks. External causes—lightning—caused 7 accidents. Spent acid decomposition was the source of 10 accidents. Here 5 cases were due to the decomposition of NG dissolved in the acid. Accidents in transportation were caused by stumbling, fall of buckets, shocks and derailments or collisions on mechanical transportation (6 cases). Transportation through water-injection was the cause of 8 accidents. This was due to adiabatic compression of air bubbles. Since the introduction of the safe water-injection method, where rapid energetic changes are avoided, the transportation by water-injection became much safer.

DIETHYLENE GLYCOL DINITRATE (DGDN) (Vol. II, p. 149)

As previously mentioned this compound was extensively used in World War II for making double base powder. It was made by the nitrating of diethylene glycol by methods similar to those used for the nitrination of glycerine, preferably at higher temperatures (Vol. II, p. 151).

PRODUCTION OF NITRATE ESTERS

The specification of diethylene glycol for nitration was given by Meyer [17]:

- Clear colourless liquid, density (20/4) 1.1157–1.1165
- Neutral to litmus
- Boiling analysis: five drops not below 241°C,
  distillation at 246.5°C,
  end not above 250°C
- Moisture: no more than 0.5%
- Residue after burning: no more than 0.02%
- Acidity (as H₂SO₄): no more than 0.01%
- Chlorides: traces
- Saponification number: not above 0.02%
- Reducing substances (test with ammonia solution of AgNO₃): none
- Viscosity at 20°C: 35.7 cP
- Content of monoethylene glycol: no more than 2%.

TRIETHYLENE GLYCOL DINITRATE (Vol. II, p. 154)

As already pointed out, the substance was used in double-base propellants in Germany during World War II.

Meyer [17] gives the specification of the glycol used for nitration (compare with the data in Vol. II, p. 154):

- Density (20/4) 1.230–1.234
- Boiling: do not start below 280°C,
  90% distilled not over 295°C
- Moisture: no more than 0.5%
- Chlorides: traces
- Acids (H₂SO₄): no more than 0.02%
- Saponification as Na₂O: no more than 0.05%
- Reducing matters: none.

MANUFACTURE OF PENTAERYTHRITOL TETRANITRATE (PETN)

(Vol. II, p. 185)

Relatively little can be added to the description of the methods of PETN manufacture. Continuous methods are mostly used in modern plants (see also Fig. 74, Vol. II, p. 188).

The nitration characteristics of pentaerythritol (PE) can be summarized as follows:

1. Use of low temperature of nitration with nitric acid (d 1.50).
2. Ease of separation of PETN from the spent acid by the fact that the product is a crystalline solid, and ease of washing it from the acid,
3. High sensitivity of PETN to impact which should always be kept in mind.
4. Instability of the spent acid.

*Pentaerythritol (PE), 'nitrating grade'.* According to 'Biazzi SA' [18] PE should possess the following characteristics:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.p.</td>
<td>263 ± 1°C</td>
</tr>
<tr>
<td>Humidity</td>
<td>max 0.2%</td>
</tr>
<tr>
<td>Crystal size</td>
<td>min dia. 0.025 mm</td>
</tr>
<tr>
<td></td>
<td>max dia. 1.0 mm</td>
</tr>
<tr>
<td>Formic acid</td>
<td>absent</td>
</tr>
<tr>
<td>Dust</td>
<td>absnt</td>
</tr>
<tr>
<td>Water insoluble parts</td>
<td>max 0.2%</td>
</tr>
<tr>
<td>Ashes</td>
<td>max 0.01%</td>
</tr>
<tr>
<td>Monopentaerythritol</td>
<td>96.5% – 98.5%</td>
</tr>
<tr>
<td>Dipentaerythritol</td>
<td>0.7% – 1.3%</td>
</tr>
</tbody>
</table>

The following is the description given by Biazzi SA [18] on the continuous nitrating of PETN – Fig. 47 with two nitrators.

The dry pentaerythritol (PE) of specified granular size and quality (see the specification above) from (1) loaded into a feeding hopper (2) is fed into the first nitrator (3) by means of a vibrating system giving a constant flow rate. The feeder is provided with a variator making it possible to modify the feeding rate. Simultaneously a continuous flow of nitric acid (98.5% HNO₃) is introduced into the nitrator in the right proportion (5:1).

From the first nitrator the suspension of PETN nitric acid enters the second nitrator (4). The temperature 15–20°C is maintained by a freon filled jacket and controlled by the cooling agent valves. The nitric acid is fed into the first nitrator from a constant-level overhead tank (5). The contents of the nitrators are stirred by paddle type stirrers, driven by electric motors which are located outside the building or in a separate motor room. Gas from the nitrator is washed with water in a column (6).

Camera [19] discussed the control of the safety of nitration of pentaerythritol with nitric acid by Redox measurement as described in Chapter X.

The PETN suspended in the spent acid overflows from the second nitrator into a continuous vacuum filter (7). The spent acid goes through a filter into an intermediate vacuum tank equipped with a strainer retaining all the PETN which may escape from the filter. From the tank the acid is pumped to storage by means of a diaphragm pump controlled by a level switch in the intermediate vacuum tank.

From the filter PETN is transferred to the dissolution neutralization and crystallization equipment by a water jet. Although the nitrating of Pentaerythritol (PE) should be regarded in itself as a relatively safe operation compared to the nitrating of glycerine and trinitration of toluene, there is a certain amount of danger particularly from the storage of spent acid for a longer time. This is the result of hydrolysis of PETN to lower nitrated PE, that is, PETN and PPDN described by Camera [20]. The lower nitrated products can be relatively readily oxidized and this of course is manifested by the formation of nitrous acid.

One of the important requirements for the safety of nitration of PE is keeping the right proportion of nitric acid to PE (5:1).

A few accidents with PETN described by Biasutti [15] were very instructive. A typical accident happened through a faulty rotometer giving a wrong dosage of the acid in the continuous method of the manufacture of PETN. Insufficient quantity of the acid produced a considerable increase in the temperature in the nitrator and a violent decomposition of PETN [21].

The sensitivity of PETN to shock was the cause of another accident. This happened when the crust of the explosive was removed from the stirrer with a steel chisel. This was against the regulation which required the use of a solvent (acetone) and either wooden or plastic tools [22].

The storage of spent nitric acid is dangerous particularly in a concentration of 75–80% [23] or from other sources 65–75% [24].
the 'fume off' of the spent acid is hydrolysis of the lower esters followed by oxidation as described above.

However, Ramaswamy and Subba Rao [23] suggested a 'controlled fume-off' as a means of avoiding the danger of keeping spent acid. Two methods were recommended both by injecting live steam:

(1) keeping the temperature at 70 ± 2°C;
or (2) at 95–100°C with an additional injection of N₂ or air.

This is fully discussed in Chapter XIII dedicated to the treatment of spent acids.

Purification of PETN

The usual method for the purification of PETN consists in crystallization from acetone (Vol. II, pp. 188–189).

A description of crystallization as given by Biazz SA [18] is as follows. PETN is continuously introduced from the filter into a stainless steel dissolving apparatus provided with a hot water heating jacket and a stirrer. The required amount of acetone is continuously fed from a constant-level overhead tank together with ammonia gas for neutralization. The neutralized solution of PETN in acetone flows continuously into a series of continuous crystallizers equipped with stirrers and jackets. The crystallization is carried out by adding a well-determined quantity of water. The contents of the last crystallizer flow continuously on a continuous vacuum filter where most of the waste acetone is removed. The dilute acetone is collected into an intermediate vacuum tank from which it is pumped to the acetone recovery unit.

The moist and recrystallized PETN falls continuously from the filter into the containers for further use.

The plant is provided with an electro-pneumatic safety system which signals all emergencies during the operation and sets the automatic safety devices in action if the intervention of personnel fails.

The material balance of the Biazz process is given below for 1000 kg of produced PETN [18].

- **PE** was used in quantity: 450 kg
- Nitric acid (as 100% HNO₃): 2250 kg (not including recovery)
- Acetone ca.: 300 kg
- Ammonia (as 100% NH₃): 1.5 kg
- Process water: 12,000 l.

By-products and wastes:

- Spent acid (81–84% HNO₃): 1650 kg for recovery
- Acidic waters: 3750 kg which should be neutralized and sent to the drains.

**Production of Nitrate Esters**

Acetone (30%): water: 9250 kg to be sent to acetone recovery plant.

Specification of the final product (PETN).

- **M.P. min. 140°C**
- Abel heat test at 30°C: min. 30 minutes
- Nitrogen content: min. 14.5%
- Insoluble in acetone: max. 0.1%
- Bulk density: max. 800 ± 80 g/litre
- Acidity: max. 0.005% (HNO₃)
- Ash: max. 0.05%
- Water (for the safety in transportation and manipulation): max. 20%.

US standards have slightly different requirements.

According to Roth [25] PETN for military use in the USA shall correspond to data as below:

- Melting point: 141°C ± 1°C
- Nitrogen content: min. 17.5%
- Acetone insoluble material: max. 0.10%
- Acidity or alkalinity: max. 0.01%

120°C vacuum stability: the max. amount of gas evolved in a 20 hour test should not exceed 5 ml.

Granulation. PETN should comply with the granulation requirements shown on Table 57.

**Table 57. Sieving of PETN (US specification)**

<table>
<thead>
<tr>
<th>US Standard Sieve No.</th>
<th>Class 1</th>
<th>Percent Passing through the Sieve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Class 2</td>
<td>Class 3</td>
</tr>
<tr>
<td>30</td>
<td>100 min</td>
<td>95 min</td>
</tr>
<tr>
<td>80</td>
<td>85 min</td>
<td>96 min</td>
</tr>
<tr>
<td>100</td>
<td>55 max</td>
<td>80 max</td>
</tr>
<tr>
<td>140</td>
<td>30 max</td>
<td>65 min</td>
</tr>
</tbody>
</table>

With regard to the safety of crystallization attention should be paid to the danger of explosive acetone-air mixtures which have been responsible for some accidents [26]. In some countries (e.g. Japan) purification of PETN is carried out by heating PETN with water in autoclaves in a manner similar to that for nitrocellulose (Vol. II, pp. 411–413). However, an explosion occurred when PETN was heated with 30% water in an autoclave [26]. The accident was probably produced by overheating.
REFERENCES

5. V. Øhman, Teknik Tidskrift Stockholm 9, 36 (1938).
6. V. Øhman, Chem. Zig. 82, 651 (1958).
22. According to [15], p. 144.

CHAPTER 12

CARBOHYDRATE NITRATES

CELLULOSE AND CELLULOSE NITRATES (NITROCELLULOSE)
(Var. II, pp. 213, 234, 293, 321, 362, 393)

With regard to cellulose two more collective volumes have appeared [1] which are the continuation of the former ones edited by Ott, Spurlin and Griffin. However, most of the text is now dedicated to the biosynthesis of cellulose and modifications of cellulose which are outside the scope of the present book. Only one chapter written by Hiatt and Rebel [2] refers to esters of cellulose, including nitrocellulose and the information given by these authors is used in the present volume.

With regard to the present advances in the chemistry of cellulose an excellent review has been given by Shafizadeh [3]. He also refers to the folded chain structure of cellulose [4, 5] and of the structure of elementary fibrils [6].

Cellulose fiber. In most European countries wood cellulose is now used for nitrating (Vol. II, p. 364). The success of the nitrating of cellulose from wood depends on a high proportion of acetyl cellulose in wood cellulose. According to Petropavlovskii, Krunchak and Vasylyeva [7] the yield of nitrocellulose highly depends on the 2-cellulose content and can be proportional to this content. Some authors [8] consider that lower quality of nitrocellulose from wood-cellulose is due to the presence of hemi-celluloses (mainly pentosanes) in it.

Nevertheless wood cellulose has a lower molecular weight than cotton cellulose, which explains the lower molecular weight of nitrocellulose from wood. Some attempts have been made to produce a higher quality nitrocellulose from wood by carrying out the nitrating in two stages, for example [9] but this technique did not seem to find a wider application although the semi-continuous method of nitrating of Bofors-Nobel-Chemnatur (see p. 346, Fig. 48) includes the nitrating in two stages:

1. Pre-nitrating,
2. After-nitrating.

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Structure of Cellulose Polymer and Determination of Molecular Weight
(Vol. II, pp. 261–278)

The structure of cellulose has only relatively recently been tackled through
the examination of its trinitrate, that is, nitrocellulose of ca. 14% N. Trinitrate
of cellulose was chosen as a readily available cellulose ester, soluble in polar
solvents, of an almost unique unbranched polymer chain structure having a
broad range of molecular weights manifested by the degree of polymerization
250–9000.

Holzzer, Benoit and Doty [45] undertook the task of fractioning samples
of nitrocellulose with 13.8–14.1% N. n-Hexane was added dropwise while stir-
ing to a 0.2% solution of nitrocellulose in acetone and several fractions were
obtained. Their molecular weight was determined by light scattering, viscosity
and osmotic pressure measurement.

Light scattering gave the following figures:

1. Weight average molecular weight: \( M_n = 2640000 \pm 77000 \)
2. Number average molecular weight: \( M_n = 1320000 \pm 4500 \)

Thus the polydispersity \( M_n/M_n \) is ca. 2. However most commercial samples
of nitrocellulose have a high polydispersity: 2.5–3.5. (For the description of
\( M_n \) and \( M_w \) and their calculation see [46].)

Measurement of viscosity gave lower figures. The above results were con-
formed by Hunt, Newman, Scharage and Flory [47]. Their figures for the mol-
ear weight of fractions were lower: 575 000–40 000. Canadian workers [48]
obtained figures of 250 000–650 000. Their method of fractionation consisted
in adding water to the solution of nitrocellulose in acetone [49].

The conclusion from the above experiments was that:

1. Molecular weight of nitrocellulose (e.g. 400 000) is much higher than
that of most vinyl synthetic polymers,
2. The cellulose skeleton in nitrocellulose is manifested by an unusually
stiff chain.

Both these characteristics are responsible for the very high viscosity of nitro-
cellulose solutions.

Recently British authors [50] described a simple method of determining
number-average and weight-average molecular weight of 12.6% N pyro nitro-
cellulose. The measurement was made with a 3% solution in acetone/ethanol.
The viscosity is related to the number-average and weight-average molecular
weight. By adding ca. 7% lead \( \beta \)-resorcylate a fractional increase in the viscosity
was found, which is a function only of number-average molecular weight. Once
the calibration has been made against osmotic pressure measurements and intrinsic
viscosity, both number- and weight-average may be measured rapidly.

Pyrolysis of Nitrocellulose

Ette and Varadi [51] examined pyrolysis of nitrocellulose (no nitrogen
content was given) between 300°C and 950°C. The decomposition yielded almost
completely gaseous products: CO, CO, nitrogen oxides, CH₄, H₂O, lesser
amounts of nitrogen (increasing with temperature) and small quantities (below
2%) of ethylene, acetaldehyde, methanol, ethanol and methyl acetate. The latter
four compounds were not found at 900–950°C. A small solid residue which
was formed between 300°C and 500°C yielded gaseous products above 500°C.

At 175–250°C a solid residue was produced which decomposed only partly
to volatile products when heated to 600°C. This indicated the difference be-
tween the composition of products formed at 300–500°C and at 175–250°C.

Osada and Hara [53] examined the action of UV radiation on nitrocellulose
and found that evolution of NO₂ and NO occurred. In oxygen atmosphere
nitrocellulose absorbed oxygen which promoted denitrification and depolymer-
ation. Also salts of di- and trivalent iron promote depolymerization.

Thermochemical Properties of Nitrocellulose (Vol. II, p. 313)

The National Bureau of Standards [41] reported their results for determining
heat of combustion and heat of formation of dinitrate- and trinitrate of cellulose
(Table 58).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of combustion cal/g</th>
<th>Heat of formation cal/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>2614.4</td>
<td>715.3</td>
</tr>
<tr>
<td>Dinitrate</td>
<td>2616</td>
<td>712.8</td>
</tr>
<tr>
<td>Cellulose</td>
<td>2188.7</td>
<td>523.4</td>
</tr>
<tr>
<td>Trinitrate</td>
<td>2178.1</td>
<td>525.4</td>
</tr>
</tbody>
</table>

Nitrination. As pointed out in Vol. II (p. 321) the only industrial method of
nitrating cellulose consists in using a nitric acid–sulphuric acid nitrating mixture.
The other nitrating mixtures, such as nitric acid/phosphoric anhydride, nitric
acid/acetic anhydride, nitric acid/chlorinated hydrocarbons were in use occasion-
ally on a laboratory scale to solve some problems connected with the nitration
of cellulose. Thus Bennett and Timell [10] confirmed the work of Bouchonnet,
Trombe and Petitpas (Vol. II, p. 344) that the nitration of cotton dust with a
mixture of nitric acid–acetic acid–acetic anhydride (in proportion 43:32:25)
at 0°C can yield fully nitrated cellulose, that is, cellulose trinitrate of 14.14% N.

With regard to the mechanism of the nitration of cellulose, two modes were suggested for the formation of esters of cellulose (Vol. II, pp. 239–242). One of the mechanisms suggests gradual introduction of NO₂ groups: at the beginning on the surface of micelles followed by a step-wise deeper penetration. Another mechanism suggests simultaneous reactions of OH groups with nitric acid. The latter mechanism seems now to be accepted according to Hiatt and Rebel [2].

Sakata and Komatsu [12] used infrared and X-ray techniques to study the mechanism of the nitration of cellulose with nitric and phosphoric or sulphuric acid. Their conclusion can be summarized as follows. Nitric acid penetrates into crystallites and most OH groups simultaneously react with the reagent in the presence of phosphoric acid. In the presence of sulphuric acid the accessibility of OH groups gradually increases. The part of the molecule which has not reacted shows the same pattern as the original ununtrated micell.

Kunz, Kompolthy and Balogh [13] examined the trend of the nitration of mechanically pulverized cellulose. They found that the nitration obeys the same rule as the nitration of starch, reported by Kunz and Toth (Vol. II, p. 430). The same dependence: reaction time on the reaction temperatures exists in both cases and the degree of nitration plot on triangle diagram (Vol. II, pp. 333–336, 429) are identical, without the typical one phase system for nitro-starch due to the solution of starch in nitratating mixture rich with nitric acid. A correlation exists between the activity of nitric acid (Vol. I, pp. 28–30) and the duration of the reaction. The reaction was fully accomplished in 8–13 minutes depending on the composition of mixed acids. It was found that the introduction of one NO₂ group into the cellulose molecule develops 1696 ± 85 kcal/mol. This figure consists of the actual heat of reaction of nitration and the heat of absorption of nitric acid by cellulose (see Vol. II, p. 358).

Mixed Esters: Nitrates and Sulphates

It is well known that the low stability of nitrocellulose is often attributed to the presence of sulphates of cellulose, usually in the form of mixed esters: nitro-sulphates (Vol. II, pp. 293–298). A number of patents [1] have attempted to obtain nitrocellulose free of sulphates by nitratating cellulose with nitratating mixtures composed of nitric acid and salts of nitric acid, such as magnesium nitrate [14] much in the way described in Vol. II, pp. 346–347.

The analytical method of determining the quantity of sulphate groups in nitrocellulose was given by Dawoud, Saad an Attia [15] who used a quick analytical method of determining sulphate esters of cellulose.

(1) by the ignition of samples in a calorimetric bomb,
(2) by titrometric determination of sulphate using Thorin titration method with BaCl₂.

The conclusion of this important work is given here. Unstabilized samples of 12.2%, 12.52% and 13.3% N have shown 0.68%, 0.44% and 0.37% SO₄ respectively.

Finished commercial products showed only trace quantities of SO₄:
- nitrocellulose of 12.2% from linters: 0.01%
- nitrocellulose of 12.16% from wood cellulose: 0.02%
- nitrocellulose of 13.2% from linters: 0.03% SO₄.

Attention should be drawn to the work of Castorina, Helf, Aaronson and Kaufman [52] who examined the nature and amount of sulphate present in nitrocellulose and mechanism of its removal during stabilization by using the radioactive tracer – sulphur 35. Thus nitrocellulose of 13.5% contained 0.84% sulphate. After 56 hours of boiling in acid it was reduced to 0.05%. The latter could not be removed. The authors concluded that ca. 90% of sulphate in unstabilized nitrocellulose is removable sulphuric acid and the remainder is sulphate ester which is difficult to remove.

Nitration of wood meal with N₂O₅ vapour at 0°C to -2°C in vacuo was also described [16].

Stabilization of Nitrocellulose

As described in Vol. II, p. 393 stabilization comprises washing and boiling nitrocellulose in kiers (if necessary an additional kiering in autoclave), pulping in heaters or mills (refiners) followed by final boiling and washing.

Hess and Trogus (Vol. II, p. 241) have shown that boiling nitrocellulose increases the regularity of the structure of the obtained molecule. A very important part of stabilization is pulping the nitratated fibres. Mechanical cutting of the fibres into shorter ones produces a depolymerization manifested by a decrease in the viscosity of the solutions of nitrocellulose (Vol. II, p. 276).

Steuer and Hess [17] have already calculated that the kinetic energy from the impact of balls (in a colloid ball mill used by Staudinger – Vol. II, p. 276) on cellulose fibres should be sufficient to rupture covalent bonds in cellulose such as C–C, C–O. Breaking such bonds requires energy of the order 80–90 kcal. This statement was substantiated by Swedish authors [18] who found experimentally that the covalent bonds in cellulose, as above, can be ruptured by mechanical action (in an agate ball mill). It has been known since 1895/96, thanks to the work of Bruley (Vol. II, p. 276), that pulping nitrocellulose reduces the viscosity of its solutions, but only now the experimental facts can be explained in terms of breaking the covalent bonds. This was done by T. Urbański.
This scheme explains both the reduction of the viscosity and a slight denitration of nitrocellulose during the pulping (Vol. II, p. 276) and the presence of Ca(NO$_3$)$_2$ and Ca(NO$_3$)$_3$ in water in beaters. Calcium salts are being formed from calcium carbonate added to the water in the course of the work of beaters.

Degradation of polymers by mechanical action (tribo- or mechano-chemistry) is now generally accepted and has been described in two monographs [20, 21].

**Knecht Compound**

The structure of "Knecht compound" has been examined by T. Urbański and Żyszczyski [54]. On the basis of infrared spectra they came to a conclusion that the cellulose moiety of the Knecht Compound is partly oxidized and shows the presence of a carbonyl group similar to that of oxycellulose (Vol. II, p. 321).

**Manufacture of Nitrocellulose. Continuous Methods**

As pointed out in Vol. II, p. 391 numerous attempts have been made to introduce continuous methods of cellulose nitration. In addition to those mentioned in Vol. II, the following continuous methods were reported by Hiatt and Rebel [2]: Plunkett [22], Plunkett and McMillan [23], Reinhardt [24], Ramsey [25] described a continuous method with nitric-phosphoric acid mixture and Bergman [26] — nitration of powdered cellulose. Diels and Orth [27] used spent acid for the first step of nitration followed by the second with fresh mixed acid.

Matuda and Matuda [28] described a number of continuous methods of cellulose nitration, among them patents by Hercules Co. [29] and Wasag Chem [30].

So far none of the above methods have received practical application, and appears that only two methods are in use on an industrial scale:

1. semi-continuous method used by Bofors-Nobel-Chematur in Sweden, and
2. continuous method used by Hercules Powder Co.

**The Semi-Continuous Method of Bofors-Nobel-Chematur [31]**

The method is depicted by Fig. 48. It was developed in the early 1960s at the Nobel Works, Karlskoga, Sweden. The process comprises continuous nitration, continuous centrifuging and batch stabilization.

Cotton, cotton linters or wood cellulose is made fluffy by a disintegrator and dried in a continuously working belt drier. Dried cellulose is continuously mixed with nitrating acid in a prenitrat. From there the mixture passes into a centrifugator where very close contact is obtained between the cellulose fibres and the acid and all enters into an 'after-nitrat' where the nitration is completed.

The method of continuous centrifuging depends upon whether low or high
FIG. 48. Semi-continuous making of nitrocellulose of Bofors-Nobel-Chematur (Courtesy Bofors-Nobel-Chematur)

FIG. 49. Continuous refiner (Courtesy Bofors-Nobel-Chematur).

Nitrocellulose plant

Grinding → Drying → Acid recirculation → After nitration → Water drumming → Stabilization viscosity reduction → Pulping → Water recirculation

Centrifuging → Precipitation → Washing → Blending → Packing

Dewatering → Removal of foreign particles

Pulped nitrocellulose is subjected to the usual operations: further boiling, washing, blending, and the removal of foreign particles. After that the nitrocellulose is dried in a centrifuge. A continuous fully automatic nitration method is shown in Fig. 50. Dried cellulosic material is introduced continuously into a reactor. The nitration mixture contains a supplemet and mixed nitration acid. The acid enters a reactor, where it is added to the material in several zones. The nitration mixture is advanced from one zone to another, in each of the succeeding zones the acid mixture is removed. In each of the succeeding zones the nitration is removed. In each of the succeeding zones the nitration is removed.
cellulose is displaced with weaker acid and finally in the last zone with water. In all zones the process occurs simultaneously. The water used for the final displacement is used for the preceding washing and so on, this is done in every step. Each effluent is used for the preceding step. Subsequently the displacing acid leaving the system is composed of spent acid of nitration.

Hercules Co. points out that the product of the continuous nitration is more uniform than from the batch processes.

**Drying Nitrocellulose**

As is known nitrocellulose is stored and transported with 30% water or ethanol. It is also known that for a single base powder (nitrocellulose powder) water in nitrocellulose is replaced by ethanol which remains in it as an ingredient of the solvent (Vol. II, p. 573). However for some types of double base powder (cordite, Vol. III, p. 642) it is necessary to dry the nitrocellulose. Drying nitrocellulose is essential in the manufacture of dynamite (Vol. II, p. 511). However it has so far been considered the most dangerous operation with dry nitrocellulose considering its ease of ignition and burning, and sensitivity to impact and friction. Mario Biazz S.A. use a Finnish method Finska Forcht [33]. The idea of the system is given in Fig. 51. It consists essentially in drying humid nitrocellulose with dry warm air which passes through the nitrocellulose from the top to the bottom.

Moist nitrocellulose in cotton sacks is put in aluminium cylinders the bottoms of which are made of metal staves, for example, of phosphorbronze wire. The thickness of the sheet of nitrocellulose should be 25–40 cm the diameter is chosen so that the content of one cylinder is used for one batch of dynamite. Dry air heated to 50°C enters the cylinders under pressure of 700 mm water. The amount of air is 30–50 nm³ per kg of dry nitrocellulose.

The end of drying is manifested by the increase above 20°C in the temperature of the air leaving the cylinders. To avoid the danger created by static electricity all cylinders should be earthed. Drying is ended after 1–2 hours. One of the advantages of the method is the fact that no nitrocellulose dust is formed.

**Safety in the Manufacture of Nitrocellulose**

Generally speaking the manufacture of nitrocellulose should be regarded as a relatively safe process. The most dangerous operation is drying nitrocellulose [34]. It also causes the largest number of accidents [35]. The explosions occurred mainly through the shock, overheating or discharge of static electricity. Another dangerous part of the work is centrifuging – the danger connected with it has been described in Vol. II, pp. 407, 389. Stabilization in autoclaves, that is, boiling nitrocellulose under pressure, also ended with explosions probably due to an insufficient quantity of water in the autoclave. As a consequence decomposition occurred with the increase of temperature to 160°C and a violent reaction occurred.

**STARCH NITRATES (NITROSTARCH)** (Vol. II, p. 418)

Attention should be paid to Abdel-Rahman Shalash [36] who nitrated both
amylose and amylpectin and gave an extensive review of the literature on nitrostarch.

Here are the main points of Shalash's work.

*Nitration of amylose.* This was achieved by using a nitrating mixture of nitric acid and acetic anhydride in volume proportions 50:50 and 60:40. Table 59 gives the main results.

<table>
<thead>
<tr>
<th>Ratio Amylose:Acid</th>
<th>Temperature °C</th>
<th>% N in the product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10</td>
<td>10</td>
<td>13.4</td>
</tr>
<tr>
<td>20</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>13.66</td>
<td></td>
</tr>
<tr>
<td>1:25</td>
<td>10</td>
<td>13.5</td>
</tr>
<tr>
<td>20</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>13.76</td>
<td></td>
</tr>
<tr>
<td>1:50</td>
<td>10</td>
<td>13.6</td>
</tr>
<tr>
<td>20</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>13.8</td>
<td></td>
</tr>
</tbody>
</table>

*Nitration of amylpectin.* The nitration was carried out with nitric acid in the presence of pyridine. The nitration is extremely fast and the esterification equilibrium is reached at a relatively low degree of nitration as denitrification intervenes.

Using nitric acid: pyridine ratio 70:30 and amylpectine: (nitric acid—pyridine) = 1:50 at 10°C, the product contained:

- after one hour: 11.45% N,
- after two hours: 12.25% N,
- after three hours: 12.7% N,
- after four hours: 12.1% N.

Among other published papers on nitrostarch is that of Vollmert [37]. He nitrated starch with N₂O₅ vapour and obtained the product with 9.7–10.0% N.

X-ray analysis was carried out simultaneously with Kołaczkowska and T. Urbański (Vol. II, pp. 422–423) by Berl and Kunze [38] and by Centola [39]. The former authors examined both: amylose nitrate and amylpectine nitrate.

**NITRATES OF VARIOUS CARBOHYDRATES**

The thesis of Delpy [40] should be mentioned. He described the nitration products as follows:

**CARBOHYDRATE NITRATES**

- Hydrocellulose nitrate, 12.61% N
- D-glucose nitrate 15.99% N (a sticky, soft substance),
- D-mannose nitrate 15.40% N (as above),
- D-fructose nitrate 13.56% N, crystals, m.p. 50–60°C,
- Saccharose nitrate 14.54% N, solid
- Maltose nitrate 12.03% N,
- Raffinose nitrate 14.36% N.

The nitration was carried out with a mixture of nitric acid (43.4%), sulphuric acid (44.25%) and water (11.85%).

**POLYVINYL NITRATE** (Vol. II, p. 173)

Efforts are being made to find an explosive polymer with properties similar to those of nitrocellulose. Naturally attention was directed towards the nitration of polyvinyl alcohol as the most accessible high molecular polyhydroxyl alcohol. It is described in the chapter dedicated to explosive polymers (Chapter XIV).

**NITRO-DERIVATIVES OF LIGNIN** (Vol. II, p. 433)

Attention is drawn to the monograph by Brauns and Brauns [42]. Although published in 1960 it contains a description of the main work on nitration of lignin.

The diagram suggested by Fraudenberg (Vol. II, p. 435) with the nitration of aromatic ring has generally speaking been confirmed.

The most important seem to be the paper published by Liersch and Schaeck [43], Ivanov, Chukasova and Sergeeva [44].

The form using the nitrating mixture with 7.4% of water at 20°C yielded the product containing 12.2% N [43]. The latter nitrated lignin with nitric acid—phosphoric acid and nitric acid—acetic anhydride and obtained the product with 7.5% N [44].

No practical application has been found for the products of nitration.

**REFERENCES**

2. G. D. HIATT and W. J. REBEL, in [1].
CARBOHYDRATE NITRATES

1278 (1956).
CHAPTER 13

N-NITRO COMPOUNDS
(N-nitramines and N-nitramides (Vol. III, p. 1)

This important group of explosives has recently received particular attention due mainly to heterocyclic nitramines—Cyclonite (RDX) and Octogen (HMX). Interest has also been maintained in Nitroguanidine and EDNA.


Darnezi and co-workers [193, 194] revealed the formation of free radicals from secondary nitramines as the result of γ and ultra-violet radiation. Recently Dubovitskii and Korsunskii [4] have reviewed nitramines from the point of view of the kinetic value of their thermal decomposition and came to the conclusion of free radical chain reaction of breaking the N−NO₂ bond. Also a monograph on octogen has appeared [5].

STRUCTURE AND CHEMICAL PROPERTIES

Very little can be added as regards the electronic spectra of nitramines (Vol. III, p. 3). Among earlier papers were those of Kortiim and Fineh [6], Mehlert [7]. The latter author reported two maxima for Cyclonite in ethanol: 202 nm and a shoulder at 236 nm. Piskorz and T. Urbanski [8] found the maxima at 232 nm. Two maxima 218−224 and 262−266 nm were present when the molecules contained other chromophores: C=O and C=NH in nitrourea and nitroguanidine (see also Vol. III, p. 25).

Infra red spectra [8, 9] were reported to show the frequencies:

\[
\begin{align*}
\text{NO}_2 \nu_{\text{sym}} & : 1630−1550 \text{ cm}^{-1} \\
\text{NO}_2 \nu_{\text{asym}} & : 1354−1262 \text{ cm}^{-1} \\
\text{N−N} & : 1000−948 \text{ cm}^{-1}
\end{align*}
\]

See also the frequencies of N-nitrosamines [10].

In primary nitramines the frequency NH can be lowered to 3253−3240 cm⁻¹ through hydrogen bonds between NH and NO₂ of neighbouring molecules or

neighbouring groups in dinitramines. In deuterated compounds it can be lowered to 2400 cm⁻¹ [11].

Primary nitramines are weak acids, for example, methyl nitramine shows 
\[ pK_a = 6.0 \] [3].

The dissociation constants of N-nitro derivatives of α, α-dinitramines also indicate their weak acid properties [12].

Nitramino compounds containing =N−NO₂ should also be included in the group of compounds belonging to nitramines and nitramides.

On the contrary a N-nitro derivative of hydrazine, the nitroimide (I) (obtained by dehydration of quaternary nitrate of substituted hydrazine) possesses weak basic properties (\[ pK_a = −4.2 \pm 0.1 \]) as shown by Epstain and Katritzky [13]:

\[
\text{(CH}_3\text{)}_3\text{N}−\text{NH}_2\text{NO}_2^− \xrightarrow{\text{Ac}_2\text{O}} \text{(CH}_3\text{)}_3\text{N}−\text{N}=\text{NO}_2^−
\]

It should be pointed out that considerable effort has been made to obtain N-nitrohydrazine from unsubstituted hydrazine. The existing descriptions in the literature [66–69] cannot be considered as conclusive. Thus the nitration of \( N,N' \)-dibenzoxyhydrazine did not yield \( N,N' \)-dinitrobenzoylhydrazine [69] but an unsymmetrical \( \alpha,\alpha' \)-dinitrobenzoyl benzoate (II):

\[
\begin{align*}
\text{II}
\end{align*}
\]

This was revealed by Lamberton and Harper [70].

Chiral nitramines—derivatives of piperidine show an optical activity according to Ferber and Richardson [14]. Symmetrical compound III is non-chiral, asymmetrical compounds IV and V are chiral and optically active:

\[
\begin{align*}
\text{III} & \quad \text{IV} & \quad \text{V}
\end{align*}
\]

The disputed existence of unstable \( \alpha,\alpha' \)-form of primary nitramines (Vol. II, p. 4) seems to be substantiated by Orton as early as 1902 [15]. Acting with alkalis on 2,4-dibromo-6-nitro-phenyl-1-nitramine he obtained a sodium salt which on acidification yielded a colourless unstable \( \alpha,\alpha' \)-product VI which was quickly transformed into the orange nitramine VII:
The nitramine group attached to the pyridine ring can readily be replaced by halogen while acting with nitrous acid and hydrochloric or hydrobromic acid [16, 17]:

\[
\begin{align*}
\text{NHNO}_2 + \text{HCl \ or \ HBr} & \xrightarrow{\text{HONO}} \text{Cl \ or \ Br} \\
\text{NHNH}_2 & \xrightarrow{\text{FCl}} \\
\text{NO}_2 & \xrightarrow{\text{Cl}} \\
\end{align*}
\]

The reaction of nitramines with α-halogenoethers was studied by Thamer and Unterhalt [22] (6):

\[
\begin{align*}
\text{R}\text{CH}_2\text{NNO}_2 \text{N}\text{A}^+ + \text{CICH}_2\text{OR}^2 & \xrightarrow{\text{CH}_3\text{CN}} \text{CH}_3\text{CN} \\
\text{R}\text{CH}_2\text{NNO}_2 \text{N}\text{A}^+ + \text{CH}_3\text{N} = \text{N OCH}_3 \\
\end{align*}
\]

The same authors described a different trend of the reaction with α-halogenoethers [23].

Primary nitramines react with formaldehyde to yield α-hydroxymethyl compounds. The reaction is reversible [24]:

\[
\begin{align*}
\text{R} \text{NH} + \text{CH}_2\text{O} & \xrightarrow{\text{NO}_2} \text{R} \text{NCH}_2\text{OH} \\
\end{align*}
\]

The next step is the Mannich reaction (8) [24] which (as pointed out by Wright [2]) was carried out with nitramines by Franchimont [25] earlier than the work of Mannich:

\[
\begin{align*}
\text{RNCH}_2\text{OH} + \text{R'}_2\text{NH} & \xrightarrow{\text{NO}_2} \text{RNCH}_2\text{NR'}_2 + \text{H}_2\text{O} \\
\end{align*}
\]

Bases VIII are soluble in water and split CH₂O through the action of alkalis, contrary to Mannich bases which are insoluble in water and stable towards alkalis.

By using primary amines R NH₂ Chapman, Owston and Woodcock [26] obtained nitramines with two nitro groups (9):

\[
\begin{align*}
\text{R} \text{NH} + \text{CH}_2\text{O} + \text{R'}_2\text{NH} & \xrightarrow{\text{NO}_2} \text{R'}_2\text{NH} \\
\end{align*}
\]

Also the same authors obtained cyclic nitramines by reacting nitramine (NH₂NO₂) (10) or primary dinitramines with primary amines:
A wide range of cyclic nitramines through the reaction of dinitramines with formaldehyde and diamines were obtained and studied by Bell and Dunstan [27] and Novikov and co-workers [28]. Bell and Dunstan reported reaction (11) and formation of compounds 1Xa, b, c:

\[ \text{NO}_2 + \text{CH}_2 - \text{NH} + 2\text{NH}_3 + \text{CH}_2\text{O} \rightarrow \text{NO}_2 \text{CH}_2\text{N} - \text{NO}_2 \text{CH}_2\text{N} - \text{NO}_2 \]

Novikov et al. [28] described a number of cyclic products from the reactions:

\[ \text{NO}_2 + \text{CH}_2\text{O} + 4\text{H}_2\text{O} + \text{NH}_3\text{RNH}_2 \rightarrow \text{R} \]

Formaldehyde can replace chlorine in N-chloro-N-nitramines to form an alcohol [29]:

\[ \text{R} \text{N}=\text{O} + \text{CH}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{R} \text{N} \text{CH}_2\text{OH} \]

The alcohols can be nitrated to yield O-nitro N′nitro compounds (X):

\[ \text{R} \text{N} \text{CH}_2\text{ONO}_2 \]

According to Major and Denkstein [30] such esters are unstable, can readily decompose and are dangerous on storage.

Acetylation of primary nitramine occurs with great difficulty. Acetyl chloride can acetylate potassium or silver salts of primary nitramines with a yield according to White and Baumgarten [31]. It is rationalized that the difficulty of acetylating metal salts of primary nitramines comes probably from the assumption that the metal salts of nitramines are chelate compounds and not true salts.

Salts of nitramine can react with fluorine to yield fluoronitramine, for example, C₄H₈N F [32]:

\[ \text{NO}_2 \]

Among other different reactions of primary nitramines alkylation should be mentioned. Methylation can be carried out with diazomethane and can yield methylated products at both nitrogen (14) and oxygen (15) [33, 132]:

\[ \text{CH}_3\text{NH} \xrightarrow{\text{N}_2} \text{CH}_3\text{NCH}_3 \]

\[ \text{C}_6\text{H}_5\text{NHNO}_2 \xrightarrow{\text{CH}_3\text{N}_2} \text{C}_6\text{H}_5\text{N} = \text{N} \xrightarrow{\text{OCH}_3} \]

Alkylation can also be carried out with alkyl halides and dimethyl sulphate. As a rule O-nitro derivatives are being formed [34], viz. (16):
PREPARATION OF NITRAMINES

The methods described in Vol. III, p. 8 remain valid. The only addition related to the formation of dinitramines is given below.

Formation of Dinitramines from Nitroguanidine

This original method was described by McKay and Wright [43] and McKay and Manchester [44]. The method consists in reacting diamines with nitroguanidine to form cyclic products, which after nitration and hydrolysis produced dinitramines (20):

\[
\begin{align*}
\text{(CH}_2\text{)}_n & \quad \text{H}_2\text{NCONHNO}_2 \\
\text{NH}_2\text{Cl} & \quad \rightarrow \quad \text{(CH}_2\text{)}_n \quad \text{C} - \text{NHNO}_2 \quad \text{HNO}_3
\end{align*}
\]

By this method 1,2-dinitraminopropane, 1,3-dinitraminobutane and 1,3-diamino-2-nitroxypropane were obtained. For more reactions of nitroguanidine see review [3].

N-NITROENAMINES

Some of this group of compounds can be subjected to an interesting 1,3-rearrangement of N-nitroenamines to C-nitro compounds according to Büchi and Wüsst [71]. A simple refluxing of N-nitroenamine in xylene under an atmosphere of argon gave the reaction (21):

\[
\begin{align*}
\text{CH}_3 & \quad \text{NO}_2 \\
\text{H} & \quad \text{H} \quad \text{CH}_3 \\
\text{X}_{1b} & \quad \text{NH}_2
\end{align*}
\]

According to N\textsuperscript{15}-NMR in aqueous solution it has nitramine structure (X\textsubscript{1b}). Naturally occurring nitramines have also been described, for example, N-nitroglycine [41] and \(\beta\)-nitrosaminealanine [42].

ALIPHATIC NITRAMINES AND NITRAMIDES (Vol. III, p. 15)

Nitramine (Nitramide)
\[\text{NH}_3\text{NO}_2\]
\[\text{m.p. 72–73°C}\]
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

Nitramine offered a considerable interest owing to the simplicity of its molecule (the simplest N-nitro compound).

Acid and base catalysed decomposition of NH₂NO₂ has already been described by Hamnett [45] who also mentioned earlier works such as that of Brønsted and Pedersen [46]:

\[
\text{NH}_2\text{NO}_2 \xrightarrow{\text{Base}} \text{N}_2\text{O} + \text{H}_2\text{O}. \quad (22)
\]

Marlies and La Mer [47] confirmed their results.

A wide examination of the base-catalysed decomposition of NH₂NO₂ was given by Kresse and co-workers [48, 49]. They suggested two parallel decomposition pathways:

\[
\text{B + NH}_2\text{NO}_2\text{H} \xrightarrow{} \text{BHNO}_2\text{H} \xrightarrow{+} \text{BH}^+ + \text{N}_2\text{O} + \text{OH}^-. \quad (23)
\]

ETHYLENE DINITRAMINE (EDNA, HALITE) (Vol. III, p. 18)

Preparation. Among different methods of preparing EDNA the method of Franchimont and Klobbie (Vol. III, p. 18) was repeated [50] by boiling dinitromethyleneurethane with alcoholic ammonia followed by acidifying the solution with hydrochloric acid and with an overall yield of 60%.

According to American sources issued in 1971 [51] the full method of making EDNA consists in the following steps:

\[
\text{CH}_2\text{O} + \text{HCN} \xrightarrow{} \text{HOCH}_2\text{CN} \xrightarrow{98\%} \text{NH}_2\text{NCH}_2\text{CN} \xrightarrow{\text{H}_2\text{O} + \text{H}_2 \text{(high pressure)}} \text{N}_2\text{O} \xrightarrow{220^\circ C/800 kg/cm}^2 \text{CO}_2 \xrightarrow{\text{220^\circ C/800 kg/cm}^2} \text{CH}_2\text{NH} \xrightarrow{95^\circ C} \text{CH}_2\text{NH} \xrightarrow{95^\circ C} \text{N}_2\text{O} \xrightarrow{98\%} \text{HNO}_3 \xrightarrow{98\%}
\]

EDNA

For nitration fuming nitric acid was used and the overall yield was 70% which made the product reasonably cheap.

N-NITRO COMPOUNDS

Physical and Chemical Properties

Pure EDNA has a m.p. of 177–179°C but begins to decompose at 175°C.

Structure by X-raying was determined by Llewellyn and Whitmore [52]. Atomic centres are confined (according to this analysis) to laminae paralleled to (001) approximately of 1.72 Å in thickness. The length of bonds are: NO 1.21 Å (as in nitromethane), C–C 1.52 Å, C–N 1.41 Å, N–N 1.33 Å. The short N–N bond is probably due to positive charges on both N atoms, as has been previously pointed out [11].

Specific gravity of crystals is 1.71 and the density of the pressed substance is

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Water</th>
<th>Solvent</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.25</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.75</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>2.13</td>
<td>5.19</td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>4.38</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>6.38</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>20</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

The solubility is given in Table 60.

EDNA is reactive owing to the presence of two primary N-nitro groups and according to Goodman [53] can readily form the imidazol ring:

\[
\text{CH}_2\text{NH} \xrightarrow{\text{paraformaldehyde}} \text{CH}_2\text{N} \xrightarrow{\text{CH}_2\text{NH}} \text{CH}_2\text{N} \xrightarrow{\text{NO}_2} \text{CH}_2\text{N} \xrightarrow{\text{NO}_2} \text{NO}_2
\]

EDNA is decomposed by hot dilute sulphuric acid (Vol. II, p. 20) and 20% NaOH [51].
Explosive Properties

EDNA is an exceptional, very strong, high explosive which is not very sensitive to impact but has a relatively low ignition temperature.

Thus initiation temperature is:

175°C after the induction of 5 sec. [54]
or 189°C after the induction of 5 sec.
216°C after the induction of 1 sec. [51]
265°C after the induction of 0.1 sec.
and 202°C on the basis of the differential thermal analysis [55].

The sensitivity to impact is similar to that of TNT.

Tomlinson [56] examined the decomposition of EDNA in water, dilute sulphuric acid and TNT at different temperatures: 60-120°C and 120°C respectively. EDNA is only sparingly soluble in molten TNT (ca. 5% solubility), but the rate of decomposition much increased in the solution. EDNA in solution decomposed by a second order mechanism with the activation energy \( E = 20-35 \text{ kcal/mol} \). High acidity favours a low value of \( E \).

In the solid state the decomposition follows a chain mechanism with \( E = 40-50 \text{ kcal/mol} \).

EDNA decomposes principally through the aci-form to yield glycol, acetaldehyde and nitrous oxide, probably according to the scheme (26):

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{NO}_2 & \xrightarrow{N_2 \text{O}} \text{CH}_2\text{OH} \quad \text{CH}_3\text{OH} \\
\text{CH}_2\text{NH}_2 & \xrightarrow{\text{CH}_2\text{OH}} \text{CH}_2\text{OH} \quad \text{CH}_3\text{OH}
\end{align*}
\]

\( \text{(26)} \)

Heat of combustion [57] was found to be \( -2464.6 \text{ kcal/kg} \).

Heat of formation at \( C_p \) is \(-148 \text{ kcal/kg} \) and at \( C_p \) \(-176 \text{ kcal/kg} \) [58]. Heat of explosion 1276 kcal/kg and volume of gases 908 l/kg [51].

The explosive properties according to Fichetroule [50] were: the velocity of detonation at the densities

<table>
<thead>
<tr>
<th>Density</th>
<th>Velocity of Detonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.15</td>
<td>6105 m/s</td>
</tr>
<tr>
<td>1.25</td>
<td>6800</td>
</tr>
<tr>
<td>1.35</td>
<td>7130</td>
</tr>
</tbody>
</table>

and lead block test 129% of picric acid, and Encyclopaedia [51] gives for the velocity of detonation 7570 m/s for pressed, unconfined charge of 25.5 mm diameter.

Nitroguanidine also described mixtures of EDNA with ammonium nitrate. The stoichiometric mixture of 42.8% EDNA and 57.2% NH₄NO₃ gave the velocity of detonation 6185 m/s at density 1.35 and lead block 113.5% of picric acid.

Specification of EDNA for US Army of 1943, amended 1947 [51] is as follows:

- **Moisture:** 0.1% max.
- **Colour:** white or buff
- **M.P.:** 174°C min.
- **Purity** (by dissolving in aqueous NaOH): 99% min.
- **Insoluble matter** (by dissolving in boiling water): 0.1% max.
- **Granulation:** US Standard Sieve No. 10 100% min
  - US Standard Sieve No. 100 20% max.

NITROGUANIDINE

Nitroguanidine became an important ingredient of treble base powder containing nitrocellulose—diglycylidinitrate—nitroguanidine (Vol. III, p. 664).

Nitroguanidine was subjected to some theoretical work, such as that dedicated to elucidating the structure:

\[
\begin{align*}
\text{NH}_2 & \quad \text{NH} & \quad \text{NH}_2 \\
\text{C}_2 & \quad \text{C}_2 & \quad \text{C}_2
\end{align*}
\]

X-ray analysis carried out by Bryden and co-workers [59] favoured the nitrinimo form. Also NMR analysis of Richards and York [60] showed that the solid nitroguanidine exists in the imino form. Owen [61] calculated the MO of several compounds containing nitrogen and among them nitroguanidine and came to the conclusion that the calculated imino form fits better to the experimental values, as shown in Table 59, with the diagram of bond lengths. The imino structure was also confirmed by Kumler and Sah [62] measurement and calculation of dipole moment.

It is currently accepted that in the solid state nitroguanidine is in the imino-form, but in a solution both forms are present and are in the equilibrium [63]. Kemula and his co-workers [64] examined the change of the ultraviolet absorption spectrum with the change of pH. The spectrum so far published revealed two maxima in aqueous or acid solution: 210 and 265 nm (Vol. II, p. 25, Fig. 4). Kemula et al. found 246 and 264 nm. The same frequencies are in the alka-
Reactions of Nitroguanidine

Very little can be added to the description of the chemical properties of nitroguanidine described in Vol. III, p. 25. Some of the reactions with nitroguanidine leading to dinitramine were given on p. 361.

Nitroguanidine in concentrated sulphuric acid can be used as a nitrating agent through the reaction:

$$\text{NH}_2\text{N} = \text{NH} + \text{H}_2\text{SO}_4 \rightarrow \text{C} = \text{NH} + \text{H}_2\text{SO}_4 + \text{NO}_3^+$$ (27)

Anthraquinone was nitrated to 1,5-dinitro-anthraquinone by T. Urbański and Żylkowski [65]. The temperature of nitration was 110–120°C for 1 hour and the yield 67%.

Specification according to Meyer [72]

The existing specifications describe nitroguanidine as a white, free flowing crystalline powder of two types. Both types should correspond to the following requirements:

- Ash content: 0.30% max.
- Acid content (as H₂SO₄): 0.06% max.
- Volatile matters: 0.25% max.
- Sulphates: 0.20% max.
- pH: 4.5–7.0
- Type I grain size: 4.3–6.0 μ
- net content: min. 98%
- Type II grain size: 3.3 μ max.
- net content: min. 99%

<table>
<thead>
<tr>
<th>Bond</th>
<th>Nitratinmo Form I</th>
<th>Nitratinmo Form II</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–NH₂</td>
<td>1.36</td>
<td>1.36</td>
</tr>
<tr>
<td>C–N</td>
<td>1.35</td>
<td>1.34</td>
</tr>
<tr>
<td>C–NH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N–N</td>
<td>1.29</td>
<td>1.35</td>
</tr>
<tr>
<td>N–O</td>
<td>1.23</td>
<td>1.22</td>
</tr>
</tbody>
</table>

NITROAMINOGUANIDINE

Nitroaminoguanidine can be obtained by acting with hydrazine on nitroguanidine [168, 184]:

$$\text{NH}_2\text{N} = \text{NH} + \text{H}_2\text{O} \rightarrow \text{C} = \text{NH} + \text{NH}_2\text{H}_2\text{O} + \text{H}_2\text{O}$$ (28)
By reacting with nitrous acid in acetic acid it yields 5-aminoazotetrazole [185]. Aminotetrazoles are related to initiating explosives obtained from aminoguanidine (Chapter XVII, and Vol. III, p. 206).

Nitrimes $R_1N=N\cdot NO_2$  

The chemistry of nitroguanidine and the work of Büchi are related to the chemistry of nitrimes, that is, compounds containing $C=N\cdot NO_2$ group. The structure of this group was given by Scholl [75], but was subject to criticism and a few structures were suggested by Fusco and Trasaghis [76] and Freeman [77]. Freeman found the confirmation of the nitrime structure by ultraviolet, infra red spectra, and the transformation of the group into the primary amino group by reducing with potassium borohydride.

$N\cdot NO_2 \xrightarrow{\text{KBH}_4} NH_2$  

NITRODIETHANOLAMINE DINITRATE (DINA) (Vol. III, p. 36)

This interesting compound was investigated by French chemists who gave thermoochemical properties: heat of combustion $\Delta H_c = 577$ kcal/mol and heat of formation $\Delta H_f = 70.5$ kcal/mol. [89].

Preparation

Desseigne [88] added some information to the method of G. E. Wright et al. (Vol. III, p. 36). Here are the main points of the process.

A nitratior was filled with 170 parts of acetic anhydride (99%) and 1.4 parts of hydrochloric of diethanolamine dissolved in 4 parts of acetic acid. Diethanolamine (52.5 parts) and 107 parts of nitric acid (97%) were added keeping the temperature at 10–15°C. After that mixing had been continued for 10–15 min, the product (DINA) began to precipitate. All was poured on ice (200 parts), filtered and washed with water followed by washing with hot 0.25% aqueous solution of sodium carbonate. At the end the solution should be neutralized with acetic acid. The product was finally purified by dissolving in acetone and precipitating with water containing a small amount (ca. 0.3%) of ammonia.

The yield was 108 parts, i.e., 90% of theoretical.
The m.p. of the product was 50.15°C.

The rate of detonation is 7730 m/s at density 1.60 and 7580 m/s at 1.55. Lead block 146% of picric acid. It shows a lower stability at 100°C and higher sensitivity to impact than tetryl [90].

Glaskova [92] in her monograph described experiments of burning DINA and the influence of various additions. The addition of dichromates of cations (particularly of potassium dichromate) increases the rate of burning.

DINITRODI-(o-HYDROXYETHYL)-OXAMIDE DINITRATE (NEO)  

Vol. III, p. 37

Desseigne [91] repeated experiments of nitration of the amide (XIIa) in two steps:

\[
\begin{align*}
\text{CO} & \rightarrow \text{NHCH(CH}_2\text{OH)}_2 \\
\text{CO} & \rightarrow \text{NHCH(CH}_2\text{OH)}_2 \\
\text{XIIa} & \rightarrow \text{CO} \rightarrow \text{NHCHCH}_2\text{ONOO}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{CO} & \rightarrow \text{NHCHCH}_2\text{ONOO}_2 \\
\text{CONCH}_2\text{CH}_2\text{ONOO}_2 & \rightarrow \text{CONCH}_2\text{CH}_2\text{ONOO}_2 \\
\text{XIIb} & \rightarrow \text{CONCH}_2\text{CH}_2\text{ONOO}_2 \\
\end{align*}
\]

The nitration was difficult and required the use of nitric acid with 60% oleum at 25°C with an overall yield of 75%. Compound XIIb can dissolve nitrocellulose and could be used according to Desseigne in double base propellants.

AROMATIC NITRAMINES

Aromatic nitramines can be subjected to 'Bamberger rearrangement' described for the first time by E. Bamberger in a number of papers since 1893 [78, 79].

\[
\begin{align*}
\text{RNO}_2 & \rightarrow \text{NHRNO}_2 \\
\end{align*}
\]

Bamberger advanced a hypothesis that the nitration of the aromatic ring of aromatic amines begins by $N$-nitration followed by a subsequent rearrangement. The hypothesis was examined by Holleman and co-workers [80] who concluded that ring nitration does not always proceed by way of an initial $N$-nitration. Also Orton with co-workers studied the mechanism of the reaction in a number of papers [81]. He concluded that the Bamberger rearrangement is an acid catalysed reaction.
Hughes and co-workers [82, 83] in a number of papers examined the mechanism of the reaction by using nitrogen isotopic [15N] and [2H] label. They came to the conclusion that the Bamberger rearrangement is an intramolecular mechanism. They rationalized it in terms of the formation of nitrites:

\[
\begin{align*}
\text{HNO}_2 + \text{H}_2\text{O} & \quad \xrightarrow{\text{H}^+} \quad \text{H}_2\text{O} + \text{NH}_2\text{NO}_2 \\
\text{NH}_2\text{NO}_2 & \quad \xrightarrow{\text{H}^+} \quad \text{H}_2\text{O} + \text{N}_2\text{O}_3
\end{align*}
\]

\[\text{(31)}\]

U.S. chemists [84] examined the action of 0.1 N hydrochloric acid on N-methyl-N-nitraniline at 40°C and obtained:

- ca. 52% o-nitro-N-methylaniline
- 31% p-nitro-N-methylaniline and
- 7% N-methylaniline.

Nitrous acid (ca. 13%) was also formed.

They also came to the conclusion that the rearrangement is an acid catalysed reaction.

**TETRYL** (Vol. III, p. 40)

In the course of the last few years the significance of tetryl has been considerably reduced. With the advent of Cyclonite (RDX) and PETN, tetryl is losing its significance in the U.S.A. It was withdrawn from use. Also compounds similar to tetryl with N-methyl-N-nitro side group have aroused less interest lately.

Nevertheless a few published papers have appeared mainly referred to thermal decomposition of the substance. Former data (Vol. II, pp. 52–53) were confirmed in general, but completed by more detailed experiments. Thus Dubovitskii, Merzhanov and co-workers [85] examined the influence of the density of loading \(m/v\), where \(m\) = the mass of the substance, \(v\) = the volume) at 150°C. Some of their results are shown in Fig. 53. It can be seen that the density has little effect on the rate of decomposition. The gases evolved were composed of \(\text{NO}_2\), \(\text{NO}\) and \(\text{N}_2\). High (1) and low (3) density.

**NITRO COMPOUNDS**

![Figure 53](image)

**FIG. 53.** Thermal decomposition of tetryl [85]. \(m/v\) in g/cm\(^3\), 10\(^{-4}\): 1–
353.5, 2–49.4, 3–6 (removal of gases); \(\eta\) (degree of decomposition).

Hara, Kamei and Osada [86] obtained similar results. Among the gases from the decomposition of tetryl they also found methane. They carried out the experiments at temperatures from 150 to 175°C. By differential thermal analysis they found the endothermic (negative) peak at 131°C due to the melting of the substance and exothermic decomposition occurred at 160°C. They calculated the activation energy as being 35 kcal/mol. This is in agreement with formerly obtained results (Vol. III, p. 53).

Pre-heating of tetryl increases the rate of burning of the substance. This was already shown by Andreev (Vol. III, Fig. 6), by his later work [94] and substantiated by M. M. Jones and Jackson [87] and Japanese authors [86]. The latter authors found for example that preheating the sample to 180°C lowers its m.p. by 20°C and the decomposition temperature by 12°C. They also examined the samples of tetryl heated at 165°C for 3 hours: by liquid chromatography, by TLC, NMR and mass spectroscopy. They found that 2,4,6-trinitroanisol and picric acid are formed on the thermal decomposition of tetryl at 160–200°C.

Burning of tetryl is discussed in the monograph by Glazkova [92] and reference is given to the early work of Hinshelwood [93] who pointed out that thermal decomposition of tetryl produces picric acid which plays the part of a catalyst of the decomposition. The rate of burning of tetryl under pressure increases by addition of potassium bichromate, according to Glazkova [92].

Thermal decomposition of tetryl was reviewed by Dubovitskii and Koronski [4].
HETEROCYCLIC NITRAMINES (Vol. III, p. 77)

Cyclonite (Hexogen, RDX) (Vol. III, p. 77)

Cyclonite (RDX in Anglo-Saxon literature, that is, Research Department Explosive) 1,3,5-trinitro-1,3,5-triazacyclohexane is at present one of the most important explosives. Over the last two decades extensive literature has been dedicated mainly to its analysis and application.

Structure

The structure of RDX has been characterized by X-ray analysis [95]. Dipole moments measurements to establish stereochemistry of nitramines have been extensively used by a few authors: G. F. Wright [96], Calderbank and Pierens [97].

The latter authors [97] found that the chair calculation 22.27 D corresponded best to experimental value 19.1 D (boat conformation and twist boat conformations gave calculations 5.81 D and 7.04 D respectively). Calderbank and Pierens also measured and calculated the Kerr effect (electric birefringence) and found the calculated value for chair conformation (−2868) fitted best to the experimental figure (−2102). The boat and twist boat conformations gave figures distant from the experiments (+172 and +164 respectively). The conclusion of these authors was that the preferred conformation of cyclonite corresponds in 70% at least of chair.

Delpuech and Cherville [98] calculated electric charges in cyclonite by CNDO method [99]. The results are given in Fig. 54.

![Fig. 54. Electron density of cyclonite](image)

Spectroscopy of Cyclonite

Electronic spectrum of cyclonite has been examined by a number of authors [7, 100, 101] who found a maximum at 202 nm and a shoulder at 236 nm. Later examination of spectra [102] confirmed these results for cyclonite dissolved in ethanol. In methanol they were slightly different: 204 and 234 nm.

Infra-red spectroscopy was given in the monograph of Bellamy [103].

Chemical Properties

Contrary to aromatic nitro compounds cyclonite does not readily give adducts. No charge-transfer complexes are formed with amines. Selig [104] established the existence of an adduct of cyclonite with hexamethylphosphoramic triamide (HMPT). Another complex with tetrahydrothiophene-1,1-dioxide (sulfolane) was described by French authors [105, 106]. Recently Selig [107] reported that a number of heterocycles with nitrogen or sulphur could form the adducts. Relatively stable equimolar complexes were obtained with:

![Complexes XIII to XVI](image)

XIII–HMPT, XIV–Sulfolane, XV–Tetrahydrothiophene-1-oxide, XVI–1,4-Butane sulone, XVII–2,6-Litidin-5-oxide, XVIII–2,2,6,6-Tetramethyl-4-piperidone-1-oxide.

Compounds XIV and XVIII are 'selective' to hexogene: they do not form adducts with octogene, whereas all others form adducts with both: hexogene and octogene.

Cyclonite is decomposed in concentrated sulphuric acid and the decomposition yielded most likely nitronium ion (Vol. III, p. 81). This is evidenced by the fact that a solution of cyclonite in sulphuric acid can nitrate aromatic compounds.

Thus Holstead and Lambertson [108] obtained p-nitroacetanilide with a 45% yield when acting on acetanilide with a solution of cyclonite in 95% sulphuric
Acid. T. Urbański and Zyłowski [65] nitrated anthraquinone with the same solution at room temperature for 24 hours. The yield of 1,5-dinitroanthraquinone was 36%.

Croce and Okamoto [109] described a cationic micellar catalysis (Chapter IV) of aqueous alkaline hydrolysis of cyclonite (and octogene). Denitration occurred in the presence of ethylhexadecyl dimethylammonium bromide. Liquid chromatography was used as the analytical method (32):

\[
\begin{align*}
\text{O}_3\text{N} & \quad \text{O}_3\text{N} \\
\text{NO}_2 & \quad \text{CH}_3 \\
\text{OH} & \quad + \text{CH}_3 \\
\end{align*}
\]

1,3,5-Triaza-3,5-dinitrocyclohexene-1-ene resulted.

**Thermal Decomposition**

Thermal decomposition of cyclonite was investigated by numerous authors (also Vol. III, p. 83): [110–115]. Maksimov [111] described several experiments of decomposition of cyclonite and octogene as solid substances and in solution. The energy of activation was calculated as \( E = 52.0 \text{ kcal/mol} \), \( \log \beta = 19.1 \).

Figure 55 shows the decomposition of cyclonite in solution in \( m \)-dinitrobenzene at 160–200°C. A concentration of 4% was used with the exception of the sample examined at 190°C where the concentration was 13%. The energy of activation was \( E = 39.7 \text{ kcal/mol} \), \( \log \beta = 14.3 \). One of the conclusions of the authors was that cyclonite decomposes faster in solution than as a solid. This is in agreement with existing views that explosives in a liquid form decompose faster than solid due to the transition of the solid to a higher energy liquid state (experiments by T. Urbański et al., Vol. II, pp. 181–183). According to Maksimov the decomposition of hexogene at 180°C in solution is 16 times faster than in the solid state.

Cosgrave and Owen [115] and Debenham and Owen [170] studied the decomposition of cyclonite at 195°C and 173–184°C respectively. They came to the conclusion that the initial decomposition takes place in the vapour phase and is followed by a more rapid decomposition in the liquid phase (e.g. a solution of cyclonite in \( 1,3,5 \)-trinitrobenzene [170]).

Major products were: hydroxydimethyl formamide and its polymers. The following is a list of products of the decomposition: \( \text{N}_2, \text{N}_2\text{O}, \text{NO}, \text{CO}_2, \text{CO}, \text{CH}_3\text{O}, \text{H}_2, \text{H}_2\text{O}, \text{HCN}, \text{HCOOH}, \text{NH}_3, \text{NO}_3^-, \text{NO}_2^- \) and the polymer mentioned above.

Other work on thermal decomposition of cyclonite was done by Wilby [171], Rosen and Deacon [172], Rauch and Fanelli [173] and Batten [174].

Recently Kishore and Laye [115] examined thermal decomposition of cyclonite by differential scanning calorimetry. The curves of the decomposition are of an 'S' shape (similar to those of tetryl – Fig. 53). Isothermal curves are similar to Figs 55 and 56. The author calculated the \( E \) value of the decomposition of cyclonite in an open vessel as being \( 41 \pm 2 \text{ kcal/mol} \). They also reported the values of \( E \) obtained by other authors. In addition to those given in Vol. III, p. 83 (by Robertson), they are those of:

- Rogers and Morris [117] 67.5 kcal/mol
- Adams [118] 45.5 kcal/mol (203.5–261°C)
- Batten and Murdie [119] 67.0 kcal/mol (179–200°C)
- Hall [120] 45.2 kcal/mol (210–261°C).

**FIG. 55. Thermal decomposition of solid cyclonite [111]**.
Kishore concluded that the figure closest to 45 kcal/mol was the most reliable. The order of the reaction is 0.6 according to the same author. See also the review article of Dubovitskii and Korsunskii [4].

**Preparation of Cyclonite (Vol. III, p. 87)**

**Nitration of hexamine.** Very little can be added to the mechanism of the reactions leading to cyclonite, as given in Vol. III.

With regard to the nitration of hexamine with nitric acid Singh [121] brought a small change to the charge distribution in compound (Vlb—Vol. III, p. 89), and Lamberton et al. [122] added some more information on compound XIX (the same as 1a, Vol. III, p. 91).

Bell and Dunstan [123] subjected reactions of hexamethylenetetramine with nitric acid, at various temperatures, to a detailed examination. Addition of water to nitrolysis solution obtained by the action of nitric acid (98%) on hexamine at -30°C yielded P.C.X., that is 3,5-dinitro-3,5-diaza-1-azoniacyclohexane or 3,5-dinitro-3,5-diazapiperidinium nitrate (XIX) (Vol. III, p. 91, 1a). The nitrolysis mixture kept at 0°C for 2 hours yielded 83% RDX and traces of the linear compound: derivative of tetra-azonanone (IX of p. 89, 91, Vol. III).

Acetanhydride reacted with hexamine by nitrolysis to yield RDX, and linear derivatives of 2,4,6-trinitro-2,4,6-triazahexane: diacetoxy compound (Vol. III, p. 91, XV and dinitroxy (XX):

\[
\text{O}_2\text{NNO}_2\text{N}-\text{NH}-(\text{CH}_2)_{16}-\text{N}-\text{CH}_2-\text{N}-\text{CH}_2-\text{N}\]

**XX

A small quantity of linear dinitroxytetra-azonanone (IX, Vol. III, pp. 89, 91) was also formed.

By adding aqueous sodium nitrite to the nitrolysis mixture at -30°C, 75% yield of 1,3-dinitro-5-nitroso-1,3,5-triazacyclohexane (XXI) was obtained.

An interesting reaction was found when cold (-30°C) nitrolysis mixture was treated with methylenedinitramine CH(NO\textsubscript{2})\textsubscript{2} and after that kept at 30°C for 15 min. The yield of RDX was almost doubled from 82 to 145% calculated on the basis of hexamine - one mole of RDX.

Larger ring nitramines - homologues of RDX were obtained by adding dinitramines such as ethylene and trimethylenedinitramine. Homologues of RDX with cycloheptane and cyclooctane ring resulted.

These experiments suggested that bis(nitroxymethyl)diaminomethyl intermediate (XIII, Vol. III, p. 91) can be a probable precursor which upon nitrating to dinitrate and reacting with methylenedinitramine eventually yielded RDX according to scheme (34).

**Preparation of Cyclonite from Hexamine Dinitrate Acetic Anhydride**

The methods by W. E. Bachmann (in the U.S.A.) and Köfler (in Germany) - Vol. III, p. 111 have now received particular attention in view of the fact that the route with acetic anhydride can lead to the formation of Octogone (HMX).

Reed [124] described the reaction of hexamine, nitric acid, trifluoroacetanhydride in the presence of liquid SO\textsubscript{3} which is a very good solvent for hexamine. The reaction yielded (85%) 1-trifluoroethyl-3,5-dinitro-1,3,5-triazacyclohexane, m.p. 131-132°C.
Explosive Properties of Cyclonite (Vol. III, p. 84)

Little can be added to the information given in Vol. III as regards explosive properties of Cyclonite. Interesting information was recently given by Institut Franco-Allemand de Recherches de Saint-Louis, France [186]. The rate of detonation of single crystals of cyclonite was found to be different along different crystal axes:

$$(001) \ 8700 \text{ m/s}$$
$$(110) \ 8587 \text{ m/s}$$
$$(111) \ 8437 \text{ m/s}$$

T. Urbański and Galas [187, 188] examined the influence of non-explosive liquids on the velocity of detonation of cyclonite. The results with two liquids: water and glycerol are collected in Table 62. The shape of the curve: velocity of detonation against the proportion of liquids is much the same as for PETN and liquids as depicted in Fig. 42.

<table>
<thead>
<tr>
<th>Proportion of liquid %</th>
<th>Total Density $\rho$</th>
<th>Real Density $\rho_r$</th>
<th>Rate of detonation $V_o$ at density $\rho_r$</th>
<th>Difference $V_o/V_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.45</td>
<td>1.45</td>
<td>7705</td>
<td>7705</td>
</tr>
<tr>
<td>10</td>
<td>1.45</td>
<td>1.31</td>
<td>7235</td>
<td>7230</td>
</tr>
<tr>
<td>20</td>
<td>1.45</td>
<td>1.16</td>
<td>7775</td>
<td>6820</td>
</tr>
<tr>
<td>30</td>
<td>1.45</td>
<td>1.02</td>
<td>7070</td>
<td>6365</td>
</tr>
</tbody>
</table>

| Glycerol               |                      |                       |                                    |                  |
| 10                     | 1.40                 | 1.26                  | 7360                                | 7125             | 235                |
| 20                     | 1.40                 | 1.12                  | 7515                                | 6885             | 820                |
| 30                     | 1.40                 | 0.98                  | 7875                                | 5240             | 1635               |
| 35                     | 1.40                 | 0.91                  | 7740                                | 6015             | 1725               |
| 40                     | 1.40                 | 0.84                  | 7555                                | 5790             | 1765               |

Apin and Velma [189] also examined the velocity of detonation and the pressure of detonation of explosives with water. Apin, Pepekín et al. [190] subjected the cyclonite-water system to a detailed thermochemical examination.

They found a straight line increase of the heat of detonation against water content from 0 to 24% of water: 1380 cal/g of dry substance and 1187 cal/g of a mixture of 76% cyclonite and 24% water. This gives a calculated value for the dry substance 1565 cal/g. It corresponds also to the maximum of the increase of the velocity of the detonation $V_o/V_r$ (Table 62) [187, 188]. Further addition of water (above 24%) does not increase the heat of detonation [190] and the increase of the velocity of detonation $V_o/V_r$ drops [187, 188].

Apin, Pepekín et al. [190] explain the phenomenon of the increase in the rate of detonation by adding water in the following way. The liquid plays the part of a confinement which prevents the dispersion of the products of detonation and prolongs the time necessary to complete the reaction in a similar way to the action of a confinement. This is certainly true but according to T. Urbański [187–188] the importance of the covalence [191] should also be taken into consideration. Another factor which should be considered is the increase of entropy (S) and Gibbs free energy (G = H−TS) which is higher in a mixture than in the individual ingredients and T. Urbański [192] advanced an hypothesis that the high entropy and free energy play an important part in properties of explosives such as their rate of detonation and sensitivity to impact. According to T. Urbański the high entropy and free energy of mixtures is one of the factors which increases the rate of detonation of a solid explosive by adding a non-explosive liquid.

Manufacture of Cyclonite (RDX) according to Mario Biuzzi S.A. (Vevey) [123]

This process consists of continuous nitration of hexamine with nitric acid (98.5%), continuous 'decomposition' of the secondary products formed during nitration and continuous filtration of RDX from its spent acid.

The hexamine, dried and sifted is fed into the first nitratir with a constant feeding rate. The nitric acid is fed from a constant level overhead tank. The feeding rate is regulated by the remote control of a pneumatic valve. The contents of the first nitratir continuously overflow into the second and then to the third (last) nitratir.

From the last nitratir all overflows to the decomposing vessels. Decomposition is initiated by filling the first decomposer with some of the nitric acid (50%) obtained from the absorption of the nitrous gases evolved during decomposition. The RDX crystallizes out and is continuously separated by vacuum filters. The RDX cake is flushed on the filter with cold water. The dilute nitric acid goes through the filter into an intermediate vacuum tank equipped with a strainer retaining all the RDX which may escape from the filter. From the tank the acid is pumped into storage. The acid washing water is collected in a separate tank from where it is evacuated by pumping.

The RDX cake washed from the filter cloth is continuously evacuated into a slurrying tank where it is mixed with water and transferred by means of water injector to another building. Reactors are cooled with Freon 12.

During nitration gases are evolved. They are drawn from the equipment vessels by means of a fan to a tower where they are met with water in a counter-current.

The acid RDX/water slurry flows into a continuous vacuum filter, the transport water is drawn through the filter into an intermediate tank with a strainer.
to retain traces of RDX. From the filter RDX falls into a suspension funnel with aqueous sodium bicarbonate. The suspension flows into the stabilization battery made of a series of steam injectors separated by cooling elements. The injector stabilization battery removes the occluded acid. The injection of steam reduces the size of crystals and removes the acid.

From the stabilization battery, the RDX/water mixture flows to the phlegmatizer or to a continuous filter. If RDX is phlegmatized, this is done in three jacketed and stirred vessels where crystals are coated with wax. The molten wax is added to the first phlegmatizer and is hardened by cooling in the second and third vessels and finally filtered. Moisture content (both unphlegmatized and phlegmatized) - 10%.

Specification for Hexamine ‘Nitration Grade’
Moisture max. 0.2%
Crystal size: over 500 μ max. 30%
300–500 μ 70–85%
less than 200 μ max. 10%
Dust, sulphates, chlorides, heavy metals — absent
Water insoluble max. 0.10%
Ash max. 0.03%
Consumption for 1000 kg RDX
Hexamine 866 kg
Nitric Acid (calculated as 100%) 8530 kg
Process water 21000 kg
Phlegmatizing agent — according to requirements (see below)
Neutralizing agent (NaHCO₃) 3–5 kg.
Steam 4500 kg
Electric energy 1440 kWh
Compressed air 100 Nm³
Specification for RDX is according to U.S. Standards for type A product.

Specification for Cyclonite (Hexogen)

According to the Encyclopedia of Fedoroff and Sheffield [126], the specifications for Cyclonite in Germany and in the U.S.A. are as follows.

Germany (Vol. III, p. 105). Hexogen should be crystalline, dry, colourless and screened. Hexogen intended for use in detonators and percussion caps should be purified by crystallization (e.g. from nitrobenzene). Hexogen intended for phlegmatization and used in boosters should contain water.

Melting point: (a) for W-, K- and SH-Salz (Vol. III, p. 104) m.p. should be above 200°C, (b) for E-Salz above 190°C.

U.S.A. Specification of 1963 covers two types of RDX and light charges based on uses and granulation.

Type A — made by the nitric acid method.
Type B — made by the acetic anhydride process.

Properties:

<table>
<thead>
<tr>
<th></th>
<th>Type A</th>
<th>Type B</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p.</td>
<td>200°C</td>
<td>190°C</td>
</tr>
<tr>
<td>Acetate insoluble max.</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Inorganic insoluble max.</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Sieve No. 60 max.</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Acidity max.</td>
<td>0.05% as HNO₃</td>
<td>max. 0.02% as CH₃COOH</td>
</tr>
</tbody>
</table>

For the use of various classes of the fineness — see Encyclopedia [126].

Disposal of Waste Cyclonite (126)

A five per cent solution of NaOH should be brought to boiling point by injecting steam. Cyclonite should be added in small portions. After adding all the cyclonite boiling should be continued to be discharged into a sump.

Toxic Properties of Cyclonite (Vol. III, p. 86)

More information was collected on toxicity of Cyclonite. Experiments with animals confirmed earlier findings of convulsions caused by Cyclonite. The important observations on humans were: the same effects were caused by inhaling the dust of Cyclonite and one fatal accident has been recorded [195].

EXPLOSIVES WITH CYCLONITE AS A MAIN COMPONENT

The Encyclopedia of Explosives [169] classifies the explosives with cyclonite into three groups: A, B and C.
Group A consists of cyclonite desensitized with waxes, this was originally used during World War II. In Great Britain cyclonite was desensitized with 9% beeswax. In Germany Montan was used (Vol. III, pp. 105, 113) in quantity 5–10%. In the U.S. synthetic waxes are used: compositions A3 and A4 are composed of 91% RDX/9% wax and 97% RDX/3% wax respectively. The composition A3 was made by heating a water slurry of RDX to 100°C and adding the wax with a wetting agent. After the wax melted, all was cooled, filtered and dried at 75°C. Composition A5 contained 1.0–1.5 stearic acid (Type I) or 1.6% stearic acid and 0.4% graphite (Type II).

Aluminized composition A of 92% RDX and 8% aluminium was originally intended for an armour piercing shell, but was found to be too sensitive to shock.

Group B are castable mixtures of RDX, TNT and some of them were known as Cyclitols. Various proportions of RDX and TNT were used, for example in Germany during World War II: Cyclitols 50/50, 53/47 for bombs and demolition charges, cyclitrol 60/40 for some shells, cyclitrol 20/80 containing 20% cyclonite, 80% TNT and the addition of 1% Montan wax.

The U.S.A. used mixture cyclonite/TNT in proportion 60/40 with 1% of synthetic wax added (composition B) or without wax (composition B-2). Other compositions of cyclonite/TNT were: 75/25, 70/30 and 65/35. The rates of detonation varied from 7840 m/s (composition B) to 8060 m/s (composition 70/30), the densities were: 1.68–1.71.

Group C are plastic explosives (Plastic explosives in Great Britain, Explosifs plastiques in France, Plastit in Germany).

U.S. Composition C contained after several modifications, such as Composition C-3: cyclonite 77%, DNT 10%, MNT 5%, TNT 4%, Tetryl 3% and Nitrocellulose 1%. The last five ingredients served as a plasticizer. It gave lead block test 177° of TNT. It could withstand being plastic between −29°C and 77°C.

Composition C-4 developed by Ottoson and Lerner (according to [169]) contains 91% cyclonite and 9% of the plasticizer composed of 5.3% di-ethyl-hexyl sebacate, 2.1% polyisobutylene and 1.6% motor oil. It remains plastic between −57°C and 77°C.

A considerable number of explosives existed in different countries during World War II. Most of them contained Cyclonite, TNT and aluminium with desensitizing waxes. Their compositions are given in the Encyclopedia [175]. An interesting substitute for TNT in Germany was a castable explosive composed of 50% methylene diamine, 30% sodium nitrate, 15% Cyclonite. A German Füllpulver N 86 consisted of ethylenediamine dinitrate 46%, RDX 18% and wax 36%. German plastic explosives contained liquid or semi-liquid nitroaromatics with nitrocellulose.

OCTOGEN (HMX) (Vol. III, p. 117)

There is a growing interest in Octogen (HMX in Anglo-Saxon literature, High

Melting-Explosive), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclo-octane. This is due to remarkable explosive properties manifested by a very high velocity of detonation — over 9000 m/s (see explosive properties, p. 390). Also in some countries it is regarded as a heat resistant explosive because of its high melting point — 276–280°C (Chapter VII).

The fact that a monograph has recently appeared [5], indicates the great interest being shown in Octogen.

Structure and Physical Properties

Octogen exists in four polymorphic modifications: I–IV or α, β, γ, δ which are most likely conformational modifications. Each of the four can be obtained by crystallization from a different solvent keeping a different rate of cooling of the solution.

<table>
<thead>
<tr>
<th>Region of stability</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>to 115°C</td>
<td>246–247°C</td>
<td>256–259°C</td>
<td>278–280°C</td>
<td>280–281°C</td>
</tr>
<tr>
<td>Molar refraction R calculated</td>
<td>56.1</td>
<td>55.7</td>
<td>55.4</td>
<td>55.9</td>
</tr>
<tr>
<td>Sensitivity to impact</td>
<td>5/15</td>
<td>1/20</td>
<td>1/20</td>
<td>1/10</td>
</tr>
<tr>
<td>energy of impact kg/cm²</td>
<td>0.75</td>
<td>0.2</td>
<td>2.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

* Compiled from [5].

Here is the description according to Fedoroff and Sheffield [127]:

The common modification, stable at room temperature α–HMX is obtained by very slow cooling of HMX dissolved in acetic acid, acetone, cyclohexanone, acetonitrile, nitric acid or nitromethane. The crystals are monoclinic.

α–HMX can be formed from the same solution as above under condition of rapid cooling. The crystals are orthorhombic.

γ–HMX are also formed from the same solution but under a very rapid cooling. The crystals are monoclinic.

δ–HMX are formed from solvents in which the substance is only slightly soluble, such as acetic acid in small amounts and by rapid cooling by pouring over ice. Selig [128] obtained δ modification by crystallizing β from N,N-dimethyl-p-toluamide. The crystals belong to hexagonal system.

As regards to crystal shape and more information on crystallographic systems – see [5].

The change of modifications at different temperatures and their relative stability is given in Fig. 57 based on the literature [129, 130].
On the abscissae is given a relative value of free energy. The most stable modifications of octogen are above the point of crossing the curves.

X-ray and ESR analysis of β-octogen gave the structure presented in Fig. 58 according to Cady, Larsen and Cromer [131].

They found that the nitro groups in octogen are in both equatorial and axial positions. The presence of axial groups was explained by Stals [133] as being due to mutual electrostatic actions of nitramino groups. The conformation of α, β and γ-octogen based on dipole moment measurements was given by G. F. Wright [96] and depicted in Fig. 59.

Charge distribution in β-octogen [98a] is presented in Fig. 60.

According to data given in the monograph by Otlova et al. [5] the following were enthalpies $-\Delta H$ of the change of modifications:

<table>
<thead>
<tr>
<th>temperatures</th>
<th>$-\Delta H$</th>
<th>cal/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha \rightarrow \delta$</td>
<td>193–201</td>
<td>5.97 ± 0.18</td>
</tr>
<tr>
<td>$\beta \rightarrow \delta$</td>
<td>167–183</td>
<td>7.91 ± 0.11</td>
</tr>
<tr>
<td>$\gamma \rightarrow \delta$</td>
<td>175–182</td>
<td>2.25 ± 0.08</td>
</tr>
</tbody>
</table>

FIG. 59. Conformation of α, β and γ-octogen [96].

FIG. 58. Structure of β-octogen [130, 131]. Data from ESR are given in brackets.
Ultraviolet spectra of octogen were examined by a number of authors [134, 135, 102]. All of them found two maxima in ethanol; 201 and 206 nm.

Infra-red spectra were also examined and gave clear differences between crystalline modifications [95, 96, 136]. According to G. F. Wright [96] this could serve as an analytical tool for distinguishing the modifications when crystalline was solid. Raman spectra were taken for β-HMX and isotopes: $^{15}$-$\text{NO}_2$, $^{15}$-$\text{N}$-$\text{NO}_2$, $^{13}$-C and de HMX [137]. One of the conclusions was the presence of hydrogen bonds between NO$_2$ and CH$_2$ groups.

Volk and Schubert [138] described mass-spectrography and Lamberton and co-workers [139] NMR spectroscopy of HMX and other nitramines.

**Solubility of Octogen**

According to the *Encyclopedia of Explosives* [127] the solubility of octogen is as follows in grams of HMX in 100 g of the solution, at 25°C:

- In acetic acid: 0.0375 g
- Acetone: 0.96 g
- Acetonitrile: 1.98 g
- Cyclohexanone: 2.11 g
- Dimethylformamide: 4.4 g
- Ethyl acetate: 0.02 g

In 1,2-dichloroethane: 0.02 at 24°C and 0.125 at 70°C.

In general, octogen is less soluble than cyclonite (Vol. III, pp. 79–80).

Specific heat of octogen at −75°C in 0.153 cal/g°C:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Specific Heat (cal/g°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.228</td>
</tr>
<tr>
<td>25</td>
<td>0.248</td>
</tr>
<tr>
<td>50</td>
<td>0.266</td>
</tr>
<tr>
<td>75</td>
<td>0.288</td>
</tr>
<tr>
<td>100</td>
<td>0.295</td>
</tr>
</tbody>
</table>

The figures are taken from the Encyclopedia [127].

**Chemical Properties**

One of the characteristic features of octogen which distinguishes that compound from hexogen is that octogen readily forms additional complexes—probably charge-transfer complexes. They have been described by a number of authors [140, 136] but mainly by Selig [141]. He described complexes of octogen in molecular ratio 1:1 with amines, for example

- Aniline: m.p. 172°C
- $\alpha$-, $m$- and $p$-toluidine: m.p. 166°, 134° and 139° respectively 1- and 2-naph-
thylemine; m.p. 203° and 148°C respectively, with some substituted phenols:

- o-cresol  m.p. 108°C
- 1-naphthol  m.p. 182°C

With some compounds, for example N-methyl-2-pyridon, N-methyl-p-toluidine, o-nitroaniline, hexamethylphosphotriamide the molecular ratio octogen: second compound is 2:1.

The X-ray analysis of octogen showed a 'sandwich' structure very common in CT-complexes.

The difference between hexogen and octogen as regards the formation of complexes can be used for the separation of octogen from hexogen.

Enthalpy of decomposition of complexes on melting is of the order of 2–3 kcal/mol.

Octogen did not decompose when boiled with 2% nitric and sulphuric acid, but concentrated sulphuric acid decomposed in a way similar to the decomposition of hexogen but slower than that of the latter [142]. Ion NO₃⁻ is probably present in the octogen–sulphuric acid solution.

On the other hand, octogen is more reactive with alkali than hexogen. A solution of 1% Na₂CO₃ decomposed octogen completely after prolonged boiling. A solution of sodium carbonate or sodium hydroxide can be used to decompose the residual octogen. The irradiation of octogen with ultraviolet light [154] liberated stable free radicals •NO₂.

**Thermal Decomposition**

Octogen is probably more stable than Cyclonite and is comparable with TNT at 150°C in the vacuum stability test [127].

A scanning calorimeter can give information on the decomposition of various forms of octogen in the temperature range 180–210°C [13]. Maksimov [111] examined the behaviour of octogen at high temperatures. The decomposition of solid samples at temperatures from 183° to 230°C was measured by determining the volume of gaseous products, some of the curves are given in Fig. 61. The energy of activation was calculated: 37.9 kcal/mol and log₁₀ B = 11.2. The decomposition of a 2% solution in m-dinitrobenzene was examined at temperatures [171] up to 215°C. Some of the curves are presented in Fig. 62. The energy of activation was found to be E = 44.9 kcal/mol and log₁₀ B = 16.0. In solution the decomposition was faster than that of the solid substance. Octogen is decomposed much slower than hexogen, in other words exhibits much better stability than hexogen.

The problem of octogen stability was tackled in similar ways by a number of authors: Baum and Shipitsin [143], Maycock et al. [144, 145], Rogers and Morris [146], Hall [147], Kimura and Kubota [148].

![Fig. 61. Thermal decomposition of solid octogen [111].](image)

![Fig. 62. Thermal decomposition of octogen in solution [111].](image)

The induction period on a heated surface for octogen was found to be [149]:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Induction Period (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>1.7</td>
</tr>
<tr>
<td>300</td>
<td>5.3</td>
</tr>
<tr>
<td>280</td>
<td>10.0</td>
</tr>
<tr>
<td>275</td>
<td>12.3</td>
</tr>
</tbody>
</table>

The statement by Henkin and McGill [150] is interesting in that octogen, placed on a copper surface of 360°C, does not decompose. There is no doubt that octogen is a heat resistant explosive.

Robertson [151] and Suryanarayana and co-workers [152] have reported that formaldehyde is one of the major products of the decomposition of HMX. Suryanarayana et al. concluded from studies on isotopically labelled HMS that
the thermal degradation of HMX is mainly accompanied by C–N rather than N–N rupture. Amongst other decomposition products, hydroxymethyl formamide was found [153]. When kept at a temperature of 200°C β-form passes into a less stable δ-form. This explains an interesting fact described by Haeuseler [167] that is, β-octogen in a hermetic container exploded after being kept for 30 min at 200°C.

It should be pointed out that the behaviour of octogen at high temperature offers some other less expected features. Thus the very high figures of the activation energy of α- and β-octogen were found to be of the order of 150–230 kcal/mol for the decomposition temperatures from ca. 190°C to m.p. (ca. 280°C) [146–148].

Kimura and Kubota [148] tried to find a tentative explanation for such high figures in terms of autocatalytic reactions. See also the review of Dubovitskii and Korsunskii [4].

Thermochemical and Explosive Properties

The following data were given in [5] and [127]:

Heat of explosion of octogen is 1356 kcal/kg (water–liquid) and 1222 kcal/kg (water–gas).

Heat of combustion 2255–2362 kcal/kg, 667.4 kcal/mol

Enthalpy of formation – ΔHf = 17.93 kcal/mol
(or 25.0 kcal/mol).

The strength of the explosive in ballisitic mortar and in lead block was: 150% and 145% respectively, velocity of detonation 9124 m/s at the density 1.84. The detonation pressure determined by the depth of the impression in a steel plate [155] was found 0.397 mm, that is 150% of that of TNT.

The rate of burning of octogen [156] depends on the pressure, but is independent of the density:

<table>
<thead>
<tr>
<th>Pressure</th>
<th>12.5</th>
<th>52.0</th>
<th>154.0</th>
<th>205.0 kg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of burning</td>
<td>0.489</td>
<td>1.48</td>
<td>3.91</td>
<td>5.20 g/cm²s</td>
</tr>
<tr>
<td>ρ = 1.66</td>
<td>0.480</td>
<td>1.43</td>
<td>3.31</td>
<td>5.13 g/cm²s</td>
</tr>
<tr>
<td>ρ = 1.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Burning can pass to the explosion. This was studied extensively by Andreev and Gorbunov [157]. Octogen of the density 0.85 and 0.93 can explode after 0.06 and 0.54 s respectively. At a density 0.94 no explosion occurred. The authors introduced the term a ‘critical density’ which forms a threshold of the possible passing burning to explosion.

The problem of burning HMX seems to gain some importance as HMX became a common component of propellants. Particularly important is HMX with aluminium described below (p. 394).

Preparation of Octogen

Octogen (HMX) is formed in the nitrilation of hexamethylenetetramine (hexamine) and is a by-product of production of cyclonite (RDX) as it was pointed out in Vol. III, p. 90. However, the statement given in Vol. III needs to be corrected. On the basis of our present knowledge, octogen which accompanies cyclonite does not reduce the power of cyclonite. On the contrary, owing to a higher velocity of detonation octogen can increase the strength of cyclonite.

W. E. Bachmann and Sheehan [158] developed a method of preparing RDX containing a small quantity of HMX. The method involved nitrolys of hexamine with ammonium nitrate–nitric acid solution and acetic anhydride. By varying parameters of temperature and acid concentration, ammonium nitrate and acetic anhydride it was shown that the ratio RDX/HMX can be altered. These results led Bachmann and co-workers to prepare mixture rich in HMX. The optimum yield obtained was 82% conversion of hexamine to HMX/RDX mixture containing up to 73% HMX.

The mechanism of the formation of octogen can be presented by scheme (35):

Low acidity and the presence of NH₄NO₃ (and paraformaldehyde – [162]) favours the formation of octogen. Without ammonium nitrate the linear compound was formed. Higher acidity helps to obtain RDX [159].

Bell and Dunstan [162] nitrated DPT at −20°C. After warming the solution to 30°C HMX resulted in a low yield.
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

By using \(^{14}\)NH\(_4\)NO\(_3\) W. E. Bachmann and co-workers [159] established that only 15% of nitrogen from NH\(_4\) enters octogen, and much more (ca. 37%) enters hexogen. Castorina and co-workers [160, 161] used C labelled hexamine, DPT and paraformaldehyde, and found that all these compounds contribute to the formation of octogen. They obtained HMX with 15% of RDX. They isolated pure HMX by dissolving all in acetone, evaporating to form a precipitate and cooling to 25°C. The crystalline solid is HMX. The presence of RDX in the substance can be detected by acting with sodium nitroso ferricyanide on the acetone solution. A blue colour reveals the presence of RDX (reaction of S. B. Wright according to [161]).

It has been found by Picard [162] that the addition of paraformaldehyde to the mixture of ammonium nitrate–nitric acid–acetic acid–acetic anhydride increases the yield of octogen.

The following is the method described by Fedoroff and Sheffield [127] as apparently used in U.S.A.

To a 6–10 l flask equipped with a stirrer and three dropping funnels add 785 g acetic acid, 13 g acetic anhydride and 17 g of paraformaldehyde keeping the temperature at 44 ± 1°C. Add over 15 min a solution of 101 g of hexamine in 165 g acetic acid, 320 g of acetic anhydride and 180 g of ammonium nitrate–nitric acid solution prepared by dissolving 840 g of ammonium nitrate in 900 g of nitric acid (99% concentration). The hexamine and nitric acid are added continuously in correct proportions. The mixture is stirred for 15 min. After that are added: 320 g of acetic anhydride and 271 g of nitric acid–ammonium nitrate solution in that proportion and then 160 g of acetic anhydride are added in bulk. The mixture is stirred for 60 min., 350 g of hot water are added and refluxed for 30 min. The content is cooled to 20°C by adding ice, the precipitate is collected and washed with three portions of cold water.

The yield of β-HMX is 95% of the theoretical and the purity 90%.

A similar method of obtaining β-HMX was given by Robbins and Boswell [163]. The composition of the product was 77.5% HMX and 22.5% RDX. The yield of HMX was 87.5%. A method was also described for nitrating hexamine with nitric acid in the presence of BF\(_3\). A yield of 96% was claimed [164].

Preparation of Octogen from DPT (3,7-dinitro-1,3,5-tetrazabicyclo[3.3.1]nonane) (Vol. III, p. 90, formula XII)

There are methods of obtaining octogen in two steps by forming DPT as the first step, followed by acting on DPT with nitric acid or nitric acid with ammonium nitrate or nitric acid, ammonium nitrate and acetic anhydride. However, the yield of DPT is not very high.

The best method of obtaining DPT consists in introducing hexamine dinitrate to 90% sulphuric acid at 8–15°C. After 45 min, all is poured on ice and the solution is filtrated. The filtrate is neutralized with 28% ammonia to pH = 5.5–6.5 DPT precipitated [165].

A-Nitro Compounds

Another method of making octogen from DPT (1 mole) consists in acting with NH\(_4\)NO\(_3\) (1.6 mole) and nitric acid (3.2 mole) at 60–65°C for one hour. Water is then added and all is heated for 12 hours in a steam-bath. The yield was 75% of the theoretical (according to [5]).

The description of the industrial manufacture of octogen in Hungary has been given [166]. In the first step DPT was obtained from hexamine, acetic anhydride, paraformaldehyde and a solution of ammonium nitrate in nitric acid. After that the rest of the reagents were added.

Altogether for 1 mole of hexamine, the following reagents were added:

- 5–7 moles of nitric acid (min. 98%),
- 3–5 moles ammonium nitrate,
- 10–11 moles acetic anhydride and
- 0.27–0.54 moles of paraformaldehyde.

The reaction was carried out at 44°C.

After that water was added and the temperature was raised to 98°C by injecting live steam. All was cooled and the product filtered. It contained 60–70% octogen and 30–40% hexogen.

To obtain pure β-form the product is dissolved in acetone and refluxed for 45 min. All forms of octogen pass into the solution. Also unstable products decompose on boiling.

If pure octogen free of cyclonite is required, octogen can be obtained due to lower solubility in acetone. By warming the product with a three times larger quantity of acetone at 40–50°C, all cyclonite passes into the solution.

The commercial grade of HMX produced in France seems to contain ca. 2.25% RDX [179].

Specification for Octogen

The U.S. specification describes two grades of octogen:

- Grade 1, min. 93%.
- Grade 2, min. 98%.

The quantity of octogen is determined by treating an 0.2 g sample with 100 ml of 1,2-dichloroethane saturated with HMX. The insoluble matter is pure octogen.

The octogen should consist of β-polymorph by examination of a 5% null of the sample in hexachlorobutadiene or tetrachloroethylene in a sodium chloride cell. Another sample of pure β-polymorph is placed in a compensating cell. The absorption is observed between 14.0 and 14.3 μ.

M.p. should be min. 270°C

Insoluble in acetone max. 0.05%
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Inorganic insoluble max. 0.03%
Acidity max. 0.02% (as acetic acid)
Granulation is different in 5 classes.

For transportation it is kept in watertight bags with a minimum 10% solution of 40% isopropyl alcohol and 60% water.

In the presence of RDX the quantitative determination of HMX is by the formation of the stable complex of HMX with dimethylformamide insoluble in CCl₄. Another method consists in the separation of HMX by low solubility in 1,2-dichloroethane. For detailed description of the methods see the Encyclopaedia [127].

The Soviet Union specification for octogen used for detonating fuses includes the items as follows (according to [5]):

m.p. min 278°C
critical and limiting diameters at density 1.65
should be 1 mm and 4 mm respectively.

The velocity of detonation is

\[ 8400 \text{ m/s at } \rho = 1.65 \text{ and } \]
\[ 8800 \text{ m/s at } \rho = 1.75. \]

When heated at 335°C the induction period should be 5 s.
For other requirements referred to charges for deep bore-holes see [5].

EXPLOSIVES WITH OCTOGEN AS A MAIN COMPONENT

Price [176] gave a description of the explosive properties of octogen (91%) desensitized with wax (9%): at density 1.71 it shows the rate of detonation 8680 m/s. Octol — a castable mixture of octogen (77%) and TNT (23%) gave the rate of detonation 8540 m/s (density 1.80). They are stronger than analogous compositions with cyclonite.

Kegeler [177] described the composition of 65% octogen with 35% TNT. It shows the rate of detonation

\[ 8254 \text{ m/s at } \rho = 1.80, \text{ and } \]
\[ 8156 \text{ m/s at } \rho = 1.77. \]

There are also compositions described, for example of 94% octogen, 3% nitrocellulose and 3% (O-chloroethyl) phosphate [178].

Of considerable importance now are mixtures of octogen with aluminium powder. Two papers have appeared recently on the ability of aluminized HMX to pass from burning to detonation. Langen and Barth [179] described the properties of Octal 70/30, that is, HMX (with wax) 70% and aluminium 30%. HMX with wax was composed of 95% of Höchst waxes 'S' and 'Kp' in equal proportions, that is 2.5% of each. The authors of the paper described the method of mixing the ingredients as follows: 100 parts of HMX desensitized with waxes were pre-heated to 90°C, 42.9 parts of aluminium degreased with carbon tetrachloride and preheated to 90°C were mixed in a vessel connected to ground potential. After that the mixture was sieved through 1 mm mesh size. The performance of Octal 70/30 was better than that of RDX/Al 70/30. This can be seen from Table 64.

<table>
<thead>
<tr>
<th></th>
<th>Heat of explosion kcal/kg</th>
<th>Lead black test cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octal 70/30</td>
<td>1650</td>
<td>555</td>
</tr>
<tr>
<td>RDX/Al 70/30</td>
<td>1635</td>
<td>470</td>
</tr>
</tbody>
</table>

Price and Clairmont [180] examined fine (5 µm) and coarse (95 µm) aluminium on the deflagration to detonation transition of HMX/Al pressed charges. They found that Al, particularly fine grain, increases the length of the pre-detonation column. However wax is more effective than Al: it is more efficient in delaying the detonation.

BSX (1,7-DIACETOXY-2,4,6-TRINITRO-2,4,6-TRIAZAHETANE)

The compound is formed as a by-product of cyclonite when made by the method of W. E. Bachmann [188–189] and Köfler (Vol. III, p. 111). This was described by G. F. Wright [2].

The remarkable property of the compound shown by Hall [181] is its ability to form complexes: with dioxane, cyclohexanone, tetrachloroethane, formamide. All in the proportion 1:1. The complex with acetophenone is in the proportion 2:1.
Sorguyl is remarkable by its high density, extremely high velocity of detonation, and positive oxygen balance. It is not hygroscopic but decomposes by hydrolysis. It decomposes in molten TNT.

**$\alpha$-Nitro-$\alpha$-Nitro Compounds**

One representative of this group of compounds merits attention. This is $1-(N$-Ethyl)-nitramino-2-ethanol Nitrate, code name Et-NENA [73]

$$C_2H_5 NH CH_2CH_2ONO_2$$

m.p. 4.0–5.5°C

This is an oil, $d = 1.32$ at $25^°/4^°C$, $nD = 1.479/25^°C$. It was prepared by Blomquist and Fiedorek [73, 74] from ethylaminoethanol. The latter was added dropwise to 98% nitric acid at $10^°C$. The resulting mixture was added dropwise to 95% acetic anhydride with some acetyl chloride to transform the nitrate salt into nitramine:

$$C_2H_5 NH CH_2CH_2OH + \text{HNO}_3 \rightarrow C_2H_5 NH CH_2CH_2ONO_2 + \text{H}_2O$$

$$\text{Et-NENA}$$

**References**

73. G. PONZIO, Gazz. chim. ital. 38 (1), 509 (1918); G. PONZIO and G. CHARRIER, ibid. 38 (1), 526 (1918).
84. E. Bamberger, Chem. Ber. 26, 471, 485 (1893); 27, 359, 584 (1894); 28, 399 (1895).
85. E. Bamberger and E. HOFF, ibid. 30, 1248 (1897); Lieb. Ann. 311, 91 (1900).
Appendix

Thermal Decomposition

Thermal decomposition of dimethyl nitramine was studied by Flournoy [11], Koroniski, Dubovitski and co-workers [2, 3].

The decomposition occurred in two steps:

\[
\text{(CH}_3\text{)}_2\text{N—NO}_2 \rightarrow (\text{CH}_3\text{)}_2\text{N}^+ + \cdot\text{NO}_2 \tag{1}
\]

\[
(\text{CH}_3\text{)}_2\text{N—NO}_2 + \text{NO}_2 \rightarrow \text{products of oxidation} \tag{2}
\]

Similar results were described by Koroniski, Dubovitski and Shurygin [4] on the decomposition of higher nitramines.

The activation energy of the decomposition of dimethyl nitramine was found to be 40.8 kcal/mole and the log of frequency factor log B = 14.1.

Koroniski, Dubovitski and co-workers [5] studied the thermal decomposition of an interesting compound: bis(2,2-dinitropropyl)-N-nitramine:

\[
\text{CH}_3—\text{C(NO}_2\text{)}_2—\text{CH}_3 —\text{N—NO}_2
\]

They examined the decomposition of 5% solution of the compound in m-dinitrobenzene at temperatures 145—196°C and found energy of activation 39.7 kcal/mole and log B = 15.7.

Thermochemistry


The data are as below:

- Cyclonite: $H_f$ crystall = 14.7 kcal/mol, $H_f$ gas = 45.8 kcal/mol
- Dinitropiperazine: $H_f$ crystall = 12.7 kcal/mol, $H_f$ gas = 13.9 kcal/mol

References

CHAPTER 14

EXPLOSIVE POLYMERS

With the present advent of polymer chemistry numerous efforts have been made on synthetic polymers containing nitro groups (whether C-, O- or N-nitro groups) with the aim of possibly replacing (or imitating) nitrocellulose and (to a much smaller extent) nitrostarch. To date it has been difficult to obtain a synthetic polymer which would possess the same mechanical properties as that of nitrocellulose.

C-NITRO POLYMERS

Nitropolystyrene and its Derivatives

In Vol. I, pp. 418–419 nitropolystyrene was described and its possible practical application is mainly in low power mining explosives and in pyrotechnic mixtures. According to [3], molecular weight is over ca. 38000.

An interesting polymer 'Peptidyl' was obtained by E. Katchalski and co-workers [1] which is poly-4-hydroxy-3-nitrostyrene, an improved version of the polymer used by Merrifield [2] for the formation of peptides. Peptidyl was obtained by nitratating a co-polymer of acetoxystyrene with divinylbenzene in proportion 100:4. Divinylbenzene is used as a cross-linking agent.

Nitroindene Polymer (p. 410)

Nitroindene polymer was obtained by the nitration of polyindene [3]. It is an amorphous solid of m.p. 230°C, and is insoluble in most solvents. Decomposition (explosion) temperature is above 360°C. It is slightly hygroscopic, taking 1.61% water from the atmosphere of 100% relative humidity. The International heat test at 75°C showed 1.1% loss of weight. A sample of 5 g evolved 11.2 cm³ of gas in 48 hours. It was considered for use in U.S. Army as a time fuse but was found to be too sensitive to impact.

POLYNITRO ALKANES

Nitroethylene Polymer (Vol. I, p. 596) (CH₂ = CHNO₂)ₙ

Nitroethylene was mentioned in Chapter VIII. Here the polymer will be described, according to Noma and co-workers [4], Perekalin and Sopova [5].

Encyclopedia of Fedoroff and Sheffield [6], Novikov and co-workers [7].

Nitroethylene polymer is a white amorphous solid which does not melt but decomposes on heating above 75°C.

During World War II in the U.S.A. [6] a method of preparing nitroethylene was developed consisting of the action of sodium bicarbonate on 1-chloro-2-nitroethane. The yield of nitroethylene was 76%.

Polymerization was carried out in aqueous medium in the presence of an emulsifier and ascaridole (a terpene peroxide) as a catalyst. Air over the liquid was replaced by nitrogen and nitroethylene was introduced gradually to the water. The reaction ended after 2 hours of mixing.

Perekalin and his co-workers [8] have done pioneering work on the polymerization of nitroethylene under γ-radiation from Co²⁵⁵. Perekalin et al. pointed out that the methods so far used to polymerize nitroethylene gave a low molecular weight of ca. 2000. When the polymerization was carried out in a solvent, for example, dimethylformamide or tetrahydrofuran, the molecular weight was higher but the product was still a powder, although the γ-radiation yielded a transparent product. The part which was not polymerized was subjected to further irradiation etc. and eventually a transparent block was obtained. Perekalin also found that polymerization continues after irradiation. On the basis of the latter fact he concluded that the polymer contains free radical of long life and the reaction of polymerization is a free-radical reaction. The molecular weight of polynitroethylene obtained by Perekalin et al. was of the order of 38000 (through measurement of viscosity) and density was 1.535. It decomposed when heated to 150°C.

In a number of papers Yamaoka and co-workers [9–14] examined polymerization. Their main conclusion was that radiation induced polymerization through the anionic mechanism involving free ions and induced post-polymerization at temperatures below −150°C.

Nitroethylene polymer is a white amorphous solid which does not melt. According to [6] it decomposed slowly at 75°C. After 2 hours of maintaining this temperature it ignited. When heated to 100°C it dehydrated with a sooty smoke in 23 min. On a hot plate of 200°C it decomposed without explosion. The sensitivity to impact is of the order of TNT. The strength (in ballistic manner) constitutes only 29% of that of TNT. Hungarian authors [15] reported the data for polynitroethylene as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of Detonation</td>
<td>720 kcal/kg</td>
</tr>
<tr>
<td>Lead Block Expansion</td>
<td>114 cm³</td>
</tr>
<tr>
<td>Impact Sensitivity (2 kg)</td>
<td>70–90 cm</td>
</tr>
</tbody>
</table>

POLYURETHANES WITH ALIPHATIC C- AND N-NITRO GROUPS

A large number of polyurethanes were made of nitro aliphatic polymers consisting in co-polymerization of nitro aliphatic diisocyanate with nitro aliphatic
diols. They were made by Aerojet General Corp., by Blatz, Gold and co-workers [16].

Two main lines were taken:

(1) to polymerize isocyanates to polyurethanes with diols (in mol. proportion 1:1) both containing C-nitro groups, and some of diols with N-nitro groups,

(2) to nitrate the above polymers ('the postnitration') to increase the number of the nitro group.

Most of the compounds are described below.

I. Co-polymers from 3,3-Dinitro-1,5-pentane Diisocyanate (I) and Nitrodiols.

\[
O = C = N - CH_2 \text{CH}_2 \text{C(NO}_2)_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 = N = C = O
\]

I

The general formula (II) gives the structure with variable \( R \) which depends on the used nitrodiol:

\[
[ O \text{C-NH(CH}_2)_2 \text{C(NO}_2)_2 \text{CH}_2 \text{CH}_2 \text{NHCO}_2 ]_n \quad (R = \ldots)
\]

II

The following were compounds IIa–IIe made of I and different diols listed below (Table 66).

**TABLE 66. Co-polymers of I with diols; polymer II**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Name of diol</th>
<th>Formulae of polymers II</th>
<th>( R = \ldots )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIa</td>
<td>2,2-Dinitro-1,3-propanediol</td>
<td>-CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
<tr>
<td>IIb</td>
<td>5,5,5-Trinitro-1,2-propanediol</td>
<td>-CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
<tr>
<td>IIc</td>
<td>2,2,4,4-Tetranitro-1,5-</td>
<td>-CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pentanehexadiol</td>
<td>-CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
<tr>
<td>IIId</td>
<td>4,4,8,8-Octanitro-1,1,-</td>
<td>-CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>undecanediol</td>
<td>-CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
<tr>
<td>IIe</td>
<td>4,4,6,6,8,8-Octanitro-1,1,-</td>
<td>-CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>undecanediol</td>
<td>-CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
<tr>
<td>IIIf</td>
<td>5,7,7,9-Trimethoxy-5,7,9-triaza</td>
<td>-CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3,11-dioxa-1,13-tridecanediol</td>
<td>-CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
</tbody>
</table>

Another group of polymers with the same diisocyanate (I) was reacted with diamine (III) to form polymer (IIIa) which is a urea derivative:

**TABLE 67. Co-polymers of IV with diol; polymers V**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Name of diol</th>
<th>Formulae of Polymers V</th>
<th>( R = \ldots )</th>
</tr>
</thead>
<tbody>
<tr>
<td>VA</td>
<td>2,2-Dinitro-1,3-propanediol</td>
<td>CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
<tr>
<td>VB</td>
<td>5,5,5-Trinitro-1,2-propanediol</td>
<td>CH( \text{CH}_2 \text{CH}(\text{NO}_2)_2\text{CH}_2\text{O} )-</td>
<td></td>
</tr>
</tbody>
</table>

Three co-polymers were made from 2-Nitro-1,4-butane Diisocyanate (VI) with diols to form polymers VII:

\[
O = C = N - \text{CH}_2 \text{N - (CH}_2)_2 \text{N = C = O}
\]

VI

Their formulae are given in Table 68.

Two co-polymers were made of 2,5-Dinitro-1,6-hexane diisocyanate (VIII) and diols which led to polymers (IX):
The sensitivity of the melting points to impact and stability are given in Table 70.

**TABLE 70. Some properties of co-polymers: diisocyanates–diols**

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p. °C</th>
<th>Impact sensitivity*</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>RDX = 2 cm</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>75–78</td>
<td>100</td>
<td>195</td>
</tr>
<tr>
<td>Hb</td>
<td>85–95</td>
<td>85</td>
<td>78</td>
</tr>
<tr>
<td>Hc</td>
<td>70–80</td>
<td>80–85</td>
<td>30</td>
</tr>
<tr>
<td>Hg</td>
<td>60–65</td>
<td>100</td>
<td>13</td>
</tr>
<tr>
<td>Hc</td>
<td>40</td>
<td>100</td>
<td>13</td>
</tr>
<tr>
<td>Hf</td>
<td>55–60</td>
<td>80–85</td>
<td>300</td>
</tr>
<tr>
<td>Hla</td>
<td>110–115</td>
<td>80–85</td>
<td>300</td>
</tr>
<tr>
<td>Va</td>
<td>75–85</td>
<td>40</td>
<td>13</td>
</tr>
<tr>
<td>Vb</td>
<td>65–75</td>
<td>65</td>
<td>20</td>
</tr>
<tr>
<td>Vla</td>
<td>90–100</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Vlb</td>
<td>70–80</td>
<td>100</td>
<td>390</td>
</tr>
<tr>
<td>Vlc</td>
<td>80–90</td>
<td>55</td>
<td>38</td>
</tr>
<tr>
<td>Ixa</td>
<td>85–95</td>
<td>100</td>
<td>90</td>
</tr>
<tr>
<td>Ixb</td>
<td>90–100</td>
<td>60</td>
<td>10</td>
</tr>
</tbody>
</table>

* Impact sensitivity is expressed in the height of 2 kg weight giving 50% probability of explosions compared with the standard Cyclonite (RDX) which requires 28–35 cm height.

**Preparation**

Polymers were prepared by adding dropwise a solution of a diol and a catalyst in absolute dioxane to an equivalent amount of a diisocyanate at 20 to 50°C depending on the substances used. The catalyst in all instances (with the exception of Hf and Hh) was ferric acetylacetonate in quantity of 0.05–0.15% in relation to the diol. With Hf and Hh it was boron trifluoride—ether complex in proportion of ca. 1.5 mol %. The temperature was kept at 20–40°C for a longer time: from 2 days to several weeks. At the end the temperature should be raised to 50°C. The product was precipitated by adding water. The solvent was removed by steam distillation or by vacuum drying. The yield in most instances was of the order of 95% (with Hf it was ca. 44%).

It can be seen from Table 70 that some of the polymers possess poor stability but show low sensitivity to impact. Some of them are remarkably stable at 134.5°C.

2. Nitration of polyurethanes containing nitro groups [16]. Several polyurethanes described above have been subjected to nitration. However, most of the products show poor stability. The previously described Hb was nitrated with 100% nitric acid at room temperature followed by gradually raising the tempera-
ture to 50°C and keeping it for 20 min. The product (X) was obtained by pouring on ice and vacuum drying the precipitated product. The impact sensitivity was 30 cm (RDX 28 cm), heat test (with KI) 5 min at 65.5°C and the relative viscosity was 1.6 cp at 25°C for 2% solution in acetone.

![Nitroimidene polymer](image)

Some co-polymers of urethanes with diols after the nitration could also not stand the test at 134.5°C. One of them exploded after 11 min of heating.

The exception from the point of view of stability shows the nitro polymer made of I and 5,5-dinitro-1,2-hexanediol. It is an amorphous powder, m.p. 55–65°C (XI) and is soluble in acetone. The polymer was prepared in two steps:

(a) the monomers were dissolved in dioxane and kept at 50°C for ca. 24 days. The product was precipitated with water.

(b) The polymer was nitratated with 100% nitric acid at 0°C. It was precipitated with water. The yield was 97%.

Impact sensitivity was 100 cm (RDX 28 cm). Thermal stability: at 65.5°C (K1 paper) 23 min, at 134.5°C no decomposition (methyl violet paper) in 5 hours.

Another product which may show some promise with regard to stability is nitrated urea derivative (XIV)

![](image)

It is an amorphous solid, m.p. 80–90°C which was obtained by hydrolysing 3-nitro-3-aza-1,5-pentane diisocyanate with water followed by nitration.

**C-NITRO POLYMERS FROM MONOMERS WITH A VINYL GROUP**

*Nitroallyl Acetate Polymer [3]*

![Diagram X III](image)

The monomer – nitroallyl acetate can be obtained from methyl nitrate and formaldehyde, followed by esterification and oxidation (1):

\[
CH_3OONO_2 + 2CH_2O \xrightarrow{\text{gas phase}} CHNO_2(CH_2O) + CH_3COOH
\]

(1)

The monomer has m.p. 17.5°C, b.p. (at 2 mmHg) 68°C.

It polymerizes on exposure to air at room temperature. The stability does not seem to be satisfactory – an explosion occurred after 10 min of keeping at 134.5°C.

**Ethyl Nitroacrylate**

\[
NO_2 CH = CH COOC_2H_5
\]

The compound was obtained by Yanovskaya, Stepanova and Kucherov [17] from formylacrylic acid ester and nitromethane. No information was given on the possible polymerization of the compound.
Nitroethyl acrylate

\[
\text{CH}_2 = \text{CH} - \text{COO} \text{CH}_2 \text{CH}_2 \text{NO}_2
\]

b.p. 100°C (5 mmHg)

This was one of the most simple acrylates obtained by Marans and Zelinski [18] (see also Chapter VIII). It can polymerize under the action of benzoyl peroxide at 100°C in the atmosphere of nitrogen. The polymer is a soft, viscous resin (contrary to the polymer of methylacrylate which is hard).

Nitroethyl methacrylate [18]

\[
\text{CH}_2 = \text{C} - \text{COO} \text{CH}_2 \text{CH}_2 \text{NO}_2
\]

b.p. 115°C (10 mmHg)

The compound gives a polymer when catalysed by benzoyl peroxide at 100°C in the atmosphere of nitrogen. The polymer is a hard resin.

Trinitroethyl acrylate

\[
\text{CH}_2 = \text{CH} - \text{COOCH}_2 \text{C(NO}_2)_3
\]

b.p. 80°C (2 mm)

This was obtained by Ville [19] by acting with acryloyl chloride on 2-trinitroethanol (Chapter VIII). No information was given on the possible polymerization.

Dinitropropyl Acrylate (DNPA) [3]

\[
\text{CH}_2 = \text{CH} - \text{COO} \text{CH}_2 \text{C(NO}_2)_2 \text{CH}_3
\]

m.p. 175°C, b.p. 96°C (0.2 mmHg)

The monomer was prepared by dissolving 2,2-dinitropropanol and acrylic chloride in carbon tetrachloride and heating for 12 hours at 55°C. The dried product was mixed with powdered silver and vacuum distilled. It can be used as a binder in propellants burning readily at a pressure of ca. 70 kg/cm². It can be polymerized in toluene in the presence of azobisisobutyronitrile as a free radical catalyst, under dry nitrogen at 80°C for 45 min. The conversion of 25% was obtained to yield the polymer:

\[
\left[ \text{CH}_2 - \text{CH} \right]_n \text{COOCH}_2 \text{C(NO}_2)_2 \text{CH}_3
\]

Poly-DNPA has an explosion temperature at 250°C, the detonation rate of 6100 m/s [19].

POLYESTERS OF DINITROCARBOXYLIC ACIDS AND DINITRODIOLS

The polymer of 4,4-Dinitro-1,7-Heptanediol Chloride and 2,2-Dinitro-1,3-Propanediol was described [20]:

\[
\left\{ \begin{array}{c}
\text{O} \quad \text{O} \\
\text{C} - \text{(CH}_2)_2 - \text{C} - \text{CH}_2 - \text{C} - \text{O} \\
\text{NO}_2 \quad \text{NO}_2
\end{array} \right\}_n
\]

The molecular weight of the polymer was 4000–9000, i.e. \( n = 11–24 \). It is a yellow coloured powder of m.p. 180–185°C.

It was prepared by dissolving equivalent amounts of the monomers in dioxane followed by maintaining the temperature of 30°C for 3 days. The solution was filtered, poured into water with ice and vacuum steam distilled to obtain the product. It shows a low sensitivity to impact: 2 kg at 85–95 cm (RDX 28 cm), and a good stability: at 65.5°C (KI paper) is 100 min, at 134.5°C (Methyl violet paper) – 80 min.

POLYMER WITH O-NITRO GROUPS

Polyvinyl Nitrate (PVN) (Vol. II, p. 173)

\[
\left\{ \begin{array}{c}
\text{CH} \\
\text{ONO}_2
\end{array} \right\}_n
\]

The polymer originally created certain hopes that it could replace (partly at least) nitrocellulose. The problem remains unsolved although a considerable amount of information on PVN was collected.

The following are references which should be added to those mentioned in Vol. II: Frank and Krüger [21], Chédin and Tribot [22], Aubenstein and Laford [23], Akopyan and co-workers [24].

Properties of PVN

Chemical and physical properties. A rather detailed description of PVN can be found in the paper by Diepold [25]. Here are the data on properties of PVN according to this author:

- Nitrogen content N 15.15% (which indicates the degree of esterification 92.8%). The other sources [29] gave 15.7% which is practically 100% nitration (99.8%).
Molecular weight $M_w$  
Viscosity of 0.5% solution in acetone at 25°C  
Included (or adsorbed) acidity max. ca. 1%  
Insoluble (in acetone) yellowish white  
Colour less than 1 mm  
Size of grains 1.6  
Density Free flowing density 0.3  
Hygroscopicity at 30%/90% relative humidity was 0.62%  
Softening temperature 30–40°C  
Freezing temperature 30°C  
Strength:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>On stretching</th>
<th>Breaking elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>-40°</td>
<td>500 bar</td>
<td>0.4%</td>
</tr>
<tr>
<td>+20°</td>
<td>450 bar</td>
<td>0.8%</td>
</tr>
<tr>
<td>+40°</td>
<td>20 bar</td>
<td>400%</td>
</tr>
</tbody>
</table>

The plastic properties of PVC plasticized with dibutyl phthalate or bis(2-fluoro-2,2-dinitroethyl) formal was examined by Michaud and co-workers [26] through pulsed NMR analysis. The purpose of this study was to find the different phases and to examine them in a function of concentration and temperature. The following were the phases found in the plasticized PVC: (1) a rigid polymer, (2) a mobile polymer, (3) a rigid plasticizer and (4) a mobile plasticizer. The work has a general significance on the insight of the nature of plasticization and mobility of macromolecular chains and on the nature of the plastic flow and exudation.

**Explosive Properties (according to [25])**

PVC (15.15% N) shows the temperature of decomposition:

- 195°C when heated at the rate of 20°C/min,
- 177°C when heated at the rate of 5°C/min.

The induction period is 7 min and over 18 hours at 175° and 165°C respectively. According to Picatinny Arsenal [27] PVC (14.86% N) gives an explosion after 5 sec at 265°C.

The sensitivity to impact was 95 cm from a weight of 1 kg.

It is easily ignited and burns readily at the rate of 3 mm/s under pressure of

\[ \text{ca. 6 kg/cm}^2. \]

The velocity of detonation slightly differs from those given in Vol. II, p. 173 [28] and according to [25] is:

- Density 0.3
- 0.8
- 1.5 (pressed)
- 1.5 (cast)
- 3,200 m/s
- 3,500 m/s
- 6,500 m/s
- 7,000 m/s.

Lead block of Trauzl 330 cm³.

The thermochemical data are as below:

- Heat of explosion 960 kcal/kg [25] and 900 kcal/kg [27]
- Heat of combustion 3016 kcal/kg [25] and 2960 kcal/kg [27]
- Temperature of explosion 2560°C
- Volume of gases 930/kg.

Stability was determined as the loss of weight of 0.3–0.4% at 75°C for 48 hours.

Picatinny Arsenal gave the following information on stability:

- Heat test (K1) at 65.5°C was over 60 min., at 134.5°C (Methyl violet) 20 min., red flames after 25 min., explosion after more than 5 hours.

The solubility of PVC largely depends on the degree of polymerization and hence on the viscosity. The larger the viscosity the lower the solubility.

The chemical stability of PVC was extensively studied by Poullain, Michaud and Poulard [29]. They examined polymers with the molecular weight $M_w$ and molecular number $M_n$ of the order of 150,000–320,000 and 120,000–140,000 respectively. They aged PVC at 90° and 65°C. They followed: (1) the decomposition of the nitrate groups, (2) the degradation of the chains followed by chromatography.

As much as (1) follows the usual trend of decomposition of nitrate esters including nitrocellulose, (2) offers a much more complicated picture which differs from that of nitrocellulose. This is the observation that during heating the length of chain of PVC decreases followed by a cross-linking. (Neither length of chains or cross-linking occurs during the aging of nitrocellulose). This is depicted in Fig. 63 referred to PVC.

The French authors [29] also examined the stabilizing action of 2-nitrodiphenylamine upon PVC. The character of ageing at 90°C was not changed by the presence of the stabilizer.

**Preparation of Polyvinyl Nitrate**


Five parts of polyvinyl alcohol (containing 10% of moisture) were introduced during ca. one hour into 100 parts of nitric acid (99–100%) at –8°C. The result-
not be lower than 95%. The temperature should be kept near 0\(^\circ\)C and the time: 15 min for introducing PVA into the acid, 30 min for the nitrating and 15 min after the nitrating at 20\(^\circ\)C. The product was precipitated by pouring into water with ice. The yield was 90% of PVN with 14.8% N (the degree of nitrating 88.7%), and the spent acid contained 50% HNO\(_3\). This method does not seem to be sufficiently economic.

**Nitration with nitric acid—sulphuric acid.** The addition of a small proportion of sulphuric acid to nitric acid prevents dissolving PVA in nitric acid. A suspension of PVA in nitric/sulphuric acid mixture is formed. The yield of PVN is best when the concentration of H\(_2\)SO\(_4\) in the mixed acid is 10–30% (Fig. 64). In such a mixed acid the solubility of PVN is negligible and the only substances dissolved in the acid are some degradation viscous products in quantity of 2–3%. They can be precipitated with water.

![Graph showing the yield of PVN against the concentration of sulphuric acid in the mixed acid: HNO\(_3\) + H\(_2\)SO\(_4\).](image)

The authors found that the determination of nitrogen in PVN in a nitrometer or by the Kjeldahl method did not give reliable results. It was necessary to use the Dumas method. According to Depold [25] the method of titration with Fe II also gives reliable results.

The method of nitrating PVA at Picatinny Arsenal, U.S.A. [27] was as follows:

PVA was mixed with acetic anhydride, the mixture cooled to −5\(^\circ\)C, a large excess of nitric acid was added keeping the temperature below 20\(^\circ\)C. All was poured into cold water. The product was collected and purified by boiling in frequently changed water.

Depold [25] described two methods of nitrating PVA: with nitric acid alone and with nitric acid/sulphuric acid mixtures.

**Nitration with nitric acid.** PVA was dissolved in nitric acid in proportion: Acid/PVA more than 20:1, otherwise the viscosity of the solution in nitric acid is too large to have an efficient mixing. The concentration of nitric acid should
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

and the grains can stick together. By adding some substances (the nature of which have not been disclosed) the sticking can be prevented and washing can be carried out even with boiling water. After the greater part of the acid has been removed the PVN should pass through a mesh filter to reduce the size of the grains and to make the removal of the last traces of the acid absorbed by PVN possible. The final product after the removal of water contained 60–70% water.

Diepold [25] gives the data as follows:

\[ M_n = 60,000 \text{–} 100,000 \]

Nitrating mixture HNO\(_3\) (1.51) H\(_2\)SO\(_4\) (1.84) 90:10 to 70:30

Nitration temperature 0–10\(^\circ\)C

Time of nitration 5–15 min

Stabilization 25–40 hours at 60\(^\circ\)C.

The yield under these conditions should be 90% and the product should contain 14.8–15.1% N (i.e. degree of the nitration 88.7–92.2%).

A patent exists [31] for stabilizing PVN by dissolving the raw, decomposable PVN in an organic solvent which will be neutralized and then PVN, free of acid, will be precipitated by adding water. Calculations should be made to see whether the method is economically feasible.

**Practical Use of Polyvinyl Nitrate**

Experiments were carried out on PVN as a component of double base propellants PVN being used instead of nitrocellulose. *Encyclopedia of Explosives* [27] gives two compositions:

1. with 82.0% PVN, 10.2% Nitroglycerine, 0.7% Dinitrotoluene, 6.1% Dibutylphthalate 1.0% Diphenylamine,
2. with 57.75% PVN, 40% Nitroglycerine, 1.5% KNO\(_3\), 0.75% Ethyl Centralite.

Heat of explosion of these propellants was much the same as with nitrocellulose instead of PVN. However, the mechanical properties are different: decrease of tensile strength, increase of elongation at break and of flexibility. PVN did not change the burning rate, but increased the pressure exponent \( \eta (\nu = k\rho^n) \). Another disadvantage was that:

1. atactic PVN which has a low melting point has a tendency to flow when mixed with other substances, (2) atactic PVN possesses a sticky nature which has created problems in extruding and shaping propellant grains.

The problem arises of how to obtain the isotactic polymer of PVN with high regularity and higher crystallinity. However, this does not seem to be possible [32].

**Explosive Polymers**

*Modifications of Polyvinyl Nitrate*

A Naval Powder Factory in the U.S.A. investigated the preparation of polyvinyl nitrate by nitration of polyvinyl acetate using epichlorohydrin as a cross-linking agent – according to Cohen [33].

The same source [33] informs us that the U.S. Naval Ordnance Test Station and Jet Propulsion studied the preparation and polymerization of glycidyl nitrate:

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{Cl} + \text{HNO}_3 & \rightarrow \text{O}_2\text{N} \text{CH}_2\text{CH}_2\text{Cl} \\
\text{O}_2\text{N} \text{CH}_2\text{CH}_2\text{Cl} \downarrow & \downarrow \text{NaOH} \\
\text{O}_2\text{N} \text{CH}_2\text{CH}_2\text{OH} & \downarrow \text{Lewis acid} \\
\text{HO} \text{CH}_2\text{CH} \downarrow \text{O} & \downarrow \text{H} \\
\text{CH}_2\text{O} \text{NO}_2 & \text{n}
\end{align*}
\]

\( n \) was 20–50 and hydroxyl terminated polymers could be cured with mixtures of diol, triol and disiocyanates.

The Naval Powder Factory, according to [33] obtained O-nitro polymers of a relatively low molecular weight:

\[
\begin{align*}
\ddot{\text{CO}} \text{CH} \text{CH} \ddot{\text{C}} \text{NHCH}_2\text{CH} \text{CH}_2\text{NH} & + \eta \\
\text{OH} \text{OH} & \text{OH} \\
& \text{HNO}_3 \\
\ddot{\text{CO}} \text{CH} \text{CH} \ddot{\text{C}} \text{NHCH}_2\text{CH} \text{CH}_2\text{NH} & + \eta \\
\text{ONO}_2 \text{ONO}_2 & \text{O} \\
& \text{ONO}_2
\end{align*}
\]

**Hydrazine and Difluoroamine Polymers**

According to Cohen [33] (Bell Aerosystem Corp. and Food Machinery Corp.) obtained polyethylene hydrazine perchlorate (XIV)

\[
\begin{align*}
\text{CH}_2 \text{CH} \text{N}_2 & + \eta \\
\text{NH}_2 & \text{ClO}_4
\end{align*}
\]
Information is given by the same source on a polymer with difluoroamino groups \((XV)\) obtained by Rohm and Haas Corp.

\[
\text{CH}_3 - \text{CH} - (\text{CH} - \text{CH}_3) \quad \text{NF}_2 \quad \text{NF}_2 \quad n
\]

\(\text{XV}\)

Pentaerythritol trinitrate (PENTRIN) is a convenient source of polymers through the esterification with unsaturated vinyl group containing acids, such as acrylic and methacrylic acid.

The monomers were described in Vol. II, p. 191 and Chapter X.

\(\text{N-NITRO POLYMERS}\)

A few polymers with \(N\)-nitro compounds were described in Chapter XIII of this book: formulæ (17) and (19).

\(\text{PLASTIC BONDED EXPLOSIVES}\) (Vol. III, p. 203)

A considerable number of explosives are composed of Cyclonite and HMX and non-explosive plastic (usually thermoplastic) polymers. Some recent compositions are given below on the basis of the literature [34]:

<table>
<thead>
<tr>
<th>Density</th>
<th>Rate of detonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/s</td>
<td>m/s</td>
</tr>
<tr>
<td>1. Cyclonite/Polyamide resin 90/10</td>
<td>1.79</td>
</tr>
<tr>
<td>2. HMX/DNP/Polyurethane (DNPAF is acetyldiformyl-2,2-dinitropropanol)</td>
<td>1.84</td>
</tr>
<tr>
<td>3. HMX/Teflon 90/10</td>
<td>1.86</td>
</tr>
<tr>
<td>4. HMX/Polyethylene 92/8</td>
<td>1.72</td>
</tr>
</tbody>
</table>

5. American plastic explosive:

Cyclonite/Polyisobutylene/2-ethylhexyl sebacate/mineral oil in proportions 91/9.1/5.3/1.6 does not lose its plasticity at \(-54^\circ\text{C}\) and retains its shape at \(+75^\circ\text{C}\).

6. British 'flexible' explosive SX-2 [35]:

Cyclonite/polyisobutylene/Teflon in proportions 88/10.5/1.5 retains its plasticity at \(-58^\circ\text{C}\).

\(\text{REFERENCES}\)


16. According to H. L. Herman, in [3], p. 144.
20. M. H. GOLDFELT et al., according to H. L. Herman in [3], p. 141.
30. W. DIEPOLD and K. MEYER, according to [25].
31. F. DAUMET and J. B. BREITENMOER, U.S. Patent 3669924 (1972) according to [27].
34. A. SIKORSKA, WIT, No. 3, 102 (1980).
CHAPTER 15

RECOVERY OF SPENT ACIDS
(Vol. II, P. 83)

The problem of recovery of spent acids has existed since the advent of nitration of glycerine and the problems of safety related to keeping the spent acid which contained a certain amount of nitroglycerine (Vol. II, p. 84, Fig. 26). The separation of nitroglycerine which can float on the surface of the spent acid created a safety problem. The method of Nathan, Thomson and Rintoul (Vol. II, p. 85) increased safety by preventing the formation of nitroglycerine on the surface. Although a small proportion of nitroglycerine is lost by solution and decomposition, the economy is satisfactory, as no costly investment is needed for the recovery of nitroglycerine from the spent acid.

However the methods being used at present for the manufacture of nitroglycerine, such as batch combined process (Vol. II, p. 95) and all continuous processes (Vol. II, p. 97) require that spent acid be dealt with correctly. Originally primitive arrangements were in use consisting in distillation of nitric acid and careful decomposition of organic products dissolved in the spent acids.

The progress was considerably speeded up with the advent of cast silicon iron as the main acid-resistant metal [1]. Some other modern materials were also introduced into the construction of the equipment, such as enamel, tantalum, teflon [1] and glass [2]. Generally speaking the spent acid from nitration of glycerine, glycols and pentaerythritol have a lot in common although they differ in some particular points. The common problems of by-products of the nitration of alcohols will be discussed below.

GENERAL PROBLEMS OF SPENT ACID FROM THE NITRATION OF ALCOHOLS

This particular problem was studied by Camera, Zotti and Modena [3, 4]. They identified some of the products of the action of nitric acid on ethyl nitrate as a model for the behaviour of nitrate esters in acid solution. They came to the conclusion that the initial process consisted in hydrolysis of the ester. The hydrolytic equilibrium was disturbed by oxidation of the alcohol by liberated nitric acid. In the instance of ethyl nitrate the freed ethanol was oxidized to acetaldehyde. Some other products were also formed. Nitric acid was reduced to nitrous acid which can serve as a catalyst of a number of reactions. Among the other products formed were: acetic and oxalic acids, carbon dioxide and nitrogen oxides from nitrous acid: NO₂, NO, N₂O and nitrogen.

Spent Acid from Nitration of Glycerine

According to Plinke [1] the average composition of spent acid of nitroglycerine is

<table>
<thead>
<tr>
<th>Substance</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>10%</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>70%</td>
</tr>
<tr>
<td>H₂O</td>
<td>17%</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>3%</td>
</tr>
</tbody>
</table>

Compared with the composition given in Vol. II, p. 84 it differs only by the presence of 3% of nitroglycerine. This should be regarded as all organic matters deriving from the nitration of glycerine, the hydrolysis of nitroglycerine, oxidation of the resulting mixtures etc., much in terms of the work of Camera et al. [3, 4].

There are three known methods of dealing with nitroglycerine spent acid:

1. Stabilization of Spent Acid according to Plinke [1]

This method is applied when the spent acid has to be re-used without the danger of keeping it for any length of time. To destroy nitroglycerine and organic impurities the acid is conveyed at a high temperature through a number of columns where nitroglycerine and other organic substances are oxidized by nitric acid. Nitric acid is reduced to nitric oxides which are directed to the absorption column washed with water yielding dilute nitric acid.

The diagrammatic presentation of the apparatus is given in Fig. 65. Nitrator (1) is fed with nitrating mixture and glycerine, nitroglycerine is separated (7) from the spent acid which enters columns (2-4). The columns are heated with steam through a heat exchanger (9). The acid freed of oxidized organic substances is cooled in (10) and flows out. Gaseous products - mainly nitrogen oxides and carbon dioxide - pass through a cooler (11) and enter column (5). Air is blown (8) into the column where cold water (12) circulates through a pump (6) and is injected additionally to the top of the column (5). Dilute nitric acid flows from the column.

2. Denitrification of Spent Acid

(A) According to Plinke [1]. The spent acid can be denitrated without adding
other acids and nitric acid of 10% can be obtained. By adding sulphuric acid of 85–96% and (in some cases) 60% nitric acid a highly concentrated nitric acid of 98% HNO₃ can be obtained and sulphuric acid of 70% H₂SO₄. All organic compounds are destroyed and gases from decomposition (nitric oxides, nitrogen, carbon dioxide) are liberated from pre-bleaching and bleaching column. The scheme for the treatment of spent acid is given in Fig. 66.

Spent acid from (1) after separation of nitroglycerine (9) enters denitration column (5). If necessary, some nitric acid (60% HNO₃) is added from container (2). Sulphuric acid (85–96% H₂SO₄) is fed from container (3) to the top of the denitration column (5). The temperature of the denitration column is controlled by injecting steam and air. Sulphuric acid (68–72% H₂SO₄) freed of nitric acid and gaseous products is collected in tank (4) and pumped out (8). Distilled nitric acid enters pre-bleaching column (6) where it is freed of nitrogen oxides through dephlegmator (10). Pre-bleached nitric acid enters bleaching column (7) where air is blown through (11) to free the acid from the traces of nitric oxides entering through (10). Here nitric acid flows back to column (6) and gases are blown into the air. A system of heat exchangers (12–20) serves for heating or cooling and keeps the proper temperature — high or low. Nitric acid of 98% HNO₃ flows through valve N 98 to a tank. After bleaching nitric acid contains less than 0.1% nitrous acid.

General views of the denitration plant are given in Figs 67–69.
(B) According to Schott, Mainz [2, 6–8]. The progress of the method of concentrating nitric acid with sulphuric acid was connected with the use of boro-silicate glass as a material for the construction plants in combination with tantalum as a heater material to carry out indirect heating of the concentration column [6]. This method of operation was realized by Messrs. Schott & Gen., Mainz, who used tantalum heat exchangers on which the acid mixture was sprayed. The exchanger was mounted on the top of the concentration column where the greatest part of the nitric acid is. The heat exchangers are heated by saturated steam and evaporate the major part (ca. 90%) of the nitric acid contained in the mixture. Figures 70–72 give general views of some parts of the equipment. An important feature was the introduction of standardized dimensions which make possible the exchange of some parts of the equipment.

3. Re-use of Spent Acid from the Nitration of Glycerine

Biauzzi S.A. [5] is using an ingenious method of utilizing spent acid from the nitration of glycerine to nitrate toluene to dinitrotoluene. Toluene is added to the spent acid at a temperature gradually increasing up to 90°C. Nitroglycerine
dissolved in the acid is decomposed and increases the concentration of nitric acid and thus participates in the nitration.

The economy of this method is based on the fact that no denitrification plant is needed.

**Spent Acid of PETN**

The main problem of spent acid after the nitration of pentaerythritol is the instability of the spent acid. Several "fume off" accidents of spent acid have occurred on its storage after the separation of PETN. Systematic study of the stability of spent acid was carried out by Ramaswamy and Subba Rao [9]. They found that the concentration of 75–80% HNO₃ made the nitric acid unstable due to the presence of organic compounds which can readily be subjected to oxidation. According to the above authors the oxidizing properties of nitric acid predominate at the critical concentration of 75–80%.

Ramaswamy and Subba Rao suggested two methods of stabilizing the spent acid of PETN manufacture.

1. In the first method live steam of low pressure was injected gradually to keep the temperature at 70 ± 2°C. The injection was stopped when no further
exothermic reaction was noticed. The concentration of the spent acid falls from
82 ± 2% to 72 ± 2% HNO₃, thus below the dangerous concentration.

(2) In the second method the spent acid was treated with steam so that its
temperature was raised to 95–100°C. A highly exothermic and vigorous reaction
was accompanied by an evolution of brown fumes and stirring was necessary by
blowing in nitrogen or air. The reaction was facilitated by the presence of
nitrous acid. The higher the concentration of HNO₂ the lower the temperature
of the reaction.

In the normal process of PETN production the content of nitrous acid and
organic by-products is below 0.2% and 0.3–0.4% respectively. Ramaswamy and

Subba Rao pointed out the ease of hydrolytic reactions in the spent acid,
followed by oxidation. They found formic, oxalic and mesoxallic acid among the
decomposition products.

Attention should be drawn to the statement by Camera [10] that PETN can
be hydrolysed to tri and dinitrate by nitric acid of 70–90% HNO₃ at 20 and
40°C (see also Chapter X, ref. 149). The unsymmetrically substituted penta-
erithritols are particularly apt to vigorous reactions [11].

Plinke [1] described the process of stabilizing spent acid of PETN which,
according to the same author contains 80% HNO₃ and 0.1–0.3% organic sub-
stances. The spent acid is distilled in a circulation evaporator to completely
destroy organic substances and to obtain pure nitric acid. To reach the full de-
composition of organic impurities, sulphuric acid of 70% H₂SO₄ is present in
the evaporator and remains there to the end of the operation.

Figure 73 is a diagram of the stabilization of residuary nitric acid of PETN
according to Plinke. Spent acid from (1) is pumped (4) to evaporator column (3)
after being heated at (6). Hot sulphuric acid (70%) flowing from column (3)
is cooled at (7) and recirculates to (3). Nitric acid distils from column (3), is
cooled through a condenser (8), collected in tank (2) and pumped out through
(5). This is nitric acid of 75–80% HNO₃. Nitrous gases escape between (8) and
(2).
Spent Acid from Cyclonite (RDX) Manufacture
(Vol. III, pp. 93, 98–102)

As described in Vol. III Cyclonite can be made by nitration hexamine (hexamethylenetetramine) with nitric acid. The product is precipitated by pouring the solution into hot water in such a way that the concentration of the acid became 50–55% HNO₃ and the temperature 70–90°C was maintained. All unstable products were decomposed and NO₂ gas evolved. This was a ‘degassing process’.

A diagram of the concentration of spent acid obtained in that way was given by Plinke [1] Fig. 74. Spent acid from tank (1) enters through heat exchanger
ing nitrous fumes through (8). A series of heat exchangers (12–17) maintain the correct temperature for the whole system. Nitric acid (98%) leaves column (6) through cooler (18) to a storage tank.

Spent Acid from Nitrocellulose (Vol. II, p. 374)

Plinke [1] gives the average composition of spent acid from the nitration of cellulose: 22% HNO₃, 62% H₂SO₄, 15.8% H₂O, 0.2% nitrocellulose. Highly concentrated nitric acid can be distilled from such an acid without adding sulphuric acid. If sulphuric acid (85–86%) is added, the process is similar to that described in Fig. 74.

This operation is seldom performed and the usual procedure consists in adding concentrated nitric and sulphuric acid to the spent acid.

Spent Acid from TNT

It is very seldom that spent acid from TNT is subjected to distillation. If so, only dilute nitric acid can be obtained according to Plinke [1]. A higher concentration of nitric acid (over 50% HNO₃) can result only after adding concentrated sulphuric and nitric acid. The apparatus is much the same as with the following.

Spent Acid from Mononitration of Toluene

It has been pointed out by Dębowski and Zieliński [12] that the spent acid from mononitration of toluene should not be reused for denitration by adding nitric and sulphuric acids. It contains 0.3–0.5% mononitrotoluenes and while adding concentrated nitric and sulphuric acids, further nitration of mononitrotoluene present can be produced but requires special precautions.

The authors suggested a simple method of dealing with the spent acid. They extracted the nitro compounds with toluene at 30°C and thus were formed:

1. Toluene with a small proportion of nitro compounds,
2. Spent acid free of nitro compounds.

Toluene (1) can be used for nitration, and (2) spent acid can be safely mixed with concentrated nitric acid and 20% oleum and re-used for mononitration of toluene.

ENVIRONMENTAL PROBLEMS OF DENITRATION

The denitration of spent acids offers some environmental problems. The major one being the escape of nitrous fumes from the denitration columns. According to Berkman [13] they can be introduced to a solution of sodium hydroxide to obtain sodium nitrate and nitrate aqueous solution. The same
monograph describes the method of absorption with water [14]. It also gives a description of the industrial method by Andrew and Hanson [15].

An original method was proposed by Kulin and Tikhonenko [16]. They suggested the reduction of nitrogen oxides escaping from the denitrification column with methane, for example:

\[
\text{CH}_4 + 2 \text{NO}_2 \rightarrow \text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O}
\]

\[
\text{CH}_4 + 4 \text{NO} \rightarrow 2\text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O}
\]

The reaction can be catalysed by Ni and Cr at 500–600°C and helped by adding some air-oxygen.

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8. SCHOTT INFORMATION 3/1978, Jenner Glasswerk Schott & Gen., Mainz, BRD.

CHAPTER 16
SALTS OF NITRIC ACID
(Vol. II, p. 450)
AND OF OXY-ACIDS OF CHLORINE
(Vol. II, p. 476)

AMMONIUM NITRATE

As is well known ammonium nitrate is the most popular oxygen carrier in explosive mixtures which is also widely used as a fertilizer. Subsequently there is voluminous literature on the properties of ammonium nitrate. Among the greatest problems is its caking. It continues to raise interest and an excellent review has appeared recently [1].

Hygroscopicity of ammonium nitrate was considered to be the major cause of caking [2–5], but later the polymorphism of crystals of ammonium nitrate (IV → III, Vol. II, pp. 450–452) was recognized as an important factor [6–8]. Particular attention should be paid to the work of Sjölin [8] who studied the phenomenon of caking using X-ray and scanning electron microscopy. His conclusions are summarized as follows: caking is mainly caused by the phase transitions IV → III at 32°C and depends on dissolution and recrystallization of the solid at the phase transition. If no pressure is applied to the sample a porous powder is formed due to volume increase [14], if pressure is applied, it will result in large crystal surfaces and the dissolution-recrystallization process gives a hard product.

Sheeerson et al. [7] drew attention to the fact that transition IV → III does not cause caking while the phase transition III → IV is of great importance and should be regarded as essential in the process of hardening. Thus hardening occurs during the process of cooling ammonium nitrate heated above 32°C.

Some substances have a great influence on the change IV → III. Particularly important is the role of water promoting the change [9–13]. Thus it has been shown by Brown and McLaren [10], Wolf and Scharr [11] that ammonium nitrate chemically pure and free of water requires a higher temperature for the transformation of form IV and at ca. 50°C it is directly transformed into form
II, whereas a trace of water favours the normal transformation $\text{IV} \rightarrow \text{III}$ at 32°C.

The above mentioned volume increase was described in the important paper by Hendricks et al. [14] and in Vol. II (p. 452, Table 110).

As the result of repeated transitions $\text{IV} \rightarrow \text{III}$ breakdown may occur of crystals or prills yielding fine particles which are readily caking through the absorption loss of moisture.

The paper by Thompson [15] should be mentioned as pointing out the importance of the capillary adhesion which can be the major factor responsible for the caking phenomenon narrow layer of the saturated solution between the particles shows a lowered meniscus of the solution, i.e. reduced pressure. Consequently the action of atmospheric pressure becomes sufficiently strong to compress the neighbouring granules into a solid block.

It can be seen from the above discussion that the phenomenon of caking is very complicated with several factors involved in it and there is practically no sufficiently simple explanation of the phenomenon. Subsequently no simple practical solution exists for preventing the phenomenon of caking ammonium nitrate and only a partial solution is known.

Some existing practical methods were mentioned in Vol. II, pp. 453–454. A more systematic description is given below:

1. Covering particles of ammonium nitrate with non-hygroscopic layers of polymers, such as polyvinyl compounds. This however should be limited to substances which could not produce harmful influence on the explosive properties of ammonium nitrate and (for underground work) would not give harmful products after detonation, such as chlorine compounds from polyvinyl chloride.

These conditions are fulfilled with paraffin wax or fuel oil if such an ammonium nitrate is used in explosive mixtures where the above substances are included in the formulation of the explosives. As pointed out in Vol. II (p. 461–2) small amounts of organic substances increase the ease of detonation of ammonium nitrate and danger of shipping.

2. Non-reactive mineral compounds, such as kaoline in powder form in proportion 2.5% [4]. Carbonates should not be advised as they can react with ammonium salts to form unstable ammonium carbonate. Also silicates are not advised as they can produce silicon oxide which is dangerous in underground work as a cause of silicosis.

3. Salts of stearic acid, such as calcium stearate.

4. Addition of anhydrous salts readily forming hydrates, such as anhydrous: $\text{Mg(NO}_3\text{)}_2$ (1%) and $\text{Al}_2\text{(SO}_4\text{)}_3$ (2%) [8]. In some patents anhydrous sulphates have been claimed.

Among the agents preventing the transformation of crystalline forms three methods are of great importance (in addition to keeping the ammonium nitrate dry):

1. Introduction of some cations which could enter the crystalline lattice, such as $\text{K}^+$ which has an ionic radius (1.33 Å) of the same order as $\text{NH}_4^+$ (1.43 Å). The presence of 3–4% $\text{KNO}_3$ suffices to stabilize form III (Vol. II, pp. 454–5).

2. Introduction of some mineral substances. Among the minerals kaoline or kieselsulphur in quantity 2.5% were suggested [4]. Brown, Green and Blanton [16] recommended adding a mixture of boric acid, diammonium phosphate and ammonium sulphate in quantity of less than 0.5%. They suggested a composition containing 0.2% $\text{Na}_2\text{BO}_3$, 0.2% $\text{NH}_4\text{H}_2\text{PO}_4$ and 0.01% $\text{NH}_4\text{H}_2\text{SO}_4$. Prills of unprecedented hardness resulted, completely stable over 32°C transitions. The authors found this mixture much superior to previously used kaoline or kieselsulphur. Engel [17] found that the volume increase due to the phase transitions $\text{IV} \rightarrow \text{III}$ at 32°C was reduced by incorporating diamine complexes of Ni and Cu into the lattice. The transition temperature raised above 50°C. The effect of complexes of Zn was less marked.

Glazkova in her monograph [18] described water resistant ammonium nitrate 'Zn V' containing 0.07–0.10% 'iron sulphate' and 0.3–0.4% of an undisclosed hydrophobic component.

3. Addition of surface active agents, such as triphenylmethane dyestuffs, can prevent caking of ammonium nitrate in quantity as low as 0.05% (see Vol. II, p. 454) and [19].

It is now accepted that surface active substances are very helpful as anti-caking agents. A review was published on the subject by Kortacekowskia and Biskupski [108]. Sodium alkylarylsulphonates and various substances with trade names were examined in quantity 0.05–0.50%. The authors draw attention to the fact that before the use of such substances experiments should be carried out on the influence of the additives on thermal stability of ammonium nitrate. Some of them appreciably lower the temperature of the decomposition of ammonium nitrate which should not be less than 220–240°C. It should also be borne in mind that the addition of an organic substance or (generally speaking) of a substance which can burn increases the sensitivity of ammonium nitrate to detonation. Small amounts, of the order of 1–4% of organic substances considerably increase the sensitivity (Vol. II, pp. 461–462 and the description of accidents on p. 441, this volume). Thus the sensitivity to detonation of ammonium nitrate with surface active agents should be examined and mixtures with additives should be handled with precaution as with explosives.

**Hygroscopicity of Ammonium Nitrate**

The hygroscopicity of ammonium nitrate is its great drawback. The problem occurred particularly with the use of ammonium nitrate mining explosives their storage and use in damp places. The usual method of reducing hygroscopicity consists in incorporating small proportions of calcium, zinc and iron salts of fatty acids, usually stearic acid.

Silicon resins can also be used (Vol. III, p. 421). The problem of the hygro-
Some organic substances (e.g., cellulose) lower the thermal stability of ammonium nitrate. According to Findlay and Rosebourne [22] an ammonium nitrate-paper combination was shown to self heat at the temperature range used in bagging and shipping the fertilizer grade of NH₄NO₃, so that it often arrived at a sea-port appreciably hotter than when it was bagged (90 ± 20°C). Bag imprudence and even charring by self-heating caused excessive spillage, contamination and required rebagging. Several spontaneous fires in rail trucks were recorded, preceding the Texas City catastrophe [23]. Immediately after the Texas City catastrophe the paraffin-wax coating of ammonium nitrate was replaced by kieselguhr – an inferior but much safer anticaking agent. Kieselguhr coated ammonium nitrate (fertilizer grade) was widely in use for AN/FO explosive mixtures [23].

A detonation of 80 tons of ammonium nitrate in plastic bags occurred in 1978 at Manouba in Tunisia [39]. The floor of the store house was covered with saw dust for the purpose of absorbing any liquid from broken bags. It was stated that saw dust mixed with oxidizing substances in the presence of moisture can undergo fermentation causing a temperature rise and ignition of ammonium nitrate. Prior to the detonation red fumes came from the store house, which indicated the beginning of the decomposition which ended in detonation.

**HYDRAZINE NITRATES (Vol. II, p. 464)**

Two hydrazine (or hydrazinium) nitrates are known: mono- and dinitrate.

**Hydrazine Mononitrate**

Mononitrate NH₅⁺NH₂NO₃ exists in two forms: α and β. α-Form is stable and has m.p. 70.9°C, β-form is unstable, has m.p. 62.1°C [24]. β-Form is obtained by keeping the substance at 110°C for 30 min and cooling slowly to 61°C. The crystal structure was examined, and so were refractive indexes of α and β-forms: 1.065 and 1.458 respectively [25]. If a concentrated solution of β-form is cooled from 100°C down to room temperature α-form was separated [26]. The transformation enthalpy ΔH of form β to α is 2.0 kcal/mol [27]. Thermal decomposition was studied by a number of authors. At 100°C the evolution of ammonia is less prominent than that of ammonium nitrate: 0.005% as compared with 0.016% [28]. Shilovskii and co-workers [29] found that the decomposition started at 180°C, increased above 240°C and became explosive at 270°C. The 'Bunce ton up and down-down' method (Vol. III, p. 445) gave 50% probability of ignition at 307°C [27]. Decomposition to 200–300°C under 1 atm. resulted in decomposition according to equation [30]:

\[
4 \text{NH}_2\text{HNO}_3 \rightarrow 2 \text{NO}_2 + 5 \text{N}_2 + 10 \text{H}_2\text{O}.
\]
Decomposition in vacuo was investigated by Breisacher and co-workers [31]. When ignited, hydrazine nitrate burns very readily, the flame is extinguished upon removal of the ignition source. Shidlovskii et al. [29] found that the addition of 10% K₂Cr₂O₇ assures steady burning.

Thermochemical and some explosive data were collected by R. Meyer [32]:

- Enthalpy of formation: -620.7 kcal/kg
- Heat of explosion: 924 kcal/kg
- Volume of gases: 1001 l/kg
- Oxygen balance: +8.6%
- Density: 1.64 g/cm³
- Decomposition temperature: 229° C.

High lead block test (408 cm³) and velocity of detonation (8690 m/s) were given.

The high figures of the velocity of detonation and of lead block aroused much interest in the compound and have been reported by several authors.

Thus explosive properties were reported by H. K. James et al. [27]: the rate of detonation of molten hydrazine nitrate 75° C was found to be 8500 m/s, and ballistic mortar 120.4 ± 0.5 (picric acid = 100) or 142 (TNT = 100).

Some other authors also reported [32] high velocity of detonation: 8500–8510 m/s with cartridges of 6.4 cm diameter, pressed to density 1.59–1.6. Price [33] found that the infinite charge diameter detonation velocity can be expressed by the equation $D = 5390 (\rho \cdot HN \cdot 100)$ where $\rho$ HN is the density in g/cm³. Kurbangalina and Timokhin [34] found that the critical diameter increases with an increase of water content and the rate of detonation can vary from 2000 to 8000 m/s.

Meyer [32] reported that mixtures of hydrazine nitrate with HMX (Octogen) pressed to high density can be over 9000 m/s.

Attention should be drawn to two monographs on hydrazine: [26] and [30].

Hydrazine Dinitrate
(Vol. II, p. 465)

Hydrazine dinitrate $\text{NH}_2\text{NH}_2(\text{HNO}_3)_2$ was described by Sabanejeff [35]. It is a substance which decomposed at ca. 80°C. When heated rapidly it melts at 103–104°C. It can be obtained by neutralizing hydrazine hydrate with two moles of nitric acid or by acting barium nitrate on hydrazine sulphate [26], [30]. It decomposed on steam bath or on standing at room temperature over sulphuric acid with the evolution of hydrazoic acid [35].

It is an explosive which is stronger, but less sensitive to impact, than Tetryl but weaker than PETN [33]. However owing to its low stability it is of little practical value.

SALTS OF NITRIC ACID AND OF OXY-ACIDS OF CHLORINE

Hydrazine Nitrate Complexes ('Hydrazinates')

Salts of bivalent metals (Ni, Co, Zn, Cd and Mn) form complexes with hydrazine nitrate of a general formula

$$[\text{M(N}_2\text{H}_4\text{H}_3\text{)}_3\text{ (NO}_3\text{)}_2\text{ and } [\text{M(N}_2\text{H}_4\text{H}_3\text{)}_2\text{ (NO}_3\text{)}_2], \text{ I II}$$

For the first time Ni salts (II) were obtained by Franzen and Meyer [36] and a number of them were prepared by Médard and Barlot [37]. According to the latter authors some of hydrazinates possess initiating properties and are described in Chapter XVII on initiating explosives.

Methyamine Nitrate (Vol. II, p. 465)

Methyamine nitrate (m.p. 111°C) recently gained much significance as an important ingredient of ‘slurry’ explosives because of its greater aptitude to detonation than that of ammonium nitrate. More data on explosive properties were recently given by R. Meyer [32]:

- Enthalpy of formation: -896 kcal/kg
- Heat of explosion: 887 kcal/kg (the given figure formerly - 1200 kcal/kg – Vol. II, p. 466 – should be corrected as being too high).
- Volume of gases: 1027 l/kg.
- Density: 1.422 g/cm³.

According to Cottrell and Gill [38] unconfined methyamine nitrate melts and boils (230°C) without decomposition.

With regard to preparation of the compound, apart from the straight forward formation from methyamine and nitric acid (66%) (as described in Vol. II) another method based on the Fösch reaction, by reacting ammonium nitrate with formaldehyde at 80–100°C, as was suggested by the author of this book [39] and brought to industrial application:

$$\text{NH}_4\text{NO}_3 + 2\text{CH}_2\text{O} \longrightarrow \text{CH}_3\text{NH}_2\text{NO}_3 + \text{HCOOH}.$$  

(2)

Although laboratory experiments have shown that methyamine nitrate is not very sensitive to impact, it gave a disastrous explosion at Potomac River, Virginia in 1976 [40] in two tank cars containing 86% solution of methyamine nitrate. The explosion probably took place due to friction in a pump or to a collision.

Tetramethylammonium Nitrate $(\text{CH}_3)_4\text{NNO}_3$ (Vol. II, p. 466)

This substance was found to be difficult to bring to explosive decomposition.
However the mixtures of tetramethylammonium nitrate with polymers can burn in the presence of ferric oxide which proved to be an efficient catalyst for burning such mixtures [41]. Fe$_2$O$_3$ has a similar catalytic effect on the combustion of guanidine nitrate.

**GUANIDINE NITRATE** (Vol. II, p. 466)

Enthalpy of formation of guanidine nitrate was determined by Krivtsov, Titova and Rosolovskii [105]. It was found to be $\Delta H_f = 93.0$ kcal/mol.

**NITRATES OF AROMATIC AMINES**

A number of nitrates of aromatic amines were recently described [42]. No information on their explosive or burning properties is available.

**AMMONIUM CHLORATE** (Vol. II, p. 476)

This substance has no practical application owing to its low stability, but it was important to study conditions influencing the decomposition and possibly the mechanism of decomposition. The early papers [43, 44] gave only a general description of the decomposition of the substance. A much more detailed account was given by Solynosi and Bánsági [45]. They studied the decomposition by measuring the pressure of non-condensable gases and the loss of weight at different temperatures. A measurable decomposition started at 50°C, but some days after the preparation of the substance according to (3),

$$\text{NH}_4\text{Cl} + \text{NaClO}_3 \rightarrow \text{NH}_4\text{ClO}_3 + \text{NaCl}$$

a slight decomposition was observed even at $-5^\circ$C. The explosion of freshly prepared substance occurred at 50°C. The activation energy was calculated as being $22-25$ kcal/mol. The addition of ammonia stabilized the substance, but the addition of chloric acid considerably increased the rate of decomposition.

Attention should be paid to the fact that the substance is dangerous and all possible reactions leading to the formation of ammonium chlorate should be carefully avoided.

**AMMONIUM PERCHLORATE** (Vol. II, p. 477)

An enormous amount of work has been done in the last 30 years on ammonium perchlorate (AP). Originally it was reflected in the monograph by Schumacher [46] (Vol. II, p. 477) and more recently – the excellent review by Jacobs and Whitehead has appeared [47]. It contains all the important information available up to 1968. The pertinent data will be repeated in the present book to obtain a full picture of this compound and some more recent descriptions will be given here. Also the monograph of Glazkova [18] on catalytic decomposition should be mentioned.

**Crystal Structure and Physical Properties**

Two crystal structures of ammonium perchlorate are known: the lower-temperature orthorhombic form existing below 240°C and cubic form above that temperature [48]. The density of orthorhombic and cubic forms is 1.95 and 1.76 g/cm$^3$ respectively [47]. Ammonium ion undergoes an almost free rotation with the potential barrier of 0.55 ± 0.05 kcal/mol [49]. The heat of transition from orthorhombic to cubic system is accompanied by a heat effect of 2.3 ± 0.2 kcal/mol [50, 110]. AP is nonhygroscopic [81].

The specific heat of ammonium perchlorate [51] is $0.309 \text{cal g}^{-1} \text{deg}^{-1}$ between 15 and 240°C and $0.365 \text{cal g}^{-1} \text{deg}^{-1}$ above 240°C. The electrical conductivity was also examined [52–54]. The activation energy of electrical conductivity changed from 45 kcal/mol at high temperature (over 255°C) to 4 kcal/mol below 92°C.

**Thermal Decomposition and Burning of AP**

**General information.** Ammonium perchlorate (AP) is stable at room temperature. It begins to decompose above 130°C [56] or 150°C [55]. According to Andreev and Sun Tsuan-tsai [55] at 160°C half-life of AP is 25,000 min and at 270°C is 225 min (for comparison they gave the half-life figures for nitrocellulose at 160°C and for TNT at 270°C: 170 min and 20 min respectively). Thus the decomposition of AP is much slower than both above mentioned explosives. The decomposition of ammonium nitrate above 170°C (i.e., above its m.p. which is 169°C) is much faster than that of AP due to the fact that AP does not melt. Thus the half-life of ammonium nitrate at 286°C and of ammonium perchlorate at 280°C is 5 min and 170 min respectively.

The decomposition of AP with temperature follows an S-curve, which is typical for autocatalytic reactions. Thus, there is an initial increase in the rate of decomposition through the formation of the products of decomposition and the fall of the rate after these products were subjected to decomposition. The formation of an unusual product at lower temperatures (220–300°C) has already been described in Vol. II, p. 479. Above 350°C the reaction is no more autocatalytic.

Numerous products are formed during the decomposition of AP. They were examined in Dodé's pioneering work [56] and confirmed by Bircumshaw and Newman (Vol. II, p. 478). Further experiments were carried out by Rosser, Inami and Wise [57]. Dodé identified the products such as chlorine dioxide (at temperatures below 300°C), nitrogen, water, oxygen, nitrous oxide, hydrogen.
chloride, nitrosyl chloride, nitrogen trioxide and nitrogen dioxide, the latter three compounds being the result of the secondary reaction of nitric oxide with chlorine and oxygen.

Wise et al. [57] gave a quantitative summary of the products of decomposition between 250° and 325°C, for example at 275°C they found:

- 0.50 O₂
- 0.047 N₂
- 0.35 N₂O
- 0.39 Cl₂
- 0.19 HNO₃
- 0.16 HCl
- 0.019 NO

Moles per mole of decomposed AP

The authors tried to rationalize the reaction in terms of a decomposition equation beginning by electron transfer followed by proton transfer (4):

\[ \text{NH₄ClO}_₄ \rightarrow \text{NH}_₄^+ + \text{ClO}_₄^- \rightarrow \text{NH}_₃ + \text{HClO}_₄ \]  

(4)

The proton transfer was earlier suggested by Davies, Jacobs and Russell-Jones [82]. A number of Soviet authors - Boldyrev et al. [118] confirmed the mechanism of proton transfer. According to Pearson and Sutton [75] perchloric acid decomposed to yield ClO₄⁻ and ClO which were detected in fragmentation in a mass spectrometer.

It appears that the reaction of decomposition of AP is too complicated to be presented in one equation. Nevertheless the deflagration of AP starting at ca. 450°C can be depicted by equation (5) according to Kaye [81]:

\[ 4 \text{NH}_₄\text{ClO}_₄ \rightarrow 2 \text{Cl}_₂ + 8 \text{H}_₂\text{O} + 2 \text{N}_₂ + 3 \text{O}_₂ \]  

(5)

Another equation for the decomposition of AP is (6) [47]:

\[ 2 \text{NH}_₄\text{ClO}_₄ \rightarrow \text{Cl}_₂ + 4\text{H}_₂\text{O} + 2\text{NO} + 1\text{O}_₂ \]  

(6)

Probably both reactions can run simultaneously.

A phenomenon of sublimation of ammonium perchlorate occurred simultaneously with decomposition as mentioned previously (Bircumshaw and Newman, Vol. II, p. 478), and suggested by Dodé [58], Jacobs and Powell [59] and made the process still more complicated.

The activation energy of thermal decomposition of AP varies from 17 to 40 kcal/mol according to various authors [47]. The wide discrepancy between their results was due to various conditions of the reactions, various techniques used and is a sign of the complicated nature of the reactions of the decomposition of AP.

Mass spectrometry fragmentation was investigated by a number of authors [60] (also references in [47]). More recent work was done by Volk and Schuhbert [61]. At 240° and 280°C they found the fragments: NH⁺⁺, NH⁺⁺, NH⁺⁺, H₂O⁺, NO⁻⁺, O²⁺, Cl⁺, N₂O⁺, NO⁻⁺, ClO⁻⁺, ClO⁺⁺, ClO₂⁺, HClO₄⁻ m/e.

**Thermal Decomposition of Irradiated Ammonium Perchlorate**

(Vol. II, p. 481)

The work of Freeman and Anderson [62] was continued and confirmed the previous observation. Irradiation increases the number of nuclei and this affects the decomposition of the substance: the decrease in the induction period and an increase in the rate constant [63a]. A detailed kinetic study of pre-irradiation was made by Harley and Levy [63b]. They also found that the activation energy of thermal decomposition of AP was unchanged by irradiation at 28.4 ± 2.5 kcal/mol.

**Influence of Pressure on Burning of AP**

Ammonium perchlorate can burn on condition that it is confined and that the pressure inside the vessel is a minimum of 45 atm. [64], or according to other authors above 20 atm. [65]. The size of crystals of AP have a decisive influence on this limit of pressure. Thus it was found that very fine substance (UFAP = ultra fine AP) can burn in the open under atmospheric pressure [81]. A number of authors examined the deflagration of ammonium perchlorate at different temperatures and pressures: Watt and Patterson [119], Bogg and coworkers [67], Glazkova [66, 18]. Glazkova examined the influence of pressures as high as 1000 atm.

All authors drew attention to a number of factors influencing the data referred to burning of AP such as: size of crystals, density, confinement (e.g. diameter of tubes), material of the tubes (e.g. glass, Plexiglas). The typical shape of curves: rate of burning/pressure is presented in Fig. 75 according to Glazkova [18]. The region below 300 atm. is depicted in Fig. 76 [67], and merits special attention. Here the analysis will be given as presented by Glazkova [66].

Four regions of burning should be distinguished, viz:

I) From 20 to ca. 55 atm. A steady increase is marked in the rate of burning. The exponent \( n \) in the formula of burning \( u = b \cdot p^n \) is ca. 0.77 according to [68].

\( \dot{u} = \text{the rate of burning in g/cm}^2 \text{ min} \)

II) From ca. 55 to 150 atm. the slope \( du/dp \) is smaller, and the exponent \( n \) has a lesser value than in (I), for example 0.55.

Both regions were described by Glazkova as those of steady burning.

III) From 150 to 300 atm. The burning is characterized by a rapid fall in the rate of burning with an increase of pressure [67]. The exponent \( n \) can acquire a negative value, for example -3.8. In some experiments Glazkova observed a plateau in this region of pressures. A plateau was also found by Manelis and Strunin [69].
position of AP. Water remains on the surface of crystals as a liquid. This follows from the temperature of boiling water under high pressure. This temperature can be higher than that of the surface of solid AP, for example: under 150 atm., the temperature of boiling water is 360°C whereas the surface has a temperature 320°C.

A factor of sublimation should also be considered. Guller and Williams [71] described the deflagration of AP at pressure between 20 and 100 atm. and suggested that a dissociate sublimation process is likely to exist at the interface between the gaseous and condensed phases.

**Density and Critical Diameter**

Bekisman, Beljakov, Lukashenya and Pelikarpov [72] studied the influence of the density of AP on the rate of burning under pressures 5–100 atm. The mass rate of burning increases with the increase of density. Thus confined samples with densities from 1.465 to 1.95 g/cm³ increased by factor 2.66. Glazkova [66] carried out wide experiments on the influence of density and obtained a somewhat complicated picture: generally the rate of burning increases with density but follows the same rule as regards the influence of the pressure as depicted by Figs 75–76. A pulsing burning was observed under pressures 160–300 atm.

Samples of AP do not burn if they are confined in tubes of a diameter below a certain limit — the critical diameter. This was investigated by Glazkova [73] for the density 1.2–1.4. The smallest critical diameter corresponds to the substance burning under 100–150 atm., that is where the rate of burning is the highest. The maximum critical diameter is at 20 atm. and further increase of the pressure reduces the critical diameter.

It should be borne in mind that the results of different authors are not in complete agreement, due to the complicated nature of burning ammonium perchlorate, which depends on so many factors mentioned already and some other factors such as the size of particles of AP, a kind of confinement. The burning of AP under different pressures indicates that the rocket propellant with AP should not be used in systems where the pressure is over 150 atm. that is, where burning is unstable (pulsating) and excludes the systems where the pressure is over 300 atm and the exponent $n > 1$.

**Decomposition (at higher temperatures) and Burning of Ammonium Perchlorate with Various Additives**

A considerable amount of work has been dedicated to the influence of additives on the decomposition of ammonium perchlorate. It started by the pioneering work of Friedman and co-workers [64] who studied the decomposition of ammonium perchlorate under pressure from atmospheric to 340 atm. They found that an addition of ca. 3% of some mineral compounds possess a
catalytic action. The best catalyst was found to be cupric chromite containing 85% CuO and 15% Cr₂O₃. Ammonium perchlorate with 3% of cupric and chromic oxides begins to burn steadily under pressure over 135 atm. and 230 atm. respectively. With cupric chromite the steady burning was much faster and started under pressure of 100 atm.

The catalysts introduce some change in the composition of the products formed during the burning of AP. The main reactions of the decomposition of NH₄ClO₄, according to Rosser and co-workers [57] consists in the sequence of the reaction already described (4).

The experiments of Rosser, Inami and Wise [57] were the continuation of their work on catalytic decomposition of ammonium nitrate [74]. They examined the action of copper chromite. They found that it acted at the early stage of the reaction and its action disappeared after copper chromite was oxidized by the products of catalytic reaction. Cobalt oxide was found to be an exceptional catalyst: it produced N₂O₃ and NO₂Cl as major products and only a trace quantity of N₂O₅. The authors came to the conclusion that copper chromite catalysed thermal decomposition of AP according to an electron transfer mechanism (4).

Pearson and Sutton [75] did not agree with this view. On the basis of their own experiments and those of other authors [77, 82] that both the catalysed and uncatalysed decomposition of ammonium perchlorate proceeds by proton transfer (4) and (7):

$$\text{NH}_4^+ \text{ClO}_4^- \rightarrow \text{NH}_3 + \text{HClO}_4.$$  (7)

An important work was done by Shimagi and Shidlovskii [76]. According to these authors the presence of HCl (equation 6) in the decomposition products is not affected by 5% of Cr₂O₃, MnO₂, Fe₂O₃, NiO, Cu₂O but these oxides suppressed the formation of N₂O and increased the concentration of NO. On the contrary, zinc oxide strongly reduced the amount of HCl and did not suppress the formation of N₂O.

Pellett and Saunders [77] studied the action of ruby laser on the AP-catalyst system. The first products evolved were NH₃ and HClO₄ and after that the products of their reaction appeared: H₂O, Cl₂O₄, NO, HClO, Cl₂ and NO₂. The decomposition of HClO₄ yielded HCl and Cl₂.

Strunin and Manelis [78] made the observation that the thermal decomposition of AP at 230–260°C was not influenced by pressure of 100 atm of an inert gas.

Kaye in Encyclopedia of Explosives [81] describes over 30 metal oxides and salts which provide a catalytic effect upon the thermal decomposition of AP. They are oxides of Al, Cd, Cr(II), Cu(I), Cu(II), Fe(III), Mg, Mn(III), Mn(IV), Mn₂O₄, Ni(II), Ni(III), V(V), Zn and chlorides: of the same metals. Also perchlorates of Cd, Cu(II), Hg(II), Mg, Zn possess a catalytic action.

**Mechanism of Low-Temperature Decomposition of AP**

The microscopic study of the formation and growth of nuclei in solid ammonium perchlorate was studied by a number of authors (Vol. II, p. 481). Raevskii and Manelis [79a] found that the decomposition centres of orthorhombic form consists of a large number of ellipsoid nuclei of 1–2 μm. They are not stationary but moving at the speed of the order 7–10 μm/min at 230°C. Their activation energy is 31 and 33 kcal/mol depending on the direction of the movement.

In the decomposition of the cubic form (above 240°C) they are spherical, randomly distributed throughout the crystals. The activation energy of their growth is 17 ± 1 kcal/mol above the transition point. The dislocation in crystals during their decomposition was revealed by etching of the surface of crystals with ethanol [79b].

A number of other works on low-temperature decomposition were subjected to a detailed review [47]. Also the monograph of Glazkova [18] should be consulted.

**Explosive Properties of NH₄ClO₄**

The following are data according to Meyer [80]:

- enthalpy of formation: -602 kcal/kg
- heat of explosion: 266 kcal/kg
- detonation rate: 350°C
- lead block expansion: 195 cm³.

According to Kaye in Encyclopedia of Explosives [81]: dry, fine grade AP can detonate from No 8 blasting cap,

- detonation rate of dry AP was 3400 m/s,
- detonation rate wet with alcohol AP 4200 m/s,
- detonation rate wet with acetone AP 4500 m/s,

(no information was given as to the density and the quantity of the liquid).

Lead block test gave 46% of picric acid, ballistic mortar – 100% of TNT.

An electrostatic discharge of over 5 joules was required to initiate a decomposition of AP.

Impact sensitivity was found to be 91 cm for 50% explosion (as compared with 61 cm with picric acid).

Heat Test at 100°C: after 48 hours 1% weight loss, between 48 and 96 hours 0.6% loss. No explosion occurred after 100 hours. The above data indicate a high stability of ammonium perchlorate.

The detonation equation (8) was given by Kaye [81]:

$$2 \text{NH}_4\text{ClO}_4 + 4 \text{H}_2\text{O} + \text{O}_2 + \text{Cl}_2 + 2 \text{NO}.$$  (8)
Price, Clairmont and Jaffe [83a] carried out an extensive investigation of detonation of ammonium perchlorate as a function of density and particle size. They expressed their results in equation (9):

$$D_i = -0.45 + 4.19 \rho_0$$  \hspace{1cm} (9)

where \( \rho_0 \) is the density in g/cm\(^3\), \( D_i \) = detonation velocity in mm/\(\mu\)s corresponding to the infinite charge diameter.

Equation (9) is valid for \( \rho_0 = 1.0 - 1.26 \).

Price and co-workers [83b] extended their results to densities below 1.0 and their equation took the shape:

$$D_i = 1.146 + 2.576 \rho_0$$

$$0.55 \leq \rho_0 \leq 1.0 \text{ g/cm}^3.$$  

For \( \rho_0 = 1.0 \) the values of \( D \) were:

<table>
<thead>
<tr>
<th>( \rho_0 )</th>
<th>( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.54</td>
<td>2.824 mm/(\mu)s</td>
</tr>
<tr>
<td>3.495</td>
<td>3.027</td>
</tr>
<tr>
<td>5.08</td>
<td>3.295</td>
</tr>
<tr>
<td>7.62</td>
<td>3.393</td>
</tr>
</tbody>
</table>

The extrapolated value \( D \) was 3.702.

At a still lower density, e.g. \( \rho_0 = 0.55 \) the \( D_i \) value was 2.530 mm/\(\mu\)s.

Decomposition occurred according to the equation

\[
\text{NH}_4\text{ClO}_4 \rightarrow 0.5 \text{N}_2 + 0.5 \text{Cl}_2 + 2 \text{H}_2\text{O} + \text{O}_2
\]

**Manufacture of Ammonium Perchlorate**

On a commercial scale AP is prepared by the interaction of ammonium chloride with sodium perchlorate. The less soluble AP precipitates and is filtered off leaving a solution of NaCl. A schematic diagram by Kaye [81] is given in Fig. 77.

According to Schumacher's patent [84] the reaction between anhydrous ammonia, concentrated hydrochloric acid and aqueous (56%) NaClO\(_4\) and recycled mother liquor from the NaCl crystallizer are heated with steam to 90\(^\circ\)C. By adding HCl the pH of the reaction is kept close to 7.0. The reaction liquor enters a crystallizer where the temperature is lowered to 35\(^\circ\)C by vacuum evaporation and brought to a supersaturation. The crystals of AP are centrifuged, recrystallized, washed with a saturated solution of AP (to remove the traces of sodium chloride). The mother liquor enters the sodium chloride crystallizer where water is removed by vacuum evaporation and the mother liquor is recycled to the reactor.

**Specification**

The U.S. specifications [81] require 99.0–99.3% purity, total moisture 0.05–0.08%, surface moisture 0.02%, NH\(_4\)Cl 0.03–0.15%, NaClO\(_4\) 0.02%, Bromates as NaBrO\(_3\) 0.0–0.004%, K\(_2\)CrO\(_4\) 0.0–0.015%, iron (as Fe) 0.001% or (as Fe\(_3\)O\(_4\)) 0.005%, ash (as sulphates) 0.25–0.30%, volatiles 0.04%.

Meyer [80] describes three grades of specification: A, B and C which are similar to the above, and in addition: water insolubles 0.01–0.03%, residue from sulphuric acid forming 0.3%, Na and K not more than 0.08%, Ca\(_3\)(PO\(_4\))\(_2\) 0–0.22%, pH 4.3–5.3 or 5.5–6.5.
Specifications also include particle size. Meyer [80] mentioned seven classes:

1. through 420–297 μ sieve, retained on 74μ sieve,
2. and (3) through 297 and 149 μ sieve respectively,
3. 50–70% through 210 μ sieve,
4. through 297 μ sieve, retained on 105 μ sieve,
5. 89–97% through 297 μ sieve,
6. 45–65% through 420 μ sieve.

PERCHLORATES OF METALS (Vol. III, p. 230)

A considerable number of perchlorates of metals have been described in the monograph by Schumacher [46] and also in the Encyclopedia by Kaye [81]. A short review of the properties of metal perchlorates was given by Shidlovskii [85]. He compared the thermochemistry of their decomposition according to the general equation:

\[ \text{M(ClO}_4\text{)}_2 \rightarrow \text{MCl}_2 + 2\text{nO}_2 - \Delta H. \]  (10)

He pointed out that three decomposition groups exist:

1. Perchlorates of K, Rb, Cs decompose with a very small thermochemical effect, for example with KClO_4: \( \Delta H = 0.6 \text{ kcal/mol.} \)
2. Perchlorates of Li, Na, Mg, Ca, Ba which decompose with a small exothermic effect: Li and Na of \( \Delta H = \text{ca.} 6 \text{ kcal/mol, and Mg and Ba of the same value for equivalent. Thus for Ba(ClO}_4\text{)}_2 - \Delta H = 12.8 \text{ kcal/mol.} \)
3. Perchlorates with a marked exothermic decomposition, for example silver perchlorate which gives \( \Delta H = 22.3 \text{ kcal/mol. Silver perchlorate possesses explosive properties (Vol. III, p. 232).} \)

It was found that when free of any organic substance, it is insensitive to mechanical action. However with a small amount of ethyl ether it shows a high sensitivity to shock and friction and has caused a few accidents.

Recently a less explicable accident has occurred [109] with cobalt (II) perchlorate. The salt had been prepared by allowing aqueous perchloric acid to react with an excess of CoCO_3, filtering off the excess carbonate, reducing the volume and crystallizing out the salt. The explosion occurred when theacked mass of crystals was placed in a mortar and tapped gently to break it up. No organic matter is thought to have been present. Extreme caution should be taken in handling Co(ClO_4)_2 and similar salts.

The mechanism of decomposition of barium perchlorate was examined by Jacobs, Solomosy and Rasko [113].

SALTS OF NITRIC ACID AND OF OXY-ACIDS OF CHLORINE 455

OTHER PERCHLORATES (Vol. II, p. 483)

**Hydrazine perchlorate (hydrazinium perchlorate)**

\[
\text{NH}_2\text{NH}_3^+\text{ClO}_4^- 
\]

Conant and Rooj [93] studied the crystal structure: they found it to be orthorhombic with m.p. 131–132° and density 1.939. Carleton and Lewis [94] studied the phase system with water and reported m.p. 142.4° and a hydrate \( N_2\text{H}_4\text{ClO}_4 \cdot \frac{1}{2} H_2O \) losing water at 61–64°. M.p. 137–138° C of the perchlorate was also reported [95].

Heat of neutralization of \( \text{HClO}_4 \) with \( N_2\text{H}_4 \) was \(-44.4 \text{ kcal/mol and heat of formation } - \Delta H_f = 42.9 \text{ kcal/mol [96] and } - \Delta H_f = 40.7 \text{ kcal/mol [97].} \)

It can be prepared by neutralizing aqueous solution of hydrazine with \( \text{HClO}_4 \) [95] or by double exchange of hydrazine salt with an inorganic perchlorate dissolved in lower alcohols [98].

The deflagration of Hydrazine Perchlorate was studied by Levy, von Elbe and co-workers [111]. They found that it could be catalysed by copper chromite, potassium dichromate and magnesium oxide. The entropy of vaporisation and dissociation:

\[
N_2\text{H}_4\text{ClO}_4 \rightarrow N_2\text{H}_4 + \text{HClO}_4 
\]

is 73 cal/deg. mole. (A similar figure was found for the entropy of dissociation of ammonium perchlorate into \( N_2\text{H}_4 \) and \( \text{HClO}_4 \); 71 cal thermal dissociation of deg. mole.) Grelecki and Cruice [112] examined also hydrazinium di perchlorate (see below) and found its decomposition to be autocatalytic. On the contrary monoperchlorate is not autocatalytic.

Volk and Schubert [61] examined the fragmentation in a mass spectrometer. They found \( \text{NH}_2\text{ClO}_4, \text{NH}_3\text{ClO}_4, \text{H}_2\text{O}^+ , \text{H}_2\text{O}^{2+}, N_2\text{H}_4^+, N_2\text{H}_4\text{ClO}_4^+, \text{ClO}_4^2-, \text{HClO}_4^+. \)

On heating it decomposes at 230°C [95], but Shidlovskii et al. [96] gives the ignition temperature 277–280°C. On detonation the volume of gases is 864 l/kg [96].

Lead block expansion is the order of 113% of Picric acid or 122% of TNT [81].

**Hydrazine Diperchlorate**

\[
[\text{NH}_3\text{NH}_3]^2^+ (\text{ClO}_4^-)_2^- 
\]

m.p. 191° C.

The compound has the density 2.21.

Salts of Hydrazine Perchlorate and Chlorate Complexes (Vol. III, p. 230)

Complex salts of hydrazine and perchlorate were described also by Maissen and Schwarzenbach [99] and in the Encyclopedia [81].
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

Nitrosyl Perchlorate (Vol. I, p. 484)

Fragmentation in a mass spectrometer was described by Volk and Schubert [61].

**Hydroxylamine Perchlorate**

\[ \text{NH}_2\text{OH} \cdot \text{HClO}_4 \]

m.p. 87.5 – 90°C

It forms hygroscopic crystals, decomposing at 120°C. Heat of formation was \( \Delta H_f = 66.2 \text{ kcal/mol} \). It was prepared by reacting hydroxylamine sulphate with BaClO_4. Impact sensitivity was of 15 cm by 2 kg falling weight [81].

**Methylamine Perchlorate** (Vol. III, p. 484)

\[ \text{CH}_3\text{NH}_3\cdot\text{ClO}_4^- \]

m.p. 255°C (d)

The crystal structure was reported by Stammier [100] and Zanazzi [101]. The substance passes through a phasic transition at 178°C. Densities of phase II at 77°C is 1.58 c/cm³, phase I at 200°C is 1.58 g/cm³.

The temperature of explosion by heating was found to be 338°C [102]. Mass spectrometry was examined by a number of authors, most complete being the study by Volk and Schubert [61]. They found fragments at 260°C: CH³⁻, CHN³⁺, CH₃N⁺²⁺, CH₃NH²⁺, CH₃NH₂⁺, Cl⁻, ClO₃⁻, ClO₂⁻, ClO₄⁻, HClO₄⁻ m/e.

**Guandine Perchlorate** (Vol. III, p. 485)

Markwald and Struwe [103] described the method of making this substance from cyanoquinidine and ammonium perchlorate. Some physico-chemical properties were reported [104]. Heat of formation according to Krivtsov and co-workers [105] was found to be \(-\Delta H_f = 74 \text{ kcal/mol}\).

Guandine perchlorate is a powerful explosive: its rate of detonation can reach 7150 m/s at \( \rho = 1.67 \), and lead block expansion 400 cm³ [106].

**Nitroguanidine Perchlorate**

This interesting substance, which is an exothermic compound, was obtained by Rosolovskii, Krivtsov and Titova [97]. Its enthalpy of formation is \(-\Delta H_f = -51.5 \text{ kcal/mol}\).

SALTS OF NITRIC ACID AND OF OXY-ACIDS OF CHLORINE

**Fluoroammonium Perchlorate**

\[ \text{NH}_3\text{F} \cdot \text{ClO}_4^- \]

This substance was prepared by Grauokusas and Baum [107]: a solution of ethyl or isopropyl-N-fluorocarbamate in 70% HClO₄ was heated until CO₂ was evolved at 68°C. The excess of perchloric acid was removed under vacuum:

\[
\text{C}_3\text{H}_7\text{O} \cdot \text{CONHF} + \text{HClO}_4^- \rightarrow \text{NH}_3\cdot\text{F} \cdot \text{ClO}_4^- + \text{CO}_2 + \text{C}_3\text{H}_7\cdot\text{OCIO}_3.
\]

**Nitronium Perchlorate** (Vol. I, p. 19)

\[ \text{NO}_2^+ \cdot \text{ClO}_4^- \]

The substance forms hygroscopic crystals which melt on decomposition at 135°C without explosion.

The original product obtained by Hauisch (Vol. I, p. 19) proved to be a mixture of nitronium perchlorate and perchloric acid monohydrate (Goddard and co-workers [116]). Nitronium perchlorate was obtained by distilling anhydrous perchloric acid onto an excess of dry dinitrogen pentoxide at 80°C and the mixture was kept in vacuo to remove volatiles. The product was composed of 89% nitronium perchlorate and 11% perchloric acid hydrate. Pure nitronium perchlorate was obtained by repeating the experiment in nitromethane with a large excess of N₂O₅ [117]. Cordes [114] examined the decomposition between 70 and 112°C and found gaseous products NO₂, Cl₂, ClO₂, NO₃Cl and O₂. M. D. Marshall and Lewis [115] established that at 65°C the major products were nitrosyl perchlorate and oxygen. Nitronium perchlorate further decomposes:

\[
\text{NO} \cdot \text{ClO}_4^- \rightarrow \text{NO}_2 + \text{ClO}_2 + \frac{1}{2} \text{O}_2
\]

\[
2 \cdot \text{ClO}_2 \rightarrow \text{Cl}_2 + 2 \cdot \text{O}_2.
\]

PERCHLORIC ACID AND CHLORINE OXIDES

Thermal decomposition of ammonium perchlorate and perchlorates of other bases raised problems of the decomposition of perchloric acid and oxides of chlorine. This was extensively reviewed by Schumacher [46], Zinov'ev [86], Jacobs and Whitehead [47], Pearson [87].
**CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES**

**Perchloric Acid** (Vol. III, p. 313)

Thermal decomposition of perchloric acid is a complicated process and the trend of decomposition depends on the temperature. The process is particularly complicated at temperatures below ca. 315°C. Above that temperature the reaction is homogeneous [8]. The following are products found in the region 200–440°C: Cl₂, Cl₂O, O₂, H₂O and chlorine oxides [60, 88, 89].

**Chlorine Oxides**

Chlorine oxides are compounds of a relatively low stability, the most stable being Cl₂O and Cl₂O₃.

Chlorine dioxide (ClO₂) is explosive if heated rapidly or overheated locally, but on careful heating the decomposition between 100° and 140°C is measurable [90].

Chlorine heptoxide (Cl₇O₇) was studied at temperatures of 100–120°C [91], it decomposed to chlorine and oxygen. The decomposition of liquid compound was examined [92] at 60–80°C.

The decomposition of other chlorine oxides are given in a review [47].

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SALTS OF NITRIC ACID AND OF OXY-ACIDS OF CHLORINE

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CHAPTER 17

PRIMARY EXPLOSIVES: INITIATORS, INITIATING EXPLOSIVES, (IE)

(Vol. III, p. 129)

INTRODUCTION

With regard to the number of primary (i.e. initiating) explosives very little can be added to those already described in Vol. III. Thus the most used initiators are: Lead Azides, Lead Styphnate, Tetracene, Mercuric Fulminate which is the oldest and so far most popular initiator is gradually being withdrawn from use in some countries (e.g. in the U.S.A.) and replaced by lead azide. The other primary explosives, such as cyanuric triazide and diazodinitrophenol are good initiators but have not yet received wider application. A few more primary explosives have proved to be efficient initiating agents such as: silver, cadmium and cupric azides, triazidotri nitrobenzene, salts of acetylene, double salts of stypnic acid (lead salt) and tetracene, hexamethylene triperoxide diamine.

A large group of explosives exists which have initiating properties. They are complex salts of metals with bases such as ammonia, amines, hydrazine etc. (Vol. III, p. 230). There is insufficient information on the properties of these compounds, their stability and their action on metals, therefore they cannot be recommended as yet for practical use.

A good initiating explosive (IE) should correspond to numerous requirements, such as:

1. Good initiating properties, that is, a small charge of IE should bring an explosive to detonation. This is usually connected with a short time of burning to detonation. A classic example is lead azide which has a remarkably short time of burning to detonation according to Patry and Laffitte [46, 47].
2. Safe handling and use in manufacture of elements of ammunition, such as pressing into the elements.
3. Ease of filling the initiating elements and ease of safe pressing.
4. Safe use of such elements, for example avoiding premature detonation when striking an object.

BURNING OF IE UNDER REDUCED PRESSURE

There has been some controversy as to whether initiating explosives can burn and eventually detonate under reduced pressure. The earlier literature reported that they do not burn in a 'high vacuum' [39]. Marsur and Schumacher [40a] found that initiating explosives can burn to detonation under pressure of $10^4$ to $10^5$ torr. This was not in agreement with the earlier finding of Burlot [41a]. Burlot [41b] reported that different initiating explosives are characterized by a critical low pressure: the explosive cannot burn and detonate if the pressure falls below that limit. The critical pressure amounts to as much as 15 torr for mercuric fulminate and $2 \times 10^2$ torr for lead azide. Belaev [42, 44], Belaev and Belaeva [43] seem to confirm the view of Burlot, although they did not examine the pressure below 2–3 torr.

T. Urbásfki and Stanuch [45] undertook experiments to clarify the existing discrepancy particularly in view of the importance of the problem. Their conclusion was that initiating explosives can be divided into five classes according to their behaviour when ignited with a resistance wire under reduced pressure. Here is their classification.

(I) IE which readily detonate when ignited either as loose powder or pressed pellets at pressure as low as $10^3$ torr. Lead, silver and mercuric azides, silver and cadmium fulminates, lead styphnate and $m$-dinitrobenzodiazonium perchlorate belong to this group of compounds. All the above substances are characterized by a very short period of burning preceding detonation.

(II) IE which readily detonate when ignited as pellets at pressure as low as $10^4$ torr. When in the form of loose powder they detonate under a pressure above 1 torr. Cyanuric triazide and hexamethylene triperoxide diamine belong to this group of compounds.

(III) IE which burn without detonation when ignited as pellets under pressure of the order of $10^4$ torr. Under atmospheric pressure they burn to detonation. When in the form of a loose powder they partially burn under pressure of 1 torr.
but under atmospheric pressure can burn to an explosion. Mercuric fulminate belongs to this group of compounds.

(IV) In the form of pellets which can detonate when ignited under atmospheric pressure, but do not detonate when the pressure is of the order 100–400 torr. At lower pressures of the order of 10^-4 torr they do not burn. In the form of loose powder they burn under atmospheric pressure but do not detonate. Dinitrodiazophenol and tetrazene belong to this group of compounds.

(V) Substances of this group do not burn to detonation even at atmospheric pressure when the pellets are not confined. A strong confinement is needed to bring their burning to detonation. Trinitrotetrazotetrazobenzene belongs to the group of compounds.

One more remark should be added to the behaviour of initiators as under (I) and (II) – still higher vacuum should be examined. Perhaps under pressure lower than 10^-5 torr the primary explosives of groups (I) and (II) may behave differently from above and decompose without explosion. Thus the classification as above is valid only in limits for vacuum application.

Recently a monograph on initiating explosives written by Bagal [1] appeared. It contains chapters on:

1. Fulminates
2. Azides
3. Styrphates
4. Diox compounds
5. Tetrazene and Tetrazoles
6. Peroxides
7. Acetylenides

Two other monographs have appeared which have been dedicated to azides: a collective volume edited by Patai [2] and two collective volumes on metal azides edited by Fair and Walker [3]. Also reviews have appeared on alkyl and aryl azides by Boyer and Canter (Vol. III, p. 196), and organic azides by L'Abbé [4].

**MERCURIC FULMINATE (Vol. III, pp. 129, 139)**

The monograph by Bagal [1] contains a detailed description of the early history of the discovery of reactions leading to the formation of mercuric fulminate which began in 1800 thanks to the work of Howard (Vol. III, p. 129). Further work was done by Liebig [5], Liebig and Gay-Lussac [6], Gérard [7] and a number of other authors [8–18]. The correct structure of fulminic acid was given by Nef [19], supported by L. Wöhler and Teodorowits [20] and later by Wieland and Hess [21].

Polymerization of fulminic acid was studied by Wieland and Hess [21] and

much later by Birkenbach and Sennewald [22]. These works led to rationalize the polymerization to a trimer given in Vol. III, p. 133 as formula VII.

Dansi [23] criticized the scheme of Wieland (Vol. III, p. 135). He could not obtain fulminates of mercury and silver by acting with their nitrates on isonitrosocetic acid. The salts of isonitrosocetic acid did not yield fulminates when acting with nitric acid (equations 5–8, Vol. III, p. 135). This casts some doubt on the accuracy of Wieland's scheme.

The structure of mercuric fulminate was also confirmed by Angelico through the ingenious formation of the compound from malonic acid (Vol. III, p. 136). Ponzo [24] found that nitrogen dioxide reacted with oxaminoacetic acid (I) yielding methylnitritol acid (II) and therefore the reaction of Angelico-Ponzo should be presented by scheme (1) according to [1]:

\[ CH_2(COOH)_2 \rightarrow \begin{array}{c}
\text{HNO}_3 \\
\text{H}_2\text{CO}_2 \end{array} \rightarrow \begin{array}{c}
\text{C=}\text{NO} \\
\text{COOH} \end{array} \rightarrow \begin{array}{c}
\text{H} \\
\text{HNO}_2 \end{array} \rightarrow \begin{array}{c}
\text{C=}\text{NOH} \\
\text{COOH} \end{array} \]

Physical Properties

The problem of difference in colour of mercuric fulminate (grey and white crystals) does not seem to be fully solved. The view of Solonina (Vol. III, p. 138), Philip [25], Langhans [26], Marshall (Vol. III, p. 138) that the grey colour mercuric fulminate is due to some organic impurities seems to be correct. Crystallization of the substance in a solvent always yielded a white substance. The coloured products are probably resinous polymers of fulminic acid. The latter contains a double bond and is liable to polymerize. Whitening of mercuric fulminate by adding cupric salts appears to be an optical effect.

The density of mercuric fulminate on pressing into a No. 8 copper detonator case is according to Wöhler and Roth [27]:

- Pressure kg/cm^2: 100, 250, 500, 1000, 2000
- Density g/cm^3: 2.36, 2.61, 2.99, 3.47, 3.76

Technical mercuric fulminate contains (according to Bagal [1]) mercuric oxalate, mercurous oxides, inclusion of the reaction liquor, mercuric chloride. Bagal also mentioned the presence of metallic mercury which proved to be not always correct according to Solonina [28]. He examined samples of grey mercuric fulminate by keeping them and frictioning on gold plates and no formation of amalgamate was noticed.
Many authors stated that keeping most of the solutions of mercuric fulminate for a longer time leads to the decomposition of the substance. According to Solonina [28] a solution of mercuric fulminate in 22% aqueous ammonia produced a decomposition of the dissolved substance and mercuric oxide precipitated after 12 hours of keeping the solution at room temperature. Pyridine—a good solvent of mercuric fulminate—may also bring about decomposition with a precipitation of metallic mercury [26, 28]. Also a yellow coloured precipitate may be formed with a low content of Hg (ca. 58.5%) [1].

Chemical Properties

As pointed out in Vol. III (p. 140) mercuric fulminate is subjected to decomposition under the action of concentrated acids. Aqua regia produces chloroplatinic. Thiocyanic acid gives an exothermic reaction with the formation of mercuric sulphide. If the temperature rises high—metallic mercury may be precipitated [1]. Nef [19] examined the action of hydrogen sulphide on silver fulminate and came to the conclusion that the salt of thiocyanohydrazolic acid (III) is formed. Cambi [29] tried to isolate the free acid. However it decomposed readily yielding this hydrocyanamide:

\[
\text{HCNO} \rightarrow \text{HCN} + \text{H}_2\text{O}
\]

The reactions of metals with mercuric fulminate was described for the first time by Chel'tsov in 1883 [30]. Dry mercuric fulminate did not react with metals—such as copper or brass—but in the presence of moisture a gradual formation of amalgamates occurs with time. Subsequently all elements containing mercuric fulminate and pressed into metal casing should be protected from moisture by varnish or air-tight casing.

Hygroscopicity of mercuric fulminate was examined by Kast [31]. He found that technical mercuric fulminate is non-hygroscopic; in 100% moisture atmosphere during 80 days at room temperature its weight increased by 0.16%. Mercuric fulminate reacted with potassium chlorate in a moist atmosphere and mercuric oxide resulted.

Sensitivity to impact. As a typical IE, mercuric fulminate is very sensitive to impact. Bubnov (according to [1]) reported that grey mercuric fulminate is slightly more sensitive to impact than the white species.

Chemical Stability and Behaviour at High Temperature (Vol. III, p. 141)

The earliest experiments on the stability of mercuric fulminate belong to Hoitsema [32] and Solonina [28]. Hoitsema examined the behaviour of mercuric fulminate under reduced pressure.

PRIMARY EXPLOSIVES: INITIATORS, INITIATING EXPLOSIVES, (II) 467

Solonina determined the ignition temperature and found it varied within the limits 157–172°C. When heating started at 100°C, the temperature was invariably 160°C.

Kast and Haid [33] found the following data: mercuric fulminate heated at the rate of 20°C/min exploded at 170–175°C, when kept at constant temperature explosion occurred:

- at 190°C after 8–10 sec.
- 200°C after 7–8 sec.
- 205°C after 5 sec.

Behaviour at Low Temperature

Kling and Florentin [34] examined the behaviour of mercuric fulminate at low temperature: from −80° to −183°C and found that the velocity of detonation does not change with temperature at the density of 1.25 the figures were: 2365 m/s and 2350 m/s at room temperature and at −183°C respectively.

Clark [35] investigated the initiating properties of mercuric fulminate at different temperatures: +25°, −80° and −183°C to test the applicability of detonators in charges with liquid oxygen. He found a lowering of initiating power of detonators with a lowering of temperature, but the velocity of detonation did not change—in agreement with the observation of Kling and Florentin.

Action of Light

The following information on the work of Farmer [36] should be added to those given previously (Vol. III, p. 146). He examined the influence of sunlight on both grey and white samples and found white samples to be more sensitive to the action of light. Thus after 320 hours of irradiation white and grey samples evolved 0.37 and 0.14 ml of gas respectively. Patry and Laffitte [37] examined the influence on the induction period of irradiation of mercuric fulminate with ultraviolet light. The induction period was very much shortened by irradiation, for example, at 160°C freshly made sample and irradiated sample gave the induction periods of 252 and 9 sec. respectively.

According to Borocco [38] mercuric fulminate irradiated with ultraviolet light in vacuo was partly decomposed with the evolution of nitrogen and carbon monoxide according to the equation:

\[
\text{Hg(ONC)}_2 \rightarrow \text{Hg} + 2 \text{CO} + \text{N}_2
\]

He also compared burning of samples: irradiated and previously heated to 100°C and found a similarity between the action of irradiation and pre-heating.
Burning under Reduced Pressure

As previously pointed out (p. 464) mercuric fulminate belongs to the group of IE which can burn to detonation under atmospheric pressure or pressure near to atmospheric. Under pressure of 10⁴ torr it burned without detonation. Murao and Wohlgemuth [48] examined the influence of the temperature of the charge of mercuric fulminate on burning under reduced pressure. At room temperature a pellet pressed under 3000 kg/cm² kept in vacuo, burned quietly. If preheated to 100°C it detonated within 10 min of keeping at this temperature without using an ignition wire.

'Dead pressing' of mercuric fulminate was described in Vol. III, p. 146. Murao and Wohlgemuth [48] explain this phenomenon in terms of 'preheated' samples of the IE. If the sample is not 'dead pressed' it is sufficiently porous for the hot gases of decomposition to penetrate inside the charge and produce 'preheating' of the substance.

Initiating Properties of Mercuric Fulminate

Gedymin [49] used an original method for determining initiating properties of a mixture of 95% mercuric fulminate with 5% KClO₃. He determined the ratio \( p \) of the smallest ('critical') mass \( m \) of the initiating charge to the surface area \( s \) of the charge of the initiated explosive pressed into a cylindrical metal tube:

\[
p = \frac{m}{s}.
\]

For tetryl and TNT \( p \) is 1.12 and 1.52 respectively. The figures express the easier initiation of tetryl than of TNT.

Extensive experiments by Koester [50] on the initiating properties of mercuric fulminate are given in Table 72.

<table>
<thead>
<tr>
<th>Initiated explosive</th>
<th>Critical charge g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETN</td>
<td>0.35</td>
</tr>
<tr>
<td>Tetryl</td>
<td>0.36</td>
</tr>
<tr>
<td>TNT</td>
<td>0.38</td>
</tr>
<tr>
<td>Tetryl + 10% paraffin wax</td>
<td>0.36</td>
</tr>
<tr>
<td>Tetryl + 20% paraffin wax</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Koester also examined the influence of the metal casing on the initiation properties of mercuric fulminate. The critical charge was found to be smaller in a hard metal (e.g. steel) than in a soft one (e.g. copper). The figures were: 0.24 g (steel) and 0.38 (copper).

Other Salts of Fulminic Acid (Vol. III, p. 157)

The only other salt of fulminic acid which was in some limited use was silver fulminate. However it no longer seems to be in use, and other salts were also of no use.

Manufacture of Mercuric Fulminate

No changes in the manufacture as described in Vol. III, p. 149 can be found. The only note of historical interest is that experiments were made by replacing ethanol with methanol in the manufacture of mercuric fulminate. Negative results were reported by Dumas and Peligot [51]. However Stahlhemsaid claimed to have obtained mercuric fulminate from methanol as early as 1860 according to [1]. The discrepancy was explained later, e.g. [20], that methanol of Stahlhemsaid contained dimethyl acetal—a derivative of acetaldehyde, and this discovery led to the finding [20] that mercuric fulminate can be obtained with a high yield and purity from acetaldehyde.

Esters of Fulminic Acid

Recently Wentrup, Winter and co-workers [182] described the reaction leading to the formation of esters of fulminic acid by vacuum flash pyrolysis (300–600°C) and matrix photolysis of 4-oximinoisoxazol-5(4H)-ones

\[
\begin{align*}
\text{CH}_3 & \quad \text{NOR} \\
\text{HO} & \quad \text{R-O-} \quad \text{N}_2 \text{C} \\
\text{CH}_3 & \quad \text{CN} \\
\text{CO}_2 & \quad \text{CO}_2
\end{align*}
\]

The esters are unstable and decomposed above -100°C: when \( R = \text{CH}_3 \), it yielded formaldehyde and hydrocyanic.

HYDRAZOIC ACID, ITS DERIVATIVES AND SALTS (Vol. III, p. 161)

The chemistry of hydrazoic acid derivatives have recently created a wide literature [2, 3, 126, 184] owing to the fact that azides are convenient starting substances in preparative chemistry. This was reviewed by L'Abbé [4] and partly by Boyer [52] in his recent paper on covalent oxygen bonding of nitrogen attached to carbon. Also a review on carbamoyle azides appeared [53].
Decomposition of Azides

Decomposition of azides very often begins with formation of nitrenes which contain uncharged nitrogen radical intermediate according to reaction (4)

\[ \text{R-N}_3 \xrightarrow{\Delta \text{ or } h\nu} \text{R-N}^+ + \text{N}_2. \]  

(4)

Chemistry of nitrenes was also reviewed [54, 55].

The formation of free radical \( \text{HN}^- \) by decomposition of hydrazoic acid has been suggested by a number of authors since 1928 (see Vol. III, p. 167). This was substantiated by experiments on the decomposition of \( \text{HN}_3 \) by the flash photolysis of Thrush (Vol. III, p. 167). The formation of nitrene radicals from azides by flash photolysis was reported simultaneously and independently by Koto [56], Reiser et al. [57–59]. Reiser rationalized the reaction derived from flash photolysis of formation of azo compounds (5):

\[ \text{RN}^- + \text{RN} \rightarrow \text{RN} = \text{NR} + \text{N}_2. \]  

(5)

Nitrenes have triplet ground states. At room or higher temperature they can behave as triplet biradical and singlet electrophilic species. They have a very short time of several microseconds, but can undergo stabilization by a number of reactions, such as: isomerization to amines, dimerization to azo compounds, ring closure to heterocyclics, various addition reactions [4]. Curtius rearrangement [60] is one of the classical examples of passing through the nitrene formation.

Infrared study of thermal decomposition of \( \text{N}_3^- \) ion (e.g. \( \text{KN}_3 \) at 345–350°C) shows the formation of \( \text{NCO}^- \) as a by-product of CO\(_2\) trapped during pressing and the possible reaction:

\[ \text{N}_3^- + \text{CO}_2 \rightarrow \text{NCO}^- + \frac{1}{2} \text{O}_2 + \text{N}_2. \]  

(6)

Azido compounds can be convenient intermediates in the synthesis of natural products containing amino group. Thus crystalline 4-amino hexoses can be formed by hydrogenation of 4-azido hexoses [70].

Heterocycles from Azides

An important reaction is 1,3-dipolar cycloaddition reviewed by Huisgen [61]. An example can be seen from the reaction of styrene (dipolarophile) and pyrrole azide (1,3-dipole) yielding a triazoline (IV):

\[ \text{N}_3^- + \text{C}_6\text{H}_5(\text{NO}_2)_3 \rightarrow \text{N} \rightarrow \text{N}^- - \text{C}_6\text{H}_5(\text{NO}_2)_3 \rightarrow \text{N} + \text{C}_6\text{H}_5(\text{NO}_2)_3 \]

\[ \text{IV} \]

Pyrolysis of vinyl azides offers an interesting method of forming azirines [62] (VI):

\[ \text{N} \rightarrow \rightarrow \text{N}_3 \]

(6)

A similar result was obtained by photolysis of vinyl azides. The reaction can lead to azepines (VII) [63] possibly through the intermediate formation of azidines [64] (as known, diazepines are an important group of tranquilizers [65]).

The reduction of vinyl azides with sodium sulphite followed by hydrolysis can lead to ketones [71].

Other Reactions of Azide Anion and Radical

An unusual reaction was recently reported by Hoz and Speizman [65] on the reaction of azides with nitrile alkenes, resulting in the formation of \( N^- \) cyano compounds (VIII):

\[ \text{NO}_2^- + \text{NaN}_3 \rightarrow \text{N} + 2 \text{NO}_2^- \]

(8)

The mechanism of the reaction is not quite clear.

Another interesting reaction comes from the fact observed by Forster and Fierz [67] that the azido-group can function under basic conditions as an intru-
An interesting azide which is in use as a source of triazolines and aziridines [72] is a cyanogen azide, $\text{CN} \cdot \text{N}_3$. It can be obtained according to Marsh and Hermes [74] as a colourless explosive oil by a simple reaction of sodium azide with cyanogen chloride. It is not stable at room temperature but in a 27% solution in acetonitrile at $0^\circ\text{C}$ to $-20^\circ\text{C}$ can be kept undecomposed (see also [75]). Later on Coppolino reported [76] that cyanogen azide can be decomposed when kept in solution even at $-20^\circ\text{C}$. With alkenes it does not give very stable triazolines.

Carbon azide $\text{C} \cdot \text{N}_3 \cdot \text{H}_3$ is not known. However Müller and Dehncke [105] succeeded in obtaining a complex salt with triazidocarbonium ion (XI) by refluxing antimony azidochloride in carbon tetrachloride:

$$\text{Sb} \cdot \text{N}_3 \cdot \text{Cl}_4 \xrightarrow{\text{CCl}_4, \text{reflux} (4 \text{ hr})} \left[	ext{CN}_3\right]^+ \cdot \left(\text{Sb} \cdot \text{Cl}_4\right)^-$$

XI

It decomposed after melting at $145^\circ\text{C}$.

### Danger of Handling Azides

The danger of handling apparently stable organic azides has recently been described [77]. Thus:

1. Ethyl azide exploded when kept at $-55^\circ\text{C}$ for a few minutes, the reason for the explosion could not be elucidated.
2. $p$-Toluene-sulphoazide exploded during distillation under reduced pressure.
3. A derivative of siladiazide ($\text{CH}_3 \cdot \text{Si} \cdot \text{N}_3 \cdot \text{Si} \cdot \text{N}_3 \cdot \text{Cl}_2$) exploded after being kept for three years when the flask with the substance was opened. Also $\text{Cl}_2 \cdot \text{Si} \cdot \text{N}_3 \cdot \text{Si} \cdot \text{N}_3 \cdot \text{Cl}_2$, $\text{Si} \cdot \text{N}_3 \cdot \text{Si} \cdot \text{N}_3 \cdot \text{Cl}_2$—residues from the distillation of the products of the reaction between $\text{SiCl}_4$ and NaN$_3$ in tetrahydrofurane—exploded. This was probably caused by $\text{H}_2 \cdot \text{N}_3$ evolved from the above products. This is not surprising in the light of the observation below.

Hydrazoic acid (Vol. III, p. 166) is relatively stable, but can explode spontaneously on handling. Curtius and Radenhausen [78] described two unexpected explosions: (1) when the substance was introduced into a barometer vacuum tube, (2) when the glass vessel containing the acid was removed from a cooling bath. A suspicion was advanced that hydrazoic acid stored for a long time in a glass container is more dangerous than the same acid freshly prepared, probably due to impurities taken from the glass [79—81].

4. Borazides: ($\text{CH}_3 \cdot \text{BB} \cdot \text{N}_3$, ($\text{Cl} \cdot \text{BB} \cdot \text{N}_3$), $\text{B} \cdot \text{N}_3$). Py exploded without any apparent reason when poured or taken with a nickel spatula.
5. Esters of azidoacetic acid, for example $\text{N}_3 \cdot \text{CH}_2 \cdot \text{COO} \cdot \text{Bu}$ can explode above $80^\circ\text{C}$ [82].

6. Acyl azides can present danger in handling, for example during distillation in vacuo. An accident with toluene-sulphonyl (tosyl) azide has been described.
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

Cyanic Triazide (Vol. III, p. 194)

No practical application has been found for this interesting compound owing to its sensitivity to handling, impact, volatility and hygroscopicity [142–144]. Nevertheless, its structure aroused a certain amount of interest and the X-ray structure was examined [145]. It confirmed the structure given in Vol. III, p. 194, formula XI.

Explosive Properties of Hydrazoic Acid

Médard [88] reported thermochemical data for hydrazoic acid:

\[
\text{heat of formation} - \Delta H_f = 71.66 \text{ kcal/mol (gas)}
\]

\[
= 64.37 \text{ kcal/mol.}
\]

According to Bagal [1] aqueous solutions of hydrazoic acid can detonate: 70% aqueous HN₃ showed the rate of detonation 7300 m/s. Anhydrous hydrazoic (liquid) gave 8100 m/s.

As previously mentioned hydrazoic acid stored for a long time is more dangerous in handling than the product freshly prepared.

Gentle friction can produce an explosion of hydrazoic acid. An accident has been described of an explosion of the substance, caused by the friction of a piece of glass in a flask put there to produce more uniform boiling [94].

Ammonium Azide (Vol. III, p. 190)

This interesting salt attracted attention as it produces a considerable amount of gas: 1148 l/kg is the highest figure for all explosives.

It is a crystalline substance, readily soluble in water and 80% ethanol, insoluble in ether and benzene. It melts at 160°C and begins to decompose. It is volatile and sublimes below 250°C under 150 mmHg. The vapour pressure at different temperatures was determined [11]:

at 48.0°C 85°C 125°C 134.2°C
was found 4.5 55.1 508.1 782.1 mm.

When heated under atmospheric pressure it decomposed while dissociating into NH₃ and HN₃ and finally the HN₃ exploded [103].

The easiest method of preparing ammonium azide [125] consists in the reaction of sodium azide with ammonium chloride in dimethylformamide at 100°C. After the reaction subsided, all was cooled to 60–70°C and dimethylformamide was distilled under reduced pressure. Ammonium azide crystallized out.

As previously mentioned (Vol. III) a practical application has not been found for the substance due to its volatility.

PRIMARY EXPLOSIVES: INITIATORS, INITIATING EXPLOSIVES, (II) 475

PHYSICO-CHEMICAL AND EXPLOSIVE PROPERTIES
OF METAL AZIDES

The fundamental problem of why some azides (e.g. KN₃) are not explosive whereas others (e.g. Pb(N₃)₂) are, is still not fully understood. Nevertheless a great amount of information has been collected to date on various physico-chemical properties of azides which can partly throw some light on the problem (see Table 73, Fig. 79 and [189]). They are assembled in Vol. I of [3] and include the chapters:

Introduction, R. F. Walker (p. 1),
(1) Synthesis and the Chemical Properties, T. A. Richter (p. 15),
(2) The Growth of Crystals, W. L. Garrett (p. 87),
(3) The Crystal Structures, C. S. Choi (p. 97),
(4) Molecular Vibrations and Lattice Dynamics, Z. Iqbal, H. J. Prask and S. F. Trevino (p. 131),
(5) Electronic Structure of the Azide Ion and Metal Azides, T. Gora, D. S. Downs, P. J. Kemney and J. Sharne (p. 193),
(6) Slow Thermal Decomposition, P. G. Fox and R. W. Hutchinson (p. 251),
(7) Imperfections and Radiation Induced Decomposition, W. L. Garrett, P. L. Marinkas, F. J. Owens and D. A. Wiegand (p. 285),
(8) Fast Decomposition in the Inorganic Azides, M. M. Chaudhri and J. E. Field (p. 383),

Vol. 2 of [3] contains a description of more practical problems:

Introduction, R. F. Walker (p. 1)
(1) Processes for the Manufacture of Lead and Silver Azide, T. Costain and F. B. Wells (p. 11),
(2) Analysis of Azides for Assay, and in Complex Media, H. Kramer (p. 55),
(3) Handling, Storability, and Destruction of Azides, B. D. Pollock, W. J. Fisco, H. Kramer and A. C. Forsyth (p. 73),
(4) The Sensitivity to Impact and Friction, L. Avrami and R. Hutchinson (p. 111),
(5) Electrostatic Sensitivity, M. S. Kirshenbaum (p. 163),
(6) Sensitivity to Heat and Nuclear Radiation, L. Avrami and J. Haberman (p. 199),

The reader, interested in the manufacture and use of azides should consult both volumes. Many problems described in the volumes are outside the scope of the present book.
Optical Properties

The optical and electronic properties of azides have been reviewed [3, (Vol. I, p. 224)]. So far it has been suggested that there are similarities between the alkali azides and halides but recently attention has been paid to the identification of defect centres formed by irradiation of azides. Deb [106] carried out experiments with thin films or single crystals of Na, K, Rb and Cs azides between 140 and 280 nm at low temperatures, such as 4–77 K. He noticed an induced luminescence in all alkali azides. Earlier work by Audubert [107] showed a faint emission of ultraviolet light from various azides during thermal decomposition. Singer and Mueller [108] observed chemiluminescence and electron emission from thermally decomposing alkali azides.

Photoconductivity of azides, including Pb(N₃)₂, was examined by a number of authors [109–111].

Slow Decomposition of Azides

Slow thermal decomposition was examined by Garner (Vol. III, p. 171). It was shown [112] that when silver azide is heated, silver is formed in an oriented way through the azide lattice. The rapid growth of nuclei by the surface migration of metal in lead azide seems to be demonstrated [113]. Choi and Boutin [114] showed the existence of azide radicals in the course of the decomposition.

Some substances, including impurities, enhance the decomposition of azides. The impurities can be present in the course of preparation of azides or formed during their storage. It is known that the presence of carbon dioxide in air may produce a decomposition of lead azide. Also water vapour in air even at room temperature may accelerate the decomposition. This problem was tackled by Reitzner [115]. He found that the induction period was the result of the reaction of water vapour with lead.

The problem of the action of radiation on azides, particularly lead and barium azide has been reviewed [116]. Irradiation prior to thermal decomposition often affects a reduction or elimination of the induction period, a decrease in activation energy and an increase in the rate of decomposition. Zakharov and co-workers [117] have found that the application of a moderate electric field can affect the rate of thermal decomposition of azides.

Through irradiation the optical density of azides increases as shown by Roth [118] and Wiegand [119]. The experimental facts supported the hypothesis that colloidal metal was produced by irradiation of lead azide and thallium azide. Colloidal disorder can be created by radiation. Lead produced by photodecomposition is reactive and can form some products on exposure to air. Thus basic lead carbonate was found lead azide irradiated with X-rays [120, 121]. Lead azide expands along one crystallographic direction under the action of X-rays [122] and nitrogen in the form of N₂ can be trapped by the irradiated lattice.

[123]. The visual colouration of lead azide was strongly suppressed by hydrostatic pressure of the order of 10 kbar [124].

Among different regularities a remarkable relationship exists between the heat of formation (ΔΗ₂₉⁸°) of a number of azides and infra-red frequency ν₅ ranging between 620 and 650 cm⁻¹. This is shown in Fig. 78 (Explosive azides) form a group separated from non-explosive ones. N₃⁻ ion becomes more asymmetric in the more covalent salts making those lattices thermodynamically less stable [102].

![Graph showing heat of formation vs. infrared frequency for various azides.]

FIG. 78. Enthalpy of formation of azides ΔΗ₂₉⁸° against infrared frequency 580–600 cm⁻¹, according to 11021.

Gray and Waddington [103, 104] determined experimentally and calculated enthalpies for the formation of azides. A great difference exists between non-explosive and explosive azides, as can be seen in Table 73.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔΗ₂₉⁸° (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaN₃</td>
<td>5.1</td>
</tr>
<tr>
<td>KN₃</td>
<td>-0.3</td>
</tr>
<tr>
<td>Ca(N₃)₂</td>
<td>-2.4</td>
</tr>
<tr>
<td>Ba(N₃)₂</td>
<td>-5.3</td>
</tr>
<tr>
<td>α-Pb(N₃)₂</td>
<td>115.5</td>
</tr>
<tr>
<td>Ag N₃</td>
<td>74.2</td>
</tr>
<tr>
<td>Cu(N₃)₂</td>
<td>140.5</td>
</tr>
</tbody>
</table>

The above figures and Fig. 78 throw some light on the problem (p. 475) of why lead and silver azides possess marked initiating properties when the others do not.
Fast Decomposition and Explosion

A considerable amount of work has been carried out on the fast decomposition of azides. This was initiated by heat, friction, impact, shock, light, electric field and atomic particles. Thermal initiation is given in Table 74.

<table>
<thead>
<tr>
<th>Azides</th>
<th>Temperature of initiation, and melting, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium azide</td>
<td>KN₃</td>
</tr>
<tr>
<td>Silver azide</td>
<td>AgN₃</td>
</tr>
<tr>
<td>Tallous azide</td>
<td>TlN₃</td>
</tr>
<tr>
<td>Cuprous azide</td>
<td>CuN₃</td>
</tr>
<tr>
<td>Mercury azide</td>
<td>or Cu₂(N₂)₂</td>
</tr>
<tr>
<td>HgN₃</td>
<td>melts at ca. 205</td>
</tr>
<tr>
<td>Mercurozide</td>
<td>Hg(N₃)₂</td>
</tr>
<tr>
<td>Cadmum azide</td>
<td>Cd(N₃)₂</td>
</tr>
<tr>
<td>Lead azide</td>
<td>Pb(N₃)₂</td>
</tr>
</tbody>
</table>

Impact sensitivity of lead and silver azides depends on the size of crystals or pellet thickness. The larger the crystals, the more sensitive they are. This and other problems related to the initiation of primary explosives are discussed by Bowden and Yoffe [125] and extensively reviewed by Chaudhri and Field [3 (Vol. 1, p. 383)].

LEAD AZIDE (Vol. III, p. 169)

Usually the advent of lead azide as a primary explosive is connected with the first patent by Hyronimus [83] in 1907. However, according to the literature [84] the first experiments with lead azide were carried out in Spandau (Germany) as early as 1893. They ended with a tragic accident and all experiments with lead azide were suspended. A number of doubts were expressed on the practical use of lead azide as an initiator [85, 86]. Also Kast [87] in his well-known book raised the problem of whether lead azide and azides of other heavy metals could be used as primary explosives.

This view has prevailed in many countries. In the U.S.S.R. lead azide entered industrial production in 1929 (Bagal [1]). Between 1920 and 1930 a considerable amount of work was dedicated to the production of lead azide which would be less hazardous to manufacture and thus dextrinated product was manufactured.

Properties of Lead Azide

It was originally thought that lead azide existed in two allotropic forms: α and β (Vol. III, p. 169). Now it is accepted that the substance is polymorphic and exists in four forms: α, β, γ and δ. The α-orthorhombic is the only one acceptable for technical application. It is the main product of precipitation with traces of the other forms present [89]. The monoclinic β-form is stable when dry, but recrystallizes as the α-form. The presence of some organic dyes (e.g. eosin) enhances the formation of β-form and hydrophilic colloids inhibit its formation. Breaking a needle of β-form may produce an explosion (contrary to the views of some authors; Vol. III, p. 173). The monoclinic γ-form is less stable than α and β [90]. It can be obtained from pure reagents at pH 3.5–7.0 or in the presence of vinyl alcohol. The triclinic δ-form precipitates from pure reagents at pH values of between 3.5 and 5.5 [90]. Both forms γ and δ are usually precipitated simultaneously and can be separated (with care) by hand.

Apin (according to [1]) described a method of preparing needle like β-modification through a slow diffusion of aqueous solutions of sodium azide and lead nitrate.

Among different modifications of lead azide, basic salt N₃Pb(OH) was prepared by Wöhler and Krupko [91] and showed less pronounced explosive properties; it deflagrated without detonating. Several basic lead azides have been prepared by Feitknecht and Sahli (Vol. III, p. 178).

An attempt was made to obtain Pb(N₃)₄ [92] from PbO₂ and hydrazic acid. The product Pb(N₃)₄ was unstable and readily lost nitrogen to form Pb(N₃)₂.

Crystal Structure of α-Pb(N₃)₂

The crystal structure of α-Pb(N₃)₂ was examined with the help of three dimensional neutron-diffraction by Choi and Bouitin [93]. These authors found four crystallographically distinct azide groups in a unit cell: azide (I), (II), (III) and (IV) — Fig. 79. Azide (I) is coordinated to four Pb atoms, two at each end. It is symmetric in both coordination and in N–N distances. Azide (II) is also surrounded by four Pb atoms but the coordination is asymmetric. The structure of azide (III) is very similar to azide (II) but the structure (III) is more symmetrical than (II). Azide (IV) is strongly asymmetric in both coordination and N–N distances.

Each Pb atom is surrounded by eight azide groups with bond lengths between 2.57 and 2.90 Å. It is further surrounded by four Pb atoms at distances 4.2–4.5 Å.

Spontaneous Explosions of Azides (Vol. III, p. 173)

Spontaneous explosions of saturated solutions of azides during crystallization
have been described. Spontaneous explosions were described for cadmium [45], cupric and mercuric [96], lead [91, 96, 97, 98] azides. Rogers [99] gave a description of his experiments with lead azides and Taylor and Thomas [100] thoroughly examined the conditions of the experiments. They prepared a 0.7% lead azide solution in 50 cm³ of hot 5% aqueous ammonium acetate and allowed it to cool to room temperature. After 11,400 sec (i.e. 1800 sec before the expected time of explosion) the crystallized out large crystals were filtered out and the liquid was left to stand. At the expected time a major explosion of the liquid occurred, but the filtered crystals remained intact. The authors tried to rationalize the phenomenon in terms of formation of nuclei and electric discharge of different layers of nuclei.

Fox, Jenkins and Taylor [101] discussed the three hypotheses which materialized to explain the phenomenon of spontaneous explosions, these are:

1. the release of stored energy which is high enough to cause an explosion [97],
2. reactive intermediates were formed in the solution [98],
3. discharge of sparks between growing crystals [100].

The third hypothesis seems at present to be the most probable. To verify it, Fox et al. [101] placed a metal electrode near the surface of the solution and measured the accumulation of electric charge. Indeed, in the solution in which explosions took place very strong charge fluctuations preceded explosions. Small lead detonators fired by Taylor and Thomas did not induce the explosion of the liquid which emanated from the crystals of lead azide. This indicated that the product – crystals of lead azide – have not yet existed in the solution. Stirring and introducing additives suppressed spontaneous explosions. Stirring dispersed the charges and did not allow their localized accumulation. The additives were absorbed by crystals at an early stage and created a lower spark sensitivity.

**Sensitivity of Lead Azide**

Sensitivity to high temperature was extensively studied [124]. Chaudhuri and Field [127] recently described a dependence on temperature of initiation of α-lead azide on crystal thickness, while studying individual single crystals of known size. There was a drop in the explosion temperature from 415 to 385°C for an increase in crystal thickness from 4 to 30 μm. Crystals of less than 3 μm thickness did not explode even up to 450°C. They did not melt at this temperature.

![Graph](image)

**FIG. 80.** Critical explosion temperature against crystal thickness, according to Chaudhuri and Field in [3, Vol. I, p. 383].

**In vacuo** no critical size of crystals was observed [128]. The previously mentioned behaviour of primary explosives at high vacuum [39–45] may explain the failure to find the critical size of lead azide under very low pressure.

As has been mentioned large crystals of lead azide are more sensitive to impact than the small ones [124]. This was noticed by Solonina as early as 1910 [1].

Direct flame (e.g. from black powder), sparks of electric discharge and glowing electric wires do not readily ignite lead azide and Claessen [129] suggested adding lead stypnate to increase its ease of ignition.

Lead azide is less sensitive to impact than mercury fulminate, as reported by Kozlov (according to [1]).
To increase the sensitivity of lead azide to impact, tetrazene was added in German detonators 'Duplex', according to Bagal [1]. Mixtures of 90--93% lead azide and 10--7% tetrazene were used.

Chaudhri and co-workers [190] determined the rate of detonation of single crystals of α-lead azide. Crystals of cross section 2 mm × 2 mm and above detonated at 8000 m/s, and smaller size (ca. 1 mm) exploded at 3000 m/s.

**Stability and Reactivity of Lead Azide**

Roux [130] kept lead azide at 50°C for 25 months, and at 80°C for 15 months and has not noticed any change of properties. Extensive experiments on the stability of lead azide were carried out by Solonina (in 1910) and Buhnov (in 1940) — according to [1]. The following are conclusions based on their work:

1. Dry lead azide does not react with metal casing made of aluminium and copper or their alloys (brass, duralumin).
2. In the presence of carbon dioxide, moist lead azide did not react with aluminium.
3. In the presence of carbon dioxide or other acidic compounds, moist lead azide can react with copper casing. Hydrazoic acid was evolved which reacted with copper or copper oxides to yield copper azides.

As recently discovered moisture without carbon dioxide can also promote reactions of lead azide.

As known copper azides are sensitive 1B and considerable work has been done to protect metals from reaction with lead azide.

**The Manufacture of Lead Azide** (Vol. III, p. 178)

The description below is based on information from [1] and [3 (Vol. 2)].

*Colloidal* lead azide. This is a pure form of lead azide (over 99% purity) in fine particles of 3--4 μm. It is non-hygroscopic but not readily pourable and hence less adaptable for mass production. It is particularly sensitive to electric discharge and hence used for electric detonators. For this purpose 'colloidal' lead azide is often mixed with a concentrated nitrocellulose solution in ethyl ether–ethanol or other solvents.

Colloidal lead azide is obtained by adding at 25°C 4% aqueous solution of sodium azide to a small excess of lead nitrate solution. The precipitate is filtered and washed with water and dried. Its density under 3000 kg/cm² pressure is 2.77 g/cm³ (as compared with 2.93 g/cm³ of crystalline lead azide).

British 'Service' lead azide. This is a crystalline lead azide containing a small proportion of lead carbonate on the surface of crystals. It is obtained by adding 1 M lead acetate and 2 M sodium azide solutions to the reactor which contains a quantity of sodium carbonate solution. The lead acetate is started a little ahead of the sodium azide so that some lead carbonate is formed which serves as a seeding agent for lead azide crystals. It contains 98.1 Pb(N₃)₂, crystals are large (ca. 55 μm), density under 15,000 kg/cm² is 3.31. Its temperature of explosion is 350°C with an induction period of 5 sec. It is non-hygroscopic, contrary to the dextrinated lead azide which is slightly hygroscopic due to the presence of dextrin.

Dextrinated lead azide. Dextrinated lead azide is made by adding, over a period of 30 min at 60°C, a dilute (3%) sodium azide to an equal volume of a lead acetate solution (7%) which contains dextrin from potato starch in a quantity of 6% to the expected yield of 6% of lead azide. The dextrin solution is made slightly alkaline with sodium hydroxide. The product contains ca. 92% of lead azide.

According to [3 (Vol. 2)] in Sweden a temperature of 75°C is maintained during the reaction, and du Pont Co. introduced 0.25% calcium stearate as an agent for coating the dextrinized particles. According to [1] the hygroscopicity of dextrinated lead azide can be higher than 0.5%.

British RD 1333 lead azide. The significant feature of this type of lead azide is the presence of sodium carboxymethylcellulose (CMC) without using sodium carbonate.

Here are the salient features of the process: 1.21 sodium CMC solution (10 g NaCMC/litre) were mixed with 0.145 litre of Empilan AQ 100 solution (10 g contains 100% ethylene derivative of lauric acid/litre) made up to volume of 15 litres with water are kept at 25°C. During a period of 60–70 min, introduced simultaneously, the solutions of sodium azide (108 g Na₃N/litre) and lead acetate (315 g (CH₃COO)₂Pb·3H₂O/litre) — 14 litres of each while stirring. The product precipitated and is washed by decantation, filtered and dried. The yield was 3.3–3.3 kg lead azide. The content of Pb(N₃)₂, 96.3%.

According to the U.S. experiments the temperature of the reaction 30–35°C should be maintained. The quantity of CMC is a critical parameter. The product should have a right viscosity and degree of etherification. The rate of stirring should not be below a certain norm (e.g. 200 rpm).

British RD 1343 lead azide. This is almost identical with RD 1333 except that the wetting agent is omitted and the sodium azide is made more alkaline. It did not cause a deposit to build up a water line in the reaction kettle, leading to reduced cleaning operation.

Special Purpose Lead Azide (SPLA) [3 (Vol. 2, p. 44)]. The Special Purpose lead azide was introduced in the U.S.A. It is of a greater sensitivity and lower
hygroscopicity than dextrinated lead azide. It does not differ much from RD 1333 preparation. The difference is in temperature $37 \pm 2^\circ$C and faster introduction of reagents (30 min).

**Polyvinyl Alcohol Lead Azide (PVA Lead Azide).** Polyvinyl alcohol was used instead of dextrin in Germany [2]. In the U.S.A. it is in use in Olin Mathison Corporation [131]. The addition of 3% PVA makes lead azide of better initiating properties, higher density and an easier inflammability than dextrinated lead azide [1].

**Gelatine Lead Azide (GAM).** Animal gelatine was used for crystal modification of lead azide with the addition of a small amount of molybdenum sulphate [132]. It is claimed that the product is safer in handling than usual lead azide.

**Spheroidal Dextrinated Lead Azide.** In the 1950s a spheroidal form of dextrinated lead azide was developed by Taylor and co-workers [185] and was named RD 1352. The method was tried in the U.S.A. and described in [3, (Vol. 2, p. 32)].

It consists essentially in reacting aqueous solutions of sodium azide and lead azide in the presence of solutions of dextrin and Tamol SN (surface active agent) at $60^\circ$C with an agitator revolving at 275 rpm. After cooling, the mother liquor was decanted, the precipitate washed with water, alcohol and dried.

The picture of the product by this interesting method is given in Fig. 81 (b, c). For comparison British Service lead azide (a) is also given.

**SILVER AZIDE (Vol. III, p. 182)**

A correction should be made to the description in Vol. III of some properties of silver azide: it is non-hygroscopic, according to C. A. Taylor and Rinkenbach [133] and Costain [3, (Vol. 2, p. 51)]. The hygroscopicity described previously was probably due to impurities.

The photosensitivity was discussed in Volume III.

Silver azide is soluble in ammonia to form a complex, upon evaporation of ammonia the azide is recovered unchanged. In nitric acid it dissolves with decomposition and the evolution of $\text{HN}_3$. On exposure to light silver azide turns first violet and finally black, as colloidal silver is formed and nitrogen evolved [3 (Vol. I, p. 58)].

A suspension of silver azide in boiling water decomposes with colouration similar to that of the photodecomposition [91]. When heat-dried the azide turns violet at $150^\circ$C, and melts at $251^\circ$C to a dark liquid. At $253^\circ$C it starts evolving nitrogen and metallic silver. When heated rapidly it explodes at $300^\circ$C emitting a green light [91, 3 (Vol. I, p. 58)].

**FIG. 81. British Service 170x (a)* and Spheroidal Dextrinated Lead Azide (Picatinny Arsenal) x 50: (b) 20 min and (c) 30 min respectively after start** [3, Vol. III].

*British Crown copyright reserved.

Silver azide crystallizes in an orthorhombic form with four molecules per unit cell. This was established by a number of authors [134–137]. The unit cell has dimensions of: $a = 5.6170\,\text{Å}, b = 5.9146\,\text{Å}, c = 6.0057\,\text{Å}$.

It has better initiating property than lead azide (Vol. III, p. 177).

Silver azide is now in use in small and strong detonators in the U.K., U.S.A., Holland, Sweden and Germany. The main obstacle against the use was originally the fact that silver azide was not in a suitable form for pouring and pressing into
detonators. During the early 1950s G. W. C. Taylor [138], Williams and Peyton [139] developed processes for making granular AgN₃.

The method used in Picatinny Arsenal [2] is as follows. The reaction was carried out in a 10-litre stainless steel kettle with a stirrer. The reagents were: 2.0 l of filtered 2N silver nitrate solution, 2.0 l of filtered 2N sodium azide solution, 1.0 l of filtered pure ammonia (28%) solution. Silver nitrate followed by ammonia was introduced into the reaction kettle. Under vigorous mixing sodium azide solution was introduced and the content was warmed to 75°C within 5 min. Silver azide started to precipitate ca. 5 min later.

At this point 50 ml of acetic acid 3N solution was added over 5 min to induce seed-crystal formation. Distilled water was added at a rate of 40–60 ml/min to maintain the original level and avoid evaporation losses.

When the total time at 75°C was 30 min, heating was increased to reach 97°C within 10 min and over the next 60 min the temperature was raised to boiling point which indicated that all the ammonia had boiled off. Cold water (3.5 l) was added and brought into the jacket to cool the content of the vessel. During the cooling, 50 ml of 3N acetic acid was introduced into the kettle. After 10 min the temperature reached 30°C, the stirring was stopped, silver azide was allowed to settle and the solution was decanted. The product was decanted with two portions of 3 l distilled water. The product was collected on a cloth-filter, washed with ethanol (95%) and dried for 40 hours at 50°C. The yield was 540 g (90%).

Vigorous stirring during the evaporation of the content of the vessel is very critical. Without stirring large flat crystals are produced. The quantity of acetic acid added for seeding was important for achieving uniform bulk density.

Cadmium Azide Cd(N₃)₂

Cadmium azide was obtained by Curtius and Risom [200] and Bassière [95]. Some work has been dedicated to its properties (Vol. III, p. 186).

According to Bowden and Singh [201] it is not decomposed by α- and γ-radiation. It shows the rate of detonation 4200 m/s. According to Wöhler and Martin [202] it is less sensitive to impact than lead azide, but more sensitive than silver azide.

Storage of Azides

Experiments on the storage of lead azide have shown [3 (Vol. 2)] that different types of lead azide withstand long storage. Some samples taken after 25 years of storage under standard storage conditions did not show any deterioration.

Toxicity

All azides are toxic, but their toxicity is due to the evolution of hydrazoic acid. The solid, insoluble azides such as lead and silver azides are practically non-toxic. Considerable studies were dedicated to the toxicity of sodium azide. It was found that the minimum lethal dose of NaN₃ is 35–38 mg/kg body weight [140]. Chronic poisoning with NaN₃ was studied by Bassendowska and co-workers [141]. They showed that the maximum permissible concentration of NaN₃ in air is 2 mg/m³, provided the skin of the worker is well protected.

Destruction of Lead Azide

Lead azide can be destroyed by acting with sodium hydroxide 10% solution at 20°C which gives Pb(OH)₂ and aqueous solution of NaN₃: (method of Kramer) [3 (Vol. 2, pp. 85–86)]

\[ \text{Pb(N₃)₂} + 2 \text{NaOH} \rightarrow \text{Pb(OH)₂} + 2\text{NaN₃}. \]  

(11)

Sodium azide can be recovered by evaporation and crystallization.

Another method was suggested by Richter [3 (Vol. 2)]. It consists in using a more concentrated (20%) sodium hydroxide:

\[ \text{Pb(N₃)₂} + 4 \text{NaOH} \rightarrow \text{Na₃PbO₄} + 2\text{NaN₃}. \]  

(12)

Here lead compound remains in solution in the form of sodium plumbate. Careful acidification of the solution with nitric acid leads to the formation of lead azide.

Data for lead azide [142] (Vol. III, p. 172)

- Enthalpy of formation: +391.3 kcal/kg
- Volume of detonation gases: 231 l/kg
- Density: 4.8 g/cm³
- Diflagration point: 320–360°C
- Lead block test: 110 cm³
- Impact sensitivity: 0.25–0.40 kpm
- Pure product: 0.3–0.65 kpm
- Dextrinated: 0.3–0.65 kpm

Specification (U.S.A.)

- Net content (by determination as PbCrO₄): min. 91.5%
- Moisture: max. 0.3%
- Mechanical impurities: nil
- Water solubles: max. 1%
- Lead content: min. 68%
- Copper content: nil
- Reaction: neutral
MANUFACTURE OF SODIUM AZIDE

It is appropriate to give a description of the basic compound used for producing azides. Below is a short description based on that of Bagal [1].

As known this is a two-step reaction (13):

\[
\begin{align*}
\text{Na} + \text{NH}_3 & \rightarrow \text{NaNH}_2 + \frac{1}{2} \text{H}_2 - 21 \text{ kcal} & (13a) \\
\text{NaNH}_2 + \text{N}_2 & \rightarrow \text{NaN}_3 + \text{H}_2\text{O} & (13b)
\end{align*}
\]

(a) Sodium Amide (Fig. 82)

Sodium should be of 99.5% purity. Gaseous ammonia — in a steel bottle (1) warmed to 30°C — should not contain more than 1% water. It is dried over

(b) Sodium Azide (Fig. 83)

The reaction is carried out in a horizontal heated electrical apparatus made of steel. Before starting the reaction it should be thoroughly dried by warming to 170–200°C. To check the tightness of the apparatus ammonia is blown through for 5–10 min. Hot melted sodium (350°C) is poured from the amide apparatus. The reaction of sodium with nitrous oxide is exothermic and there is little need of heating the reactor. The best temperature of the reaction is 200–220°C. At 250°C the reaction is too fast and may lead to an explosion. To achieve the uniformity of the reaction nitrous oxide is introduced into both ends of the reactor.
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

An analysis of outgoing gases should be carried out. They should contain 35–40% N₂O and 25–30% NH₃. The end of the reaction is manifested by the fall in the ammonia content to 3–5% NH₃ and the fall of temperature. The time to carry out the reaction of one batch is ca. 30 hours and the yield is 28–30 kg.

The content of the reactor is cooled to 100°C and washed with water. Care should be taken with this process, as water reacts vigorously (exothermic reaction) with unreacted sodamide. Sodium azide with sodium hydroxide is taken by water (200 l), filtered and evaporated to a density of 1.55–1.57 at 20°C. Sodium azide is collected, washed with a small quantity of water and finally with ethanol.

Sodium Azide Formation in Liquid Ammonia

This method was worked out in the U.S.S.R. [1] and based on a reaction at relatively low temperature in liquid ammonia. Both reactions: amidation and azidation can be carried out in the same reactor – autoclave of 200 l capacity and pressure up to 100 kg/cm².

Liquid ammonia dissolved sodium and the solution (under the action of catalysts) reacted to form sodamide. Sodamide is practically insoluble (ca. 0.1%) in liquid ammonia and precipitated as a fine powder. The catalyst is ferric oxide in quantity 3–5% (relative to sodium). The reaction takes 30 min to 1 hour at ca. 50°C. Hydrogen escapes from the autoclave at 40–60 kg/cm² through a safety valve working at this pressure.

The suspension of sodamide in liquid ammonia can readily react with nitrous oxide. Nitrous oxide kept in steel bottles under pressure is introduced into the autoclave under 25 kg/cm² maintaining the reaction temperature of 50°C.

The reaction of N₂O with NaN₃ in liquid ammonia is a somewhat complicated reaction. At first the reaction forms a complex 2 NaN₃, N₂O. In the presence of an excess of ammonia over 0°C sodium azide is formed. However in the presence of sodium hydroxide the basic sodium azide (NaN₃, 2NaOH) results. A higher temperature (e.g. 30–50°C) favours the formation of the basic compound, while a temperature of ca. 0°C prevents the formation of this substance.

Finally, a good solubility of sodium azide and practically no solubility of sodium hydroxide in liquid ammonia makes the separation of sodium azide from sodium hydroxide possible. Sodium azide retained on a filter should be washed with liquid ammonia. After ammonia has been evaporated, pure sodium azide remains with a yield of 99%.

TETRAZENE (TETRACENE) (Vol. III, p. 206)

Relatively recent X-ray analysis by Duke [147] confirmed the structure given by Patinkin, Horowitz and Lieber (formula I, Vol. III, p. 207). This is depicted

![Structure of TETRAZENE](image)

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by formula (XII) where the substance is presented as a zwitterion of 1-amino-1-(1H-tetrazol-5-yl)azo guanidine hydrate.

\[
\text{NH}_2
\]

XII

The heat of explosion is 558 kcal/kg and heat of formation \(-H_f = -70\) kcal/mol.

The following properties are according to the U.S. Military Specification [148]:

- Colour and appearance: white to light yellow coloured needle shaped crystals
- m.p. and explosion: 130 ± 2°C
- Granulation: 100% should pass through No 45 sieve
- Specific gravity: 1.65 ± 0.05
- Heavy metals: absent
- Meyer [142] gives some additional requirements:
  - moisture: max. 0.3%
  - aqueous extract: no acid present (on universal paper)
  - pouring density: 0.3
  - deflagration point: min. 138°C
  - lead block test: 155 cm²

It is slightly more sensitive to impact than mercuric fulminate.

Bubnov (according to [1]) gave the figures of density depending on the pressure applied:

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.052</td>
</tr>
<tr>
<td>200</td>
<td>1.179</td>
</tr>
<tr>
<td>300</td>
<td>1.289</td>
</tr>
<tr>
<td>400</td>
<td>1.304</td>
</tr>
<tr>
<td>500</td>
<td>1.377</td>
</tr>
<tr>
<td>600</td>
<td>1.401</td>
</tr>
<tr>
<td>1000</td>
<td>1.493</td>
</tr>
<tr>
<td>1600</td>
<td>1.503</td>
</tr>
</tbody>
</table>

Pouring density was given as 0.45.

It is non-hygroscopic: at 30°C and relative humidity 90% it absorbed 0.77% water. It does not attack metals at room temperature [149], and does not react with concentrated ammonia at room temperature, sodium and potassium hydroxides decompose the substance and ammonia is evolved.
With concentrated acid it forms salts: hydroxide, perchlorate, sulphate nitrate. They are all explosive and their initiation temperature is ca. 140°C.

The practical use is limited to detonators which are initiated by another primary explosive and tetryl is used as an intermediate booster or when mixed with another primary explosive to increase its sensitivity to flame or spark. The mixture tetryl was used in explosive rivets (Vol. III, p. 240). Dynamit A.G. patented [150] mixtures of tetryl with lead azide for this purpose.

A few initiating compositions with tetryl have been described in the Encyclopedia [148]. The most important seems to be 'Sinonydsatz' developed in Germany as a replacement for mercury fulminate mixtures. It proved to be non-corrosive and did not erode barrels of firearms. Their composition was: lead styphnate 25–55, tetryl 1.2–5.0, barium nitrate 25–45, lead dioxide 5–10, antimony sulphide 0–10, calcium silicide 3–15, powdered glass 0–5%.

Duplex-Cap (detonators) contained 0.3 g of a mixture of lead azide (92.5%) tetryl (7.5%) pressed at 100 kg/cm² over 0.05 g of unwaxed PETN pressed at 300 kg/cm².

Tetryl Derivatives and their Salts (Vol. III, p. 210)

Since the advent of Tetryl attention has been paid to other compounds which contain tetryl ring. An excellent review on Tetrylates was given by Herman in the Encyclopedia [190]. Silver and mercury salts of 5-nitrotetryl were suggested in Germany during World War II to replace the fulminates. According to the same source [190] mercuric salt of 5-nitrotetryl proved to be a powerful initiating explosive. It is sensitive to friction, has an explosion temperature of 210°C. It seems that it is too sensitive for practical use.

The chemistry of tetryl derivatives was reviewed by Bensen [192]. The simplest and most versatile derivative is 5-aminotetryl (Vol. III, p. 210). It is usually obtained by the method of Stolle and Schick [151] from cyanoguanidine and sodium azide in an acid medium:

\[
\begin{align*}
\text{NH}_2 & \quad \text{NH} \\
\text{H}_2 & \quad \text{CN} \\
\text{N} & \quad \text{N}
\end{align*}
\]

\[
\text{XIII} \quad \text{m.p. 203°C}
\]

Nitramino derivative of 5-aminotetryl (XIV)

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{NH} & \quad \text{O} \\
\text{N} & \quad \text{NH}
\end{align*}
\]

\[
\text{XIV}
\]

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was claimed [152] to yield a lead salt with initiating properties. The N-nitro compound (XIV) was described by Lieber et al. [153].

**Azotetrazol**

According to Thiele [154] oxidation of 5-aminotetryl with potassium permanganate in the presence of an excess of sodium hydroxide yielded sodium salt of azotetrazol:

![Diagram](image-url)

Basic lead salt of azotetrazol (bulk formula C₇H₁₀Pb·5H₂O) was used in Germany during World War II. A description of the method of manufacture according to Bagal [11] is given here. The starting substance was sodium salt of 5-aminotetryl (XIII). The sodium salt dissolved in a solution of sodium hydroxide at 70–80°C was charged with a 25% excess of potassium permanganate at the rate which would maintain the temperature 95–100°C. The solution should be brown. The filtered solution was cooled, the precipitated sodium salt was collected and dried at a temperature below 30°C.

To obtain the basic lead salt a solution of 3% sodium salt of XV containing 0.775% NaOH was prepared. The solution was poured into 7.5% solution of lead nitrate in a filled reactor at 43–44°C. The precipitated basic lead salt was collected, washed with water of 30–30°C, ethanol and kept as ethanol moistened product. The yield was a 78% based sodium salt of XV.

The salt was used for electric igniters. The substance was mixed with nitrocellulose varnish and fixed on the resistance bridge.

Another important derivative of tetryl is 1,3-ditetrazyltriazine (XVI)

![Diagram](image-url)

This was obtained by K. A. Hofmann and Hock [155] as described in Vol. III, p. 210. The compound forms colourless thin plates, crystallizing with 1 mole of water. It has masked acidic properties and can readily form salts with metals. On boiling with dilute hydrochloric acid it yielded 5-aminotetryl (XIII) and nitrogen. The compound was described in review [156]. Sinha, K. R. K. Rao and Sankaran [157] made an extensive study of the properties of the substance and its salts. Lead salt has an explosion temperature of 185°C. Bahadur [158]
described lead double salt of XVI and stypnic acid as an initiator. Practical experiments have shown that the salt is too dangerous to handle.

**FUROXANE DERIVATIVES**

Attention was recently drawn to the initiating properties of some salts of nitro derivatives of benzo-furoxane. Potassium and barium salts of 4,6-dinitrobenzofuroxane as primary explosives were suggested by Piechowicz [193].

\[
\begin{align*}
\text{O}_2\text{N} & \rightarrow \text{N} \rightarrow \text{O}^+ \\
\text{N} & \rightarrow \text{O} \\
\text{NO}_2 & \rightarrow \text{NO}_2
\end{align*}
\]

No information is available as to the practical application of this salt.

The potassium salt was described as early as in 1899 by Drost [194], and a number of authors [195, 196] mentioned explosive properties of the salts of the above compound.

Benzofuroxane can be obtained according to Green and Rowe [195] by oxidation of o-nitroaniline with sodium hypochlorite. Nitration of benzofuroxane at 5–20°C yielded 4,6-dinitrofuroxane [194–196].

An excellent review on furoxanes was given by Kaufman and Picard [197].

Pepekin, Apin and co-workers [203] determined the energy of dissociation of the bond \(\text{N} \rightarrow \text{O}\) in benzofuroxane. They found a value of 59.5 kcal/mol.

**NITRO DERIVATIVES OF PHENOLS** (Vol. III, p. 212)

An experimental work on thermal decomposition of the salts of picric and stypnic acids has been carried out by Andreev and Lu-Bao-Fen [159]. Ammonium, potassium and lead salts were examined, and the results summarized in Table 75.

The curve: rate of decomposition/temperature shows an autocatalytic trend of reactions.

The decomposition of stypnates occurs at a lower temperature than that of picrates.

**Lead Mononitroresorcintol (LMNR)**

The lead salt of mononitroresorcintol was in use in electric detonators for making fuseheads. Some of them may be composed of this salt and dextrinated lead azide [159, 160].

The main problem in making LMNR is the use of 2-mononitroresorcintol.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Interval of temperature (\text{res}^\circ\text{C})</th>
<th>(E) kcal/mol</th>
<th>Half-life time at (230\circ\text{C}), minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium picrate</td>
<td>250–300</td>
<td>41.2</td>
<td>8600</td>
</tr>
<tr>
<td>Lead picrate</td>
<td>230–260</td>
<td>60.2</td>
<td>920</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td></td>
<td>explosion at (260\circ\text{C})</td>
</tr>
<tr>
<td>Potassium Stypnate</td>
<td>170–200</td>
<td>47.6</td>
<td>262</td>
</tr>
<tr>
<td>Dipotassium Stypnate</td>
<td>200–240</td>
<td>51.7</td>
<td>210</td>
</tr>
<tr>
<td>Lead Stypnate</td>
<td>200–230</td>
<td>36.4</td>
<td>143</td>
</tr>
</tbody>
</table>

which should be obtained by very careful nitration of resorcinol. Resorcinol is heated with fuming sulphuric acid at \(100\circ\text{C}\) for 30 min. The solution is cooled to \(25\circ\text{C}\). After adding mixed acids it is allowed to stand for 30 min. The addition of water follows, and distillation of the product with steam. It forms orange coloured prisms, m.p. 84–88°C, boiling p. 232–234°C [161, 162a].

**Lead 2,4-Dinitroresorcinate** (Vol. III, p. 220)

The Encyclopedia of Fedoroff and Sheffield [162b] gives some figures on the properties of lead dinitroresorcinate. It explodes at \(265\circ\text{C}\) (induction 5 sec), heat of explosion is \(270\) kcal/kg. It is slightly hygroscopic: at \(30\circ\text{C}, 90\%\) relative hygrosopicity is 0.73%. It has low initiating property: \(0.4\) g did not initiate tetryl pressed at \(70\) kg/cm\(^2\).

**Basic Lead 4,6-Dinitroresorcintol**

The salt was developed in Great Britain during World War II [162c]. Finely ground (40 g) resorcinol was gradually introduced to 98% nitric acid (400 g) at \(-15\circ\text{C}\) to \(-20\circ\text{C}\). The low temperature was kept by adding solid carbon dioxide to the nitration vessel. After all the resorcinol was introduced, the nitra-
tion mixture was cooled to $-50^\circ$C and then drawn into 5 times its volume of water with ice.

The crude product was purified by dissolving in 5% NaOH solution and pouring the solution into hot boiling 12% sulphuric acid. The precipitated dinitroresorcinol was washed with water. The yield was 27.5 g, that is, ca. 40% of theoretical.

The product reacted with an excess of freshly precipitated lead hydroxide suspended in water at 90°C.

According to existing information [162c] large scale manufacture of the salt in Great Britain was carried out by reacting dinitroresorcinol freshly filtered from nitric without purification with lead hydroxide at 90°C.

**Lead Stypnate (Vol. III, p. 213)**

No relevant facts can be added to those reported previously. The following are data taken from Meyer’s textbook [142]:

- density 3.0
- deflagration point 275–280°C
- heat of explosion 370 kcal/kg
- lead block test 130 cm³ (according to [162d])
- detonation velocity 4900–5200 m/s

**Specification**

| net content | min. 98% |
| moisture | max. 0.15% |
| lead content | 43.2–44.3% |
| (determined as PbCrO₄) | max. 0.05% |
| Heavy metals other than lead | max. 0.5% |
| Ca and Mg | max. 0.07% |
| Na | 5–7 |
| pH | 8.8% |
| nitrogen content | 1.3–1.5 |
| bulk density | min. 270°C |

**Deflagration point**

According to the authors the salts are less sensitive to heat, impact, friction and electric discharge than the corresponding salts of phenol and resorcinol.

**Complex Salts (Vol. III, p. 230)**

In addition to complex perchlorates (Vol. III) Ni, Co and Cd form the following complex salts with hydrazine nitrate:

- Ni (N₂H₄)₃(NO₃)₂ − deflagration at 215°C
- Co (N₂H₄)₂(NO₃)₂ − deflagration at 210°C
- Cd (N₂H₄)₃(NO₃)₂ − deflagration at 245°C

According to Mérard and Barlot [164] they could be recommended as primary compounds. They possess the advantage that they are less sensitive to impact than mercury fulminate and lead azide. Their disadvantage is that they are difficult to ignite.

Nickel salt was examined in detail. It expands in lead block of ca. 85% of picric acid. The velocity of detonation in an 8 mm diameter plastic tube was found to be 2900–3100 m/s.

**1,3,5-Triazido-2,4,6-Trinitrobenzene (Vol. III, p. 193, formula IX)**

The substance is readily transformed into benzotrisfuroxane (Vol. I, pp. 603–604, formula II and Vol. III, p. 193, formula X). Kinetics of the transformation was studied by Korsunskii and Apina [181] — see Chapter IV.

**Dinitrobenzenediazoxoide (Dinitrodiazophenol DDNP, DINOL) (Vol. III, p. 201)**

Little can be added to the information given in Vol. III. According to Fordham [183] it has a velocity of detonation of 6900 m/s at a density of 1.58. As compared with other initiating explosives it is relatively insensitive to impact and
friction. It has good storage properties and an application has been found in both commercial and military detonators, particularly in the U.S.A.

Salts of Acetylene (Vol. III, p. 227)

Silver acetylide. Although silver acetylide has not received practical application it has been the subject of a few published papers. Stettbacher [165] was first to draw attention to the very strong initiating properties of silver acetylide. He found that the initiating charge is 0.07 g (for AgN₃ and mercuric fulminate he found 0.02 g and 0.29 g respectively).

Tamman and Kröger [166] compared the properties of the acetylide and the double salt Ag₃C₂·AgNO₃. The latter was obtained by acting with acetylene on a solution of AgNO₃ in dilute nitric acid. The initiation temperature was found to be 202–207°C (depending on the rate of heating). Silver acetylide gave a range of 143–148°C. A wide description of the properties of the double salt Ag₃C₂·AgNO₃ was given by Stadler [167]. It was obtained by introducing acetylene into a solution of 50 g AgNO₃ in 200 cm³ water and 30 cm³ nitric acid (d 1.4) at 80–90°C. The velocity of detonation was 2250 m/s and 4450 m/s at densities of 2.51 and 5.36 respectively. The lead block expansion was 136 cm³. The heat of explosion for the double salt was 183 kcal/mol (for silver acetylide 70.3 kcal/mol).

MANUFACTURE OF PRIMERS

One of the leading explosives factories in Europe, Vihtavouri Works in Finland, has developed a modern process for the manufacture of primers after the explosion in 1951 [180]. The main novelty being remote control.

The building for the manufacture of primers has a corridor running through the middle and on both sides of the corridor are steel–concrete chambers. The outer walls of the chambers are lightly built. In the corridor walls, part of the concrete is replaced by 30 mm steel plate, to simplify the fixing of the control apparatus. The explosives – lead styphnates, lead azide and tetrazene are kept and transported from one stage to another in 1 kg canisters. They are grasped with tongs and transported from one chamber to another by trolleys moved by a cable. Steel trapdoors in the dividing walls are opened and closed by remote control.

Lead styphnate and lead azide are precipitated in correct proportion and mixed by a continuous process.

The five production operations: precipitation, mixing, filtration, drying and sieving are carried out in one chamber. Drying is carried out in the filtration apparatus by washing with solvents and drying with warm air. The explosive is transferred from one apparatus to another by tongs and levers fitted through the armour plating.

PEROXIDES (Vol. III, pp. 225, 299)

Peroxides as explosives have no practical application with the exception of concentrated hydrogen peroxide, containing over 80% and 90% H₂O₂ (Vol. III, p. 299) as an oxidant in rocket fuel. It also became an important oxidant with a wide application – among reactions with concentrated hydrogen peroxide the reaction H₂O₂ → NO₂ was achieved to obtain hexanitrobenzene (Chapter VI). The reactions of radical polymerization under the catalytic action of acyl and ketone peroxides are well known. Among the latter use has been found for propioene peroxide and peroxyacetic acid became one of the most important epoxidation agents.

A number of monographs and reviews have been published on peroxides in addition to those mentioned in Vol. III (p. 227) [168–176, 168–175]. The problems of peroxide reactions are outside the scope of the present book and only those related to explosives will be described here.

Some peroxides, such as BaO₂, SrO₂ are in use in pyrotechnical compositions [176]. This is outside the scope of the present book.

Propioene Peroxide (XXI)

found a wide application as an initiator of radical polymerization. It is much less sensitive to impact and friction than acetone peroxide (Vol. III, p. 225).

Hexamethylenediamine peroxide which has two assigned formulae (Vol. III, p. 225, formulae I and II) was examined with NMR technique by T. Urbanśki [174], who found that formula I by Baeyer and Villiger [177] was the correct one.

Among peroxides with explosive properties are those from 1,2-diketones (XXII) [178]. They were prepared by ozonolysis or by the action of singlet oxygen on alkanes, or by sodium hydroxide action on bromoperoxide.

XXII

XXIII
The name 'superoxide' was introduced in 1934 to signify an exceptional degree of reactivity of superoxide radical anion \( \text{O}_2^- \) in \( \text{K}_2\text{O}_2 \) [187]. It was obtained by acting with dioxygen on metals such as potassium (and Rb, Cs). It is marked by nucleophilicity. In aprotic media it reacts rapidly with primary and secondary alkyl halides to yield dialkyl peroxides and with acyl chlorides to yield acyl peroxides. Superoxides are reduced to peroxides under some experimental conditions. They were recently reviewed by Sawyer and Valentine [188]. No explosive properties of metal superoxides or their mixtures have been recorded.

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Appendix to Chapters XIII and XVII

An interesting organic azide related to hexogen (HMX) was recently described by Frankel and Woolley [204].

\[
\begin{align*}
\text{NO}_2 & \\
\text{CH}_3 & \quad \text{N} & \quad \text{CH}_3 \\
\text{O}_2 & \quad \text{N} & \quad \text{N} & \quad \text{NO}_2 \\
\text{CH}_3 & \quad \text{N} & \quad \text{CH}_2 & \\
\text{CH}_2 & \text{N}_3 & \\
\text{m.p.} & 130-131^\circ 
\end{align*}
\]

CHAPTER 18

BLACK POWDER (GUN POWDER)
(Vol. III, p. 322)

Black powder is still little known as regards the mechanisms of reactions occurring during its burning, although it has been known for more than 2000 years.

Owing to new tools such as differential thermal analysis [1], and advances in solid-state chemistry [2-5], advances in free radical chemistry and ESR technique [6] and catalysis, theoretical and experimental approaches to the problems of mechanism were made possible (Vol. III, p. 335).

Concling [7] recently gave an interesting review on burning black powder and pyrotechnic compositions. He presented diagrams of differential analysis of the behaviour of potassium nitrate, sulphur and their mixture when heated. Figure 84 shows a diagram of KNO₃ + S mixture.

![Diagram](image)

FIG. 84. Differential calorimeter diagram of KNO₃ + S according to Concling [7].

One of the problems in burning black powder is: at which moment does the main reaction begin (e.g. Vol. III, p. 338) and whether the reaction occurs in the condensed phase or the gas phase.

Andreev [8] in his monograph pointed out that the burning of black powder occurs mainly in the condensed phase. This explains the experimental facts that the rate of burning depends very little on the pressure and the heat transfer does not go through the gas phase but through the solid or liquid (melted) phase. Also the transformation of the solid phase to liquid occurs through endothermic processes which do not favour the reaction. Glazkova et al. [9, 10] systematically examined the deflagration and thermal decomposition of mixtures of potassium nitrate with carbon, sulphur and both these components. Here are her main conclusions:

1. The rate-controlling reactions of potassium nitrate with charcoal occurred in the condensed phase.
2. The stoichiometric mixture of sulphur with potassium nitrate indicated that the burning does not depend on density and the rate-controlling reaction occurred in a gas-phase.

The rates of burning of mixtures of potassium nitrate with sulphur are higher than those of potassium nitrate with carbon.

It follows from Fig. 85 on the mixture of three components: KNO₃, carbon and 5% sulphur, that the rate of burning was greater in the samples pressed to the theoretical than to the lower density.

![Graph](image)

FIG. 85. The rate of burning of a mixture of KNO₃, carbon and 5% sulphur at a lower (1) and higher (2) density, according to Glazkova et al. [10].

This meant that the rate-controlling reaction occurs mainly in the condensed phase.

Glazkova also examined the action of catalysts such as lead chromate; it leads to an increase in the importance of reactions in the condensed phase.

Bowden and Blackwood [11] pointed out the important part played by charcoal in the process of burning black powder and the role of soluble constituents present in charcoal.
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

It is known that unpaired electrons and free radicals are present in charcoal [12]. Also another fact is that the grinding of polymers and charcoal produce the break of covalent bonds \( \geq C - C \leq \) to form free radicals \( \geq C \). [13].

T. Urbaski advanced the view [14, 15] that free radicals in charcoal considerably influence the properties of black powder. The concentration of free radicals in charcoal depends very much on the temperature of carbonization in the range 245–650°C (Fig. 86). ‘Ammonpulver’ – a mixture of 85% \( \text{NH}_4\text{NO}_3 \) and 15% charcoal – was prepared from charcoal made at various temperatures of carbonization of cellulose.

Numerous modifications have been introduced, some with the aim of reducing the rate of burning.

One of the modifications consisted in partially (or completely) replacing potassium nitrate by sodium nitrate. Sodium nitrate changed some properties of the mixtures, in spite of the similarity to potassium nitrate. As pointed out previously (Vol. III, p. 329), sodium nitrate mixtures for mining (in Germany ‘Sprengsalpeter’) gave a better performance than potassium nitrate mixtures (in Germany ‘Sprengpulver’). This has never been investigated and explained, but recently a few notes have appeared which point out the difference between sodium and potassium nitrate. Thus according to Touse [17] the difference between these two nitrates can be found in their behaviour at a temperature of ca. 900°C. Sodium nitrate decomposed mainly according to equation (1a) but ca. 8% reacted in the sense of equation (1b):

\[
2 \text{NaNO}_3 + \text{O}_2 \rightarrow 2 \text{NaNO}_3 + \text{NO}_3 + \text{NO}_2 + \text{O}_2
\]  

(1b)

Reaction (1b) does not occur with potassium nitrate. In the light of the above it seems that sodium nitrate is more reactive than potassium nitrate at high temperature.

Various modifications of black powder are known. One of the most popular is sulphurless black powder (Vol. III, p. 331). Fedoroff and associates [18] mentioned over twenty different modifications of black powder.

Here are a few modifications introduced with the aim of lowering the rate of burning.

1. Addition of silicate dust (e.g. brick dust) and graphite. Such mixtures do not burn uniformly and leave a considerable residue.

2. Addition of resin, which reduces the rate of burning of black powder under atmospheric pressure ca. 20 times.

3. Substitution of pitch for charcoal slows down the burning 4 to 10 times.

FIG. 86. Spin concentration in charcoal against the temperature of carbonization of cellulose, according to T. Urbaski et al. [16].

FIG. 87. Rate of burning (‘coefficient of vivacity’, \( \frac{dp}{dt_{\text{max}}} \)) of ‘Ammonpulver’ against the temperature of carbonization of cellulose, according to T. Urbaski et al. [6].

Modifications of Black Powder

One of the characteristics of black powder is that it is a fast burning mixture.
(4) Substitution of cuprene (acetylene polymerized on copper as a catalyst) for charcoal.

(5) Introduction of triphenyl phosphate, camphor substituted ureas (as suggested by F. Olsen).

(6) Mixing black powder with nitrocellulose dissolved in a usual solvent, with the ratio black powder/nitrocellulose being 60/40. The resulting dough was extruded in much the same way as cannon propellants. This was known as Benite, developed by Hassmann and improved by Huselton and Kaplowitz according to [18]. The composition of Benite was: 40% Nitrocellulose (13.15% N), 44.3% KNO₃, 6.3% Sulphur, 9.4% Charcoal. Ethyl Centralite was added to this mixture in a proportion of 0.5%.

According to Stettbacher [19] the addition of 1–6% of BaSO₄ is strongly advised to slow down the rate of burning of black powder.

Among recent modifications of black powder a patent [20] should be mentioned. The mixture is composed of potassium perchlorate (60–80%), salts of benzoic acid (40–20%) and a small proportion of water (ca. 2%). Water is probably combined with benzoic acid salts in the form of hydrates.

By replacing charcoal with bit (fossil) coal an increase in the rate of burning can occur.

Considerable work is being carried out by Glazkova et al. [21, 22] on the burning of mixed explosives and the catalysis of burning. She considered sulphur in black powder to be a catalyst.

Here are the main conclusions of the work of Glazkova et al. [22] related to the burning of mixtures of inorganic nitrates with charcoal.

1. Inorganic nitrates can play the part of catalysts and their effectiveness can be arranged in the following way:

   Na > Pb > K > Ba > Al > Ca, Mg, Cu.

2. A stoichiometric mixture of ammonium nitrate and charcoal reacts in the condensed phase and a similar mixture of sodium nitrate with charcoal in a gas phase (see above for the statement on burning a mixture of potassium nitrate).

3. The burning rate of the mixtures depends mainly on the catalytic activity of cations and not on their concentration.

4. The most effective catalytic action on the burning of mixtures with ammonium, potassium and sodium nitrates possess salts of Cr(VI), Cu(II), Pb(II) and sulphur. They are acting mainly on reactions in condensed phase, that is, with ammonium and potassium nitrate.

**Explosive properties**

A paper by Isaksson and Rittfeldt [23] described the examination of black powder of different origins. They came to the conclusion that samples of different origins can be identified on the basis of their combustion parameters.

**Hygroscopicity of Black Powder**

Potassium nitrate is non-hygrosopic, but black powder is relatively hygrosopic. Charcoal is responsible for the hygroscopicity of the mixture because of the high absorption power of charcoal. One of the methods of reducing the hygroscopicity is to mix charcoal with non-hygrosopic substances. This however may reduce the burning properties of the powder.

The method of mixing charcoal with sulphur (binary mixture) can be beneficial under the following conditions:

1. all charcoal is mixed with sulphur,
2. the temperature of mixing should be kept for a short time at approximately 120°C, that is, above the m.p. of sulphur,
3. mixing is carried out in the air-tight container in an atmosphere of nitrogen, to prevent the oxidation of sulphur.

**Manufacture of Black Powder**

The classic method of manufacturing black powder comprises mixing the ingredients in a ball mill and finally in edge runners. The process has not changed in nearly a hundred years. However, recently an improvement has been introduced by Løvold [26] in the factory of Dyno industries A.S., Nittedal Krutfactory, Nittedal in Norway. This method consists of mixing and milling all three ingredients in a single operation in a Jet-Mill (Fig. 88 [24]). The mill has no moving parts which is one of the safety factors. Compressed air is blown through a specially designed nozzle in the lower part of the mill and into the grinding chamber. The air leaves the nozzle with a very high velocity. The material to be crushed—a mixture of all three components as a continuous stream—is fed into the chamber where the collision of particles causes pulverization to the size distribution as follows [26]:

- 100% finer than 25 μm
- 95% finer than 15 μm
- 90% finer than 10 μm
- 83% finer than 5 μm
The Use of Black Powder

1. Black powder with potassium nitrate and with sodium nitrate (the latter-German 'Sprengsalpeter') is widely used for mining when a low strength of explosive is required, for example in quarries where large and undamaged blocks are needed or when the material is soft (e.g. slate).
2. For slow burning fuses, delay charges.
3. For small rockets (signal, distress and life-saving at sea rockets), rockets for rain-making (Vol. III, p. 324).

Pyrotechnics

Pyrotechnics is strongly connected with black powder. This is however outside the scope of the present book. The existing literature is recommended [27–30].

Accidents with Black Powder

As mentioned earlier (Vol. III, p. 361) the manufacture of black powder is one of the most dangerous operations in the production of explosives. Before the advent of the manufacture of nitroglycerine it was considered to be the most dangerous type of manufacture. It still remains dangerous in spite of considerable improvement in the methods of production. In his book Biasutti [31] described an explosion in the edge runner at the factory in Modderfontein, South Africa in 1980. Nobody was injured thanks to the remote control operation.

History of Black Powder

The following are published monographs dealing specifically with the more recent history of black powder in various countries to complete the references in Vol. III, pp. 363–364: [32–36].

REFERENCES

   Izd. 'Nauka', Moscow, 1966.
INTRODUCTION

The early history of the use of explosives in mines and in various branches of civil engineering has been described in Vol. III. The growing use of explosives for peaceful application has been described in a number of monographs. Here are some of them (in addition to those mentioned in Vol. III):

- Assonov [1], Samuiro [2], Rossi and Pozdniakov [3], Cybulski [4], Charewicz, Krawiec et al. [5], Dubnov, Bakharevich and Romanov [6], Fordhain [7], Mining Research, Two Collective Vols (Ed. G. B. Clark) [8], the book on Explosive Working of Metals by Reinhardt and Pearson [9].


It should be added that in the U.S.A. commercial explosives can be classified as blasting agents and explosives [11]. The former are those which do not detonate from a detonator No. 8 but require a stronger initiator, while explosives detonate readily.

PRINCIPLES OF COMPOSITION OF COMMERCIAL EXPLOSIVES

The principles of the design of commercial explosives were described in Vol. III, pp. 420-440. Some of the principles will now be discussed in detail on the basis of more modern literature.

Oxygen Balance

The composition of commercial (mining) explosives should correspond to two requirements:

(a) production of non-toxic gases,
(b) full utilization of the energy of the reaction between the oxygen carrier and combustible ingredients.
The oxygen balance is usually calculated on the unwrapped explosive and, as Fordham [7] pointed out, only a part of the wrapper (waxed paper, polyethylene or other polymers) – usually a half – takes part in the chemical reaction. As pointed out in Vol. III (p. 424) both negative and positive balance can produce toxic gases: carbon monoxide and nitrogen oxides respectively. Dubnov et al. [6] pointed out that the explosive can also react with the medium surrounding the shot-hole.

Rossi [11] and Khudyakov [12] studied this problem and came to the conclusion that coal can react with CO₂ to yield CO, apatites and potassium salts can bind NOₓ, molybdenum and some copper ores bind carbon monoxide. Some iron ores can catalyse the oxidation of carbon monoxide to carbon dioxide. Dubnov [6] pointed out that sulphur containing ore may be responsible for the formation of such toxic gases as SO₂ and H₂S.

Dubnov et al. gives the results of experiments in an apatite mine with Ammonit 6 as follows:

**TABLE 76. Toxic gases produced by detonation of Ammonit 6 [6]**

<table>
<thead>
<tr>
<th>Combustible of the wrapper in g for 100 g of explosive</th>
<th>Oxygen balance %</th>
<th>Found in the atmosphere of the borehole in l/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper, Paraffin wax, Explosive, Cartridge</td>
<td>CO</td>
<td>NO</td>
</tr>
<tr>
<td>1.7, 2.3</td>
<td>+0.3</td>
<td>-9.8</td>
</tr>
<tr>
<td>1.7, 4.8</td>
<td>+0.3</td>
<td>-18.3</td>
</tr>
</tbody>
</table>

Rossi, according to Dubnov, reported that by replacing paraffin wax paper with polyethylene, the concentration of carbon monoxide was reduced from 39–42 to 12–20 l/kg, after the detonation of Ammonit No. 6.

Subsequently the official regulation in U.S.S.R. [13] reduced the amount of paper to 2 g and paraffin wax (or similar hydrophobic product) to 2.5 g/100 g of explosive.

Other factors influencing the formation of CO and nitrogen oxides:

The fineness of particles of ammonium nitrate reduces the amount of CO and NO, as given by Svetlov [11]: see Table 77.

Another factor influencing the composition of the products is the ratio between the diameter of shot-hole and the diameter of the cartridge. The following are data for Ammonit 6 ZhV [11]: see Table 78.

The composition of fumes produced by detonation of explosives used in Poland: Barbaryt A and Metanit D2 (Vol. III, pp. 478–479) was examined by Cybulskia and Sobula [14]. The fumes were analysed after the detonation in both laboratory conditions and in shot-hole underground. Samples of gases

**TABLE 77. Influence of the fineness of ammonium nitrate of the amount of toxic gases, according to Svetlov as reported by Rossi [11]**

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Concentration of toxic gases, l/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonit No. 6</td>
<td>CO</td>
</tr>
<tr>
<td>large particles</td>
<td>28</td>
</tr>
<tr>
<td>fine particles</td>
<td>22.9</td>
</tr>
<tr>
<td>Ammonit ZhV-20</td>
<td>CO</td>
</tr>
<tr>
<td>large particles</td>
<td>22.8</td>
</tr>
<tr>
<td>fine particles</td>
<td>21.4</td>
</tr>
</tbody>
</table>

**TABLE 78. Influence of the diameter of shothole and of the cartridges [11] explosive: Ammonit No. 6 ZhV**

<table>
<thead>
<tr>
<th>Diameter in mm</th>
<th>Cartridges</th>
<th>Concentration of toxic gases, l/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shothole 42</td>
<td>32</td>
<td>49–57</td>
</tr>
<tr>
<td>34</td>
<td>32</td>
<td>30–31</td>
</tr>
</tbody>
</table>

These concentrations decrease very quickly through the blowing ventilation. Overcharging of shot-holes produced a marked increase in the above gases. When fired in coal more fumes are produced than in stone.

Volk [15] examined the detonation fumes, between the detonation of Ammonit 1 in an atmosphere of air and argon. In the former case the amount of NO was higher than in argon, and the method of determining toxic gas products in the Federal Republic of Germany was described [16]. G. Persson and P. A. Persson [106] and Lindqvist and Johnson [107] found that experimental firing of charges of AN–FO explosives in steel-tubes gave results comparable with those in rocks. Similar results of firing charges in mortar were also reported [108].

**HYGROSCOPICITY OF MINING EXPLOSIVES**

The hygroscopicity of ammonium nitrate is a great drawback in explosives containing this salt. It limited the use of ammonium nitrate explosives, and only relatively recently methods were found of reducing the hygroscopicity of ammonium nitrate explosives.
One of the methods of protecting explosives against moisture consists in using a hydrophobic envelope, such as paper impregnated with hydrophobic substances more efficient than paraffin, such as paraffin with added substances containing polar groups—pitch, asphalt, petroleum tar etc. or using a polyethylene envelope.

A recent method of protecting ammonium nitrate against moisture, is mixing it with substances such as calcium or zinc stearate, petroleum tar, asphalt, barium sulphate and guar gum powder. According to Dubnov [6] stearates are in powder form of 5–20 μm size, whereas ammonium nitrate is of 70–120 μm. Owing to such sizes a very small proportion of stearates suffices to cover the surface of particles of ammonium nitrate. To evaluate the efficiency of the hydrophobic substances—Pozdnjakov in the U.S.S.R. [17] developed a hydrostatic apparatus which determines the pressure of water which is required to penetrate through a thin layer of explosive enclosed in a capsule. Dubnov [6] gives the figures for water pressure in centimetres needed to pass through a standard explosive composed of ammonium nitrate (80%), TNT (19%) and hydrophobic substance (1%). Some of his figures are collected in Table 79.

### Table 79. Water column (in cm) needed to penetrate Pozdnjakov apparatus [6]

<table>
<thead>
<tr>
<th>Substance</th>
<th>Water Column (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium stearate</td>
<td>90</td>
</tr>
<tr>
<td>Zinc stearate</td>
<td>88</td>
</tr>
<tr>
<td>Paraffin wax—petroleum tar (4:1)</td>
<td>85</td>
</tr>
<tr>
<td>Paraffin wax—asphalt (1:2)</td>
<td>82</td>
</tr>
<tr>
<td>Ferric stearate</td>
<td>78</td>
</tr>
<tr>
<td>Paraffin wax</td>
<td>70</td>
</tr>
<tr>
<td>Paraffin wax—calopheny (4:1)</td>
<td>68</td>
</tr>
<tr>
<td>Paraffin wax—soot (1:2)</td>
<td>67</td>
</tr>
<tr>
<td>Paraffin wax—graphite (1:2)</td>
<td>67</td>
</tr>
<tr>
<td>Paraffin wax—calopheny (3:1)</td>
<td>66</td>
</tr>
<tr>
<td>Paraffin wax—dinitronaphthalene (1:2)</td>
<td>64</td>
</tr>
</tbody>
</table>

Shestakov [18] introduced an original method of protecting ammonium nitrate which consists in mixing ammonium nitrate with Fe₂(SO₄)₃ (0.5%) and fatty acids (stearic, palmitic acid) (0.25%). A thin layer of ferric stearate or palmitate is formed on the surface of crystals of ammonium nitrate. It is now customary to use 0.3–0.4% fatty acids and 0.07% iron salts. Part of the fatty acids can be replaced by paraffins. Explosives containing fatty acids and iron salts are marked with symbol Zh V.

The mixing of ammonium nitrate with hydrophobic components is usually achieved in edge runners used extensively in black powder manufacture (Vol. III, p. 350, Figs 93, 94) or in disc mixers (Vol. III, p. 504, Fig. 166).

Water resistance of commercial explosives is examined in Germany at Test Station Dortmud – Deine [69].

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### STABILITY OF COMMERCIAL EXPLOSIVES

#### Physical Changes

Ammonium nitrate commercial explosives are stable at a moderate temperature and dry atmosphere and should not be kept at temperatures above 32°C when a change in the crystal habit of ammonium nitrate occurs and the change of temperature may harden the cartridges. The same can occur if explosives are kept in a humid atmosphere and a change of temperature can produce cracking of ammonium nitrate.

Explosives with nitroglycerine should be protected from freezing and the thawing of frozen nitroglycerine can cause disasters (Vol. III, p. 518). Currently in most countries a non-freezing mixture of nitroglycerine with nitroglycol is used. The change of explosive properties on storage was discussed in Vol. III, pp. 436–438.

#### Chemical Changes

Ammonium nitrate is usually slightly acid owing to the loss of ammonia leading to the presence of free nitric acid. This can possess a deteriorating effect on nitrate esters present in the explosive. It is therefore advisable to include neutralizing agents, such as CaCO₃ and Centralites (Vol. III, p. 645). The latter in proportion of 0.5%. Diphenylamine can be used only in mixtures without aromatic nitro compounds, as diphenylamine reacts with higher nitrated aromatics. Ammonium nitrate explosives with nitrate esters and dynamites are usually subjected to the Abel-test at 80°C to verify their stability [19].

Apart from the reaction of the decomposition of nitrate esters some other changes can occur in mixed explosives, such as the reaction of the oxidation of aluminium, particularly marked in water–gel explosives. Also permitted (permissible) explosives containing ion exchange mixtures of sodium nitrate with ammonium chloride a double exchange reaction can occur:

\[ \text{NaNO}_3 + \text{NH}_4\text{Cl} \rightleftharpoons \text{NaCl} + \text{NH}_4\text{NO}_3 \]

The reaction is reversible and ammonium nitrate can react with sodium chloride.

All the above considerations lead to imposing a limited storage time on mining explosives. In Poland ammonium nitrate permitted explosives should be used within 1½–3 months from the production date. Non-permitted ammonites
and dynamites 2–4 months. In the U.S.S.R. ammonium nitrate explosives in cartridges should be used within 3 months.

RATE OF DETONATION AND CRITICAL DIAMETER

As is well known the rate of detonation of explosives depends on the density and diameter of cartridges. Figure 89 gives the rate of detonation against the diameter of cartridges of some mining explosives according to Cybulski [4].

![Graph showing rate of detonation vs. diameter of cartridges](image)

**FIG. 89.** Rate of detonation of typical mining explosives against diameter of cartridges [4].

Below a certain diameter detonation is not propagated. A definition of the critical diameter is as follows. The critical diameter is larger when the cartridges detonate in the open, and smaller when confined in metal tubes. Table 80 gives the figures according to Cybulski [4].

As is known, the rate of detonation depends on the confinement of the charges. Cybulski [4] gives some data collected in Table 81.

"GAP TEST" (TRANSMISSION OF DETONATION)

The gap test values depend, among different factors, on the density (see Vol. III, p. 436, Fig. 144), diameter (Table 82) and confinement (Table 83).
Gap Test and Temperature

The gap test depends on the temperature of explosives. Thus for a permitted explosive with 10% nitroglycerine-nitroglycerol the gap was found to be 5 cm at -10°C, 6 cm at 0°C, 8 cm at 10°C and 10 cm at 20°C (see Dubnov et al. [6]).

A remarkable difference exists between the gap test in the open and in a mortar with the chlorate explosive Miedzianit. When initiated in open space with detonator No. 8 the detonation died away 7–10 cm beyond the detonator. On the contrary, in a mortar, no limit was found owing to the short borehole.

The problem of the cause of such a difference between ammonium nitrate and chlorate explosive has not been examined but certainly merits a special study.

Potassium chlorate is no longer used in explosives and is limited only to pyrotechnic compositions and match-head formulation [21]. Sodium chlorate is produced to manufacture chlorine dioxide as a bleaching agent of wood pulp and cellulose fibres.

The transmission distance of picric acid charges was examined by Burtlot [22]. This is however outside the scope of the present book. Also the method of determining the transmission detonation through an inert solid medium, such as a number of card-boards ('card-gap test') [116, 117], cellulose acetate [121, 122] or Plexiglas layer is discussed in the literature on the theory of detonation, for example [34].

CHANNEL EFFECT

T. Urbański in 1926 [20] described the phenomenon currently known as channel effect (Vol. III, pp. 435–436). He found that several ammonium nitrate explosives in a steel tube produce a shock wave which moves at a velocity higher than the detonation wave. This is summarized in Table 84.

The author observed that in a long bore-hole 'end' cartridges can be compressed to a high density ('dead pressed') which detonate with difficulty.

<table>
<thead>
<tr>
<th>TABLE 84. Shock wave in open space and in a steel tube.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation with detonator No. 8 according to T. Urbański [20, 33]. Explosive Bradyt F (see Table 83), cartridge 30 mm diameter</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Detonation velocity m/s</th>
<th>In the open</th>
<th>In a steel-tube 35/42 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2740</td>
<td>3220</td>
</tr>
<tr>
<td>Shock-wave m/s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–50 mm</td>
<td>1815</td>
<td>–</td>
</tr>
<tr>
<td>50–100 mm</td>
<td>560</td>
<td>3830</td>
</tr>
</tbody>
</table>

An unfavourable opinion of this work was given in [23]. The phenomenon was described in 1965 by Ahrens [24], Woodhead and Titman [25], and by Johansson and Persson [26]. Tribute was paid to the priority of the author of the present book by Golbinder, Svetlova and Tyshievich [27]. The latter authors contributed a considerable number of experimental facts on channel effect.

POSSIBLE SPIRAL WAY AND DETONATION OF MIXED EXPLOSIVES

Photographs of the detonation of ammonium nitrate explosives with an open lens camera were taken by T. Urbański [28]. The image was composed of light and dark bands with a sinusoidal shape. An hypothesis was advanced by the author of the possible spiral way of the detonation. At the same period British authors — Campbell, Bone et al. [29, 30] published a number of papers in which they indicated the spiral way of the propagation of detonation of gas mixtures. Their results were substantiated by Laffite et al. [31].

T. Urbański continued his experiments with a camera giving images at 10⁻⁴ s intervals [32].

The conclusion was [33] that only mixed explosives, for example ammonium nitrate — TNT give the described pattern.

The latter fact was also observed by P. A. Persson and G. Persson [34] and they claimed that the pattern on the photographs was due to glass cracking. An argument against such a suggestion is that if a glass-tube is filled with an homogeneous explosive, for example TNT, Picric Acid or PETN, no sinusoidal pattern is observed, although the cracking is the same.

Another experiment by T. Urbański [33, 34] throws some light on the detonation of explosives, if the detonation was carried out in a plastic tube put concentrically inside another tube made of glass and suspended in air (Fig. 90). If the inner tube was filled with homogeneous explosive not a mixture, the inner tube remained undamaged after the detonation. If the inner tube is filled with a mixture (e.g. NH₄NO₃ and TNT) the inner tube was covered with holes (Fig. 91).

The success of the experiment depends on the choice of the correct dimensions of the outer (glass) and inner (plastic) tube.

The fact that the inner tube filled with mixtures is perforated indicates that

FIG. 90. Detonation in two concentric tubes: T — outer glass tube, 1 — inner celluloid tube filled with an explosive, D — detonator [32, 33].
the two solid phases forming an explosive mixture do not detonate simultaneously and this fact has some bearing on the pattern seen in the photograph.

It should also be recalled that the slow explosion of nitroglycerine can manifest a spiral mode of propagation [35].

DEFLAGRATION OF EXPLOSIVES IN COAL-MINES (Vol. III, p. 417)

The deflagration of explosives in coal mines was examined for the first time by Audibert and Delmas [36] and independently by Cybulski (Vol. III, p. 418) and showed that the decisive factor is the admixture of coal-dust to the explosive, particularly in the vicinity of the detonator. Explosives containing nitroglycerine are more liable to deflagration and particularly chlorate explosives can create such a danger.

The problem of deflagration of ammonium nitrate explosives was extensively investigated by Andreev and co-workers [37]. Their conclusion was that the presence of wood meal increases the ability of such explosives to deflagrate and reduces the critical diameter of burning. Also the replacement of $\text{NH}_4\text{NO}_3 + \text{NaCl}$ by $\text{NaNO}_3 + \text{NH}_4\text{Cl}$ (Vol. III, p. 421) in mixtures containing TNT and nitroglycerine slightly increased the ability to deflagrate. Andreev and Glazkova [38] found that the ammonium nitrate/TNT mixture 80/20 burned faster under the action of the addition of potassium nitrate or potassium perchlorate. Further experiments by Glazkova and Zhadan [39] suggested replacement of ammonium chloride by ammonium oxalate.

According to Dubnov [6] the conditions of shot-firing which lead to a deflagration of mining explosives were recently established by Galadzhil and co-workers [40, 41], Dubnov and Romanov [42]. In principle deflagration can occur when the gap between cartridges is larger than that required to produce the detonation. Thus Dubnov and Romanov [42] describe three gap regions:

(a) transmitting the detonation,
(b) producing the deflagration,
(c) refusing any action.

This is depicted in Fig. 92 based on experiments [6].

![Fig. 92: Experimental curves of the probability $p$ of detonation (1), burning (2) and no reaction (3) of a passive cartridge of cyclonite (dia. 35 mm, density $\rho = 1.2$) as a function of the distance $L$ cm from the active cartridge of TNT (dia. 35 mm, $\rho = 1.0$) according to Dubnov et al. [6].](image)

In the U.K. the ability of explosives to deflagrate is examined with the gap test by filling the gap with coal-dust.

The papers by Zimmermann [43] and Murray et al. [44] pointed out once more that the penetration of coal-dust into the explosive increases the danger of deflagration of the explosive. Further experiments on deflagration confirmed the influence of coal-dust on the ease of deflagration [102]. Some experiments were carried out to show the influence of deflagration on methane-air explosion [103].

EVALUATION OF THE STRENGTH OF MINING EXPLOSIVES

In addition to the laboratory methods which comprise mainly lead block expansion and the rate of detonation different methods of a more practical character are in use. Thus Cybulski [4] reported the method used in Poland which is essentially the method of bench firing and determining the burden which can be brought down by a charge of 200 g of explosive in a bore-hole of 80 cm length and stemming of 60 cm. This is presented in Fig. 93. In (a) the correct burden is shown and in (b) an overlarge burden is shown. The dimensions for a rock are referred to 200 g of Metanit D2 and stemming with lime.

Apart from such a practical method of determining the strength of explosives the following are the laboratory methods of examining the strength of explosives...
SAFETY AGAINST METHANE AND COAL-DUST

This problem was fully discussed in Vol. III, pp. 409–491. A few more recent items of information will be given here.

The modern testing gallery in India is presented in Fig. 94.

As mentioned previously the result obtained in a gallery depends on the mode of initiation.

In the usual test the detonator is inserted last into the cannon, this is called direct initiation. If the detonator is placed at the opposite end of the train of cartridges and is inserted first into the cannon the initiation is called inverse and the probability of ignition of a methane–air mixture is very high. Figure 95, illustrates the difference between direct and inverse initiation according to Taylor and Gay [52].

More severe tests, known as 'Break Tests', exist in the U.K. a description of which was given in Vol. III, p. 419, Fig. 140. Here is the description according to Fordham ([7], pp. 79–82).

The tests were devised in the United Kingdom for studying the safety of explosives intended for use in ripping, i.e. increasing the height of roadways in mines after the coal has been extracted. The extraction of coal relieves stresses in the surrounding rocks and is therefore liable to cause breaks which can contain methane–air mixtures.

Break Test 1 consists of a shot-hole in which a break occurred across the hole in the middle of the explosive charge. It is simulated by placing a train of explosive across the gap between two steel plates in a test gallery.

Break Test 2 consists of a break parallel to the shot-hole in such a way that half of the shot-hole is in one piece of rock and the remainder of the explosive in the space between the rocks. It is simulated by two parallel plates of which the lower is grooved as a bore-hole – Fig. 96.
The most severe of these is Break Test No. 2. In the U.S.S.R. a cannon spraying coal dust in quantity of 6 kg by means of a small (50 g) explosive charge. Coal dust of 400–600 g/m³ is formed and the shot of the examined explosive is fired 2–10 s after spraying the dust. The mechanism of the ignition of methane and coal-dust was summarized in diagram — Fig. 97 depicted by Cybulski [4].

Here three elements are shown of the projection from the mortar:
1. Shock wave,
2. Gas products of detonation,
3. Particles of the explosive mixture: undecomposed explosive, sodium chloride, metal parts of the detonator. Some of them are projected in front of the shock wave.

The necessity for standardization of gallery-tests as carried out in different countries has also arisen [109]. Gorol and Sobala [110] drew attention to their observation that the results against methane–air was a better practical criterion of the safety of explosives than the test against coal-dust.

The Theory of Safety Against Methane and Coal-Dust

The theoretical aspect of inhibition of explosions of methane–air and coal dust–air is mainly regarded from the view point of the action of alkali metals in flame and particularly on the action of potassium ion [53–55].

Ashton and Hayhurst [56] rationalized it in terms of collisional ionization and recombination of electrons with alkali metal ions in flame, for example:

$$M + X \rightarrow M^+ + e^- + X.$$  

Where X is a flame species.
AMMONIUM NITRATE–FUEL OIL MIXTURES (AN–FO)
(Vol. III, pp. 482, 508)

As described in Vol. III, p. 482 the cheapest ammonium nitrate explosives (AN–FO) were introduced in open cast mines. Diesel fuel-oil was used as a cheap combustible ingredient — originally in 1954 and eventually on a larger scale in 1960 in the U.S.A. [57, 72] and almost simultaneously in Canada, Scandinavia and Germany [58], Japan and in U.S.S.R. [59].

The following are figures on the use of AN–FO explosives in the U.S.A. in 1979 and 1980: over 1300 and nearly 1400 million pounds respectively. Their use was mainly in quarrying, non-metal mining and construction work [10].

An International Symposium on Mining Research took place in 1961 [60] and was partly dedicated to AN–FO explosives. Hino and Yokogawa [61] described the action of surfactants on the detonation ability of ammonium nitrate and its mixtures with coal tar in proportions 93.3/6.2. The addition of 0.5% of surfactant increased the detonation ability of the mixtures. Particularly effective were sodium dinaphthylmethane disulphonate, sodium laurylsulphonate and sodium dodecylbenzene sulphonate.

Grubb [62] drew attention to the importance of the intimacy of mixing ammonium nitrate with fuel oil by using fine and porous particles of ammonium nitrate. Clark et al. [63] described the use of micro-prilled ammonium nitrate of less than 20 mesh size. They found the AN–FO made of such ammonium nitrate can readily detonate but the rate of detonation is limited by characteristic low bulk density — the consequence of micro-prills.

The possible use of AN–FO explosives for underground work was described by Henning [64] and Bullock et al. [65]. The authors came to the conclusion that AN–FO can replace dynamite in blasting operations even in small diameter holes (e.g. 23 mm [64]). An important problem for underground work is fumes produced by AN–FO. This was investigated by Van Dolah et al. [66]. Their main conclusions are in agreement with general rules: the negative oxygen balance favours the formation of CO but does not reduce the amount of NO2. The positive balance appreciably increases the concentration of NO2. The strength of the primer also has an influence on the composition of the products. The concentration of oxides of nitrogen increased as the strength of the primer decreased.

According to Schiele [58] the maximum rate of detonation is with 5.5% diesel oil. Chatken, E. B. Cook and Ruhe [114] used the large closed gallery to examine both the rate of detonation of AN–FO and the composition of gaseous products. Figure 98 gives the rates of detonation of AN–FO made of prilled and powdered ammonium nitrate. Ammonium nitrate was catalysed by 4% of undisclosed catalyst. The formation of nitrogen oxides was favoured by inadequate initiation and propagation of detonation, as already known [115]. The rate of detonation against the diameter of cartridges is changing as depicted in Fig. 99.

![Graph](image-url)  
FIG. 98. Rate of detonation of AN–FO (with prilled and powdered AN) as a function of the proportion of Diesel oil diameter 14 cm [114].

![Graph](image-url)  
FIG. 99. Rate of detonation of AN–FO as a function of bore-hole diameter (Schiele [58]).
EXPLOSIVE WORKING OF METALS

A low rate of detonation is required for most operations connected with explosive working of metals. It is usually achieved by mixing explosives marked for their ease of detonation (such as PETN, Cyclonite) with a relatively large quantity of such oxygen carriers as NaNO₃, KNO₃, Ba(NO₃)₂.

Plastic explosives are particularly suitable for the working of metals.

Most problems connected with explosive working of metals are outside the scope of the present book and the monograph [120] should be consulted.

MINING EXPLOSIVES USED IN VARIOUS COUNTRIES

Below are listed mining explosives used in some countries which complete the list given in Vol. III, pp. 446–489. In addition to the list a separate group is described:

Water gel (Slurries), p. 545.

Bulgaria

Bulgarian Permitted Explosives are characterized by the presence of potassium sulphate as the agent giving safety to methane and coal-dust [68]: Table 85.

TABLE 85. Bulgarian permitted explosives

<table>
<thead>
<tr>
<th>Components</th>
<th>Skalinit 1</th>
<th>Skalinit 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>69</td>
<td>64</td>
</tr>
<tr>
<td>KNO₃</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>TNT</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Charcoal</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

Oxygen balance % 1.37 +2.63
Heat of detonation (calculated) Kcal/kg 720 685
Calculated temperature of explosion °C 2295 2295
Rate of detonation m/s 3435 3200
Lead block cm³ 300 280
Gap test cm 4 3

Germany (Vol. III, p. 455)

German Permitted Explosives are, as before, divided into three classes. Their composition still remains undisclosed and the method of manufacture is kept secret.

Two main groups of Permitted Explosives are known: those made by Vasag-chemie Synthen GmbH: Wetter-Devonit A, Wetter-Roburit B, Wetter-Salit A,

COMMERCIAL (MINING) EXPLOSIVES


Their properties are collected in Meyer Dictionary [69].

Great Britain (Vol. III, p. 461)

Permitted explosives. The five groups of permitted explosives used in the U.K. are now called P explosives with numbers P1 to P5.

P1 Explosives should pass the following test [7]

(a) 26 shots fired of 142 g of explosive with inverse initiation, unstemmed should not give more than 13 ignitions of methane–air mixture
(b) 5 shots fired of 795 g with direct initiation, stemmed, should not ignite methane–air mixture
(c) 5 shots fired of 795 g with direct initiation stemmed, should not ignite coal dust–air mixture.

Their power should not be larger than 58–66% of blasting gelatine [7].

Polar Ajax and Polar Viking are typical representatives of this group of explosives (Vol. III, pp. 466 and 468 respectively).

One more explosive P1 should be mentioned: Hydrobel of the composition given in Table 86.

TABLE 86. British permitted explosives

<table>
<thead>
<tr>
<th>Components</th>
<th>Hydrobel (P1)</th>
<th>Explosives Unipreff (P3)</th>
<th>Carrifrax (P4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>20</td>
<td>53</td>
<td>10</td>
</tr>
<tr>
<td>NaN₃</td>
<td></td>
<td></td>
<td>46.5</td>
</tr>
<tr>
<td>Liquid nitrate esters</td>
<td>40</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Nitrocellulose</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaCl</td>
<td>27</td>
<td>29</td>
<td>-</td>
</tr>
<tr>
<td>NH₄SO₄</td>
<td>9.5</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Combustible (e.g. wood meal)</td>
<td>1</td>
<td>9.5</td>
<td>6</td>
</tr>
<tr>
<td>Others (e.g. hydrophobic compounds)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

P2 Explosives are sheathed explosives (Vol. III, p. 431).

They have been almost entirely withdrawn owing to the danger of breakage of the sheath and therefore loss of safety. According to Fordham [7] they have been superseded by P3 explosives.

P3 Explosives are so called Eg.S. explosives – Vol. III, p. 429. Currently these explosives should pass the following [7] test:
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

(a) 26 shots fired of 397 g with inverse initiation, unstemmed should not give more than 13 ignitions of methane–air mixture.
(b) 5 shots fired of 1020 g with direct initiation stemmed should not give an ignition of methane–air mixture.
(c) 5 shots fired of 567 g with inverse initiation unstemmed should not give an ignition of coal dust–air mixture.

Their power should not be higher than 42–50% of blasting gelatine. Unigel and Unigex are typical representatives of this group of explosives (Vol. III, p. 466).

One more explosive P3 should be mentioned: Unipur (Table 86).

P4 Explosives were designed for ripping with delay detonators. They should satisfy the following tests [7]:

(a) as with P3 explosives,
(b) 5 shots fired of the maximum permitted charge weight in Break Test I should not give an ignition of methane–air mixture.
(c) 26 shots are fired in Break Test II in a gas mixture of 3.6% propane with air and nitrogen which is more easily ignited than methane–air. Preliminary shots determine the most hazardous charge of explosive not exceeding 227 g. No more than 13 ignitions may occur.
(d) 5 shots of a cartridge of 30.5 cm long and 3.7 cm diameter are fired in Break Test III and no ignition should occur.

Carrifrax is the typical explosive P4 (Table 86).

P3 Explosives are designed for blasting solid coal with millisecond delay.

26 shots of 567 g are fired into methane–air mixture and no ignition should occur. In addition the explosives should pass the second (b) and third (c) test applied to P3 explosives.

Italy

Italian mining explosives are described in the Encyclopedia by Federoff, Sheffield and Kaye [70].

Four groups of explosives are listed.

(1) Mining explosives with nitroglycerine. These contain 43–77.5% nitroglycerine with colloidion cotton (1.5–5.0%) and oxygen carriers: NH₄NO₃, NaN₃ or KNO₃. An exception exists with 7.0% nitroglycerine, 0.8% colloidion cotton, 44% ammonium perchlorate, 32.2% sodium nitrate, 10% DNT, 5% TNT, 1% wood meal.

Another group consists of gelatinous explosives with 82.5–92% nitroglycerine and 5.5–8% colloidion cotton. The former contains sodium nitrate (8.5%) and wood meal (3%).

(2) Mining explosives with 4–14% nitroglycerine, and 0.1–1.5% colloidion cotton. A characteristic feature is the presence of a large quantity of ammonium picrate: 51–89% and one of the mixtures has 65% cyclonite.

(3) Mining explosives without nitroglycerine with ammonium nitrate and TNT. The aromatic nitro compounds are sometimes replaced with 10–30% PETN or Cyclonite. The names are: Ager, Vulcania, Vulcanite.

(4) Mining explosives with ground smokeless powder. These are mainly ballistic mixed with oxygen carriers, mainly ammonium nitrate.

Novel Mining Explosives used in Poland

As previously described (Vol. III, p. 475), mining explosives in Poland are divided into four groups:

I. Rock explosives (wrapped in red paper) (Tables 85–87)
II. Coal Explosives (Karbonits) (wrapped in blue paper)
III. Permitted explosives (Barbarits, Metanits) (in yellowish paper)
IV. Permitted special explosives (Special Metanits) (in yellowish paper with two black bands) (Tables 87–91).

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Saletrol A</th>
<th>Amonit Stainy I/II</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃ (grilled)</td>
<td>94.5</td>
<td>90</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>5.5</td>
<td>–</td>
</tr>
<tr>
<td>Petroleum tar</td>
<td>–</td>
<td>2</td>
</tr>
<tr>
<td>Wood meal</td>
<td>–</td>
<td>8</td>
</tr>
<tr>
<td>Oxygen balance %</td>
<td>0.0</td>
<td>+0.06</td>
</tr>
<tr>
<td>Lead block expansion cm³</td>
<td>205</td>
<td>235</td>
</tr>
<tr>
<td>Rate of detonation m/s</td>
<td>3560</td>
<td>2630</td>
</tr>
</tbody>
</table>

According to their composition they are marked with letters:

G — denotes the presence of glycol dinitrate ('nitroglycol'),

J — means that they are ion exchanging mixtures (Vol. III, p. 421) containing Na⁺NO₃⁻ + NH₄⁺Cl⁻ → Na⁺Cl⁻ + NH₄⁺NO₃⁻,

H — denotes hydrophobic properties of the ingredients, particularly that ammonium nitrate contains hydrophobic compounds, such as calcium stearate.

Most of the explosives described overleaf were introduced between 1975 and 1978.
### TABLE 88. Polish rock explosives (Amonits)

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>6 G</th>
<th>11</th>
<th>11 G</th>
<th>12 GH</th>
<th>14 GH</th>
<th>15 GH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>81</td>
<td>85</td>
<td>85</td>
<td>81.4</td>
<td>86.5</td>
<td>82</td>
</tr>
<tr>
<td>Nitroglycerin</td>
<td>2</td>
<td>5.5</td>
<td>2.75</td>
<td>3.5</td>
<td>2.25</td>
<td>2.88</td>
</tr>
<tr>
<td>Nitroglycol</td>
<td>2</td>
<td>-</td>
<td>2.75</td>
<td>3.5</td>
<td>2.25</td>
<td>2.87</td>
</tr>
<tr>
<td>DNT</td>
<td>-</td>
<td>1.5</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TNT</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Petroleum tar</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
<td>1.25</td>
<td>-</td>
</tr>
<tr>
<td>Wood meal</td>
<td>2</td>
<td>7.5</td>
<td>7.5</td>
<td>2</td>
<td>7.2</td>
<td>4</td>
</tr>
<tr>
<td>Al</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Ca Stearate</td>
<td>-</td>
<td>0.15*</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen balance %0</td>
<td>+3.35</td>
<td>+3.97</td>
<td>+4.61</td>
<td>+4.92</td>
<td>+4.20</td>
<td>+0.85</td>
</tr>
<tr>
<td>Lead block expansion cm³</td>
<td>420</td>
<td>330</td>
<td>310</td>
<td>370</td>
<td>315</td>
<td>400</td>
</tr>
<tr>
<td>Rate of detonation m/s</td>
<td>3030</td>
<td>2480</td>
<td>2000</td>
<td>3000</td>
<td>2600</td>
<td>2800</td>
</tr>
<tr>
<td>Gap test cm</td>
<td>13</td>
<td>9</td>
<td>5</td>
<td>14</td>
<td>4</td>
<td>8</td>
</tr>
</tbody>
</table>

* Over 100%

### TABLE 89. Polish rock explosives (Dynamites)

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>3 GH</th>
<th>5 GH</th>
<th>5 G1</th>
<th>5 G3</th>
<th>8 GH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>47.9</td>
<td>50</td>
<td>50</td>
<td>47.4</td>
<td></td>
</tr>
<tr>
<td>NaNO₃</td>
<td>-</td>
<td>14.8</td>
<td>15.5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>22.5</td>
<td>11</td>
<td>11.5</td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td>Nitroglycol</td>
<td>22.5</td>
<td>11</td>
<td>11.5</td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td>DNT</td>
<td>2</td>
<td>4</td>
<td>10</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>TNT</td>
<td>-</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Collodion cotton</td>
<td>2</td>
<td>0.8</td>
<td>1.0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Wood meal</td>
<td>3</td>
<td>1</td>
<td>0.5</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Ca Stearate</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Glycol</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Oxygen balance %0</td>
<td>+43.5</td>
<td>+45.87</td>
<td>+45.3</td>
<td>+2.02</td>
<td></td>
</tr>
<tr>
<td>Lead block expansion cm³</td>
<td>430</td>
<td>320</td>
<td>320</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>Rate of detonation m/s</td>
<td>2370</td>
<td>2120</td>
<td>2800</td>
<td>2200</td>
<td></td>
</tr>
<tr>
<td>Gap test cm</td>
<td>7</td>
<td>6</td>
<td>8</td>
<td>11</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 90. Polish coal and permitted explosives (Karbonits and Metanits respectively)

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Karbonit węglowy D6G</th>
<th>Metanit powietrzny D5G</th>
<th>W2A</th>
<th>Metanit powietrzny specjalny J1</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>77</td>
<td>63.5</td>
<td>56</td>
<td>-</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>-</td>
<td>2</td>
<td>2.5</td>
<td>53.8</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>4</td>
<td>2</td>
<td>2.5</td>
<td>7.8</td>
</tr>
<tr>
<td>Nitroglycol</td>
<td>4</td>
<td>2</td>
<td>2.5</td>
<td>2.2</td>
</tr>
<tr>
<td>DNT</td>
<td>5</td>
<td>3.5</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Wood meal</td>
<td>3.5</td>
<td>3</td>
<td>4</td>
<td>2.2</td>
</tr>
<tr>
<td>NaCl</td>
<td>10.5</td>
<td>26</td>
<td>25</td>
<td>34</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>Soot</td>
<td>0.1*</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dyestuff</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen balance %0</td>
<td>+4.5</td>
<td>+4.96</td>
<td>40.4</td>
<td>47.55</td>
</tr>
<tr>
<td>Lead block expansion cm³</td>
<td>265</td>
<td>200</td>
<td>180</td>
<td>100</td>
</tr>
<tr>
<td>Rate of detonation m/s</td>
<td>2150</td>
<td>2035</td>
<td>1900</td>
<td>1700</td>
</tr>
<tr>
<td>Gap test cm</td>
<td>7</td>
<td>4-6</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>

* Over 100%

### TABLE 91. Polish permitted explosives (Dynamite type)

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>FGH</th>
<th>Barbarat FGH 2</th>
<th>KG</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>14.2</td>
<td>12.2</td>
<td>15</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>-</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>26.5</td>
<td>28</td>
<td>11</td>
</tr>
<tr>
<td>Nitroglycol</td>
<td>7.3</td>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>Collodion cotton</td>
<td>0.5</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>NaCl</td>
<td>40</td>
<td>43</td>
<td>34.5</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>-</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>BaSO₄</td>
<td>10</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.3</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
</tr>
<tr>
<td>Oxygen balance %0</td>
<td>+2.15</td>
<td>+1.8</td>
<td>+3.56</td>
</tr>
<tr>
<td>Lead block cm³</td>
<td>175</td>
<td>160</td>
<td>130</td>
</tr>
<tr>
<td>Rate of detonation m/s</td>
<td>2250</td>
<td>2000</td>
<td>2150</td>
</tr>
<tr>
<td>Gap test cm</td>
<td>12</td>
<td>4-5</td>
<td>4-5</td>
</tr>
</tbody>
</table>
Spain

According to Fedoroff and Sheffield [71] original types of explosives were developed during World War II by Otto-lauchits. Esplosivo F.E.1, F.E.2 and F.E.3.

They were composed of 65–70% $\text{NH}_4\text{NO}_3$, 17–25% TNT and 10–15% $\text{Na}_2\text{HPO}_4+\text{H}_2\text{O}$.

Sweden

A few AN—FO Type explosives used in Sweden are given in Table 92 [67].

<table>
<thead>
<tr>
<th>Components</th>
<th>AN—FO—0</th>
<th>AF—FO—2</th>
<th>AN—FO—4</th>
<th>AN—FO—8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_4\text{NO}_3$</td>
<td>94.5</td>
<td>92.9</td>
<td>91.4</td>
<td>88.2</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>5.5</td>
<td>5.1</td>
<td>4.6</td>
<td>3.8</td>
</tr>
<tr>
<td>Al</td>
<td>–</td>
<td>2.0</td>
<td>4.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>


Mining explosives in U.S.S.R. are divided into six groups.

I. For open cast work: Akvatols, Igdanit (AN—FO), TNT, TNT + Al (Table 93).

II. For open-cast and underground work, where no dangerous coal-dust and methane are present (Tables 94, 95).

III. Permitted explosives safe to methane but not for coal mines. (Table 96).

IV. Permitted explosives safe to methane and coal-dust (Table 96).

V. High safety permitted explosives (Table 97).

VI. Highest safety permitted explosives in particularly dangerous coal mines (Table 97).

Ammonit and ammonals. These are used in cartridges of 32 and 90 mm diameter. Most popular is Ammonit 6Zh V with ammonium nitrate protected by fatty acids and iron salts.

Some of the most popular compositions are given in Table 94.

The density of the explosives is comprised between 0.95 and 1.15 Ammonit Skalnyi No. 1 is also manufactured in compressed cartridges of density 1.43–1.53.

A modification of Ammonit are Zemogranulits. They contain ammonium nitrate in prills mixed with molten TNT. Those with a negative oxygen balance are used obviously in open-cast work only. Thanks to a high TNT content they are relatively hydrophobic. Some of Zemogranulits are described in Table 95.

### Table 93. AN—FO type explosives used in U.S.S.R. [6]

<table>
<thead>
<tr>
<th></th>
<th>Dynamo</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_4\text{NO}_3$</td>
<td>87.7</td>
<td>89.4</td>
<td>91.8</td>
<td>92.8</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>2.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Diesel Oil</td>
<td>–</td>
<td>3</td>
<td>4.2</td>
<td>4</td>
</tr>
<tr>
<td>Al</td>
<td>10</td>
<td>8</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>Wood meal</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3</td>
</tr>
<tr>
<td>Oxygen balance</td>
<td>60.25</td>
<td>60.34</td>
<td>60.41</td>
<td>60.06</td>
</tr>
<tr>
<td>Heat of deto</td>
<td>1295</td>
<td>1240</td>
<td>1080</td>
<td>915</td>
</tr>
<tr>
<td>Volume of gases</td>
<td>800</td>
<td>845</td>
<td>910</td>
<td>985</td>
</tr>
<tr>
<td>Lead block cm$^3$</td>
<td>425</td>
<td>460</td>
<td>430</td>
<td>390</td>
</tr>
<tr>
<td>Rate of deto m/s</td>
<td>1–1.3</td>
<td>3000 – 3600</td>
<td>2600 – 3200</td>
<td>2400 – 3200</td>
</tr>
<tr>
<td>40 mm dia. in steel 10 g booster</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>2–3</td>
</tr>
</tbody>
</table>

Dynamon AM–10 differs from Dynamon AM–10 by a lower aluminium and higher mineral oil content: 8% and 3% respectively.

The density is comprised between 0.80 and 0.95.

Permitted explosives are described in Tables 96 and 97.

Detonits and dynamites. Detonits are rock explosives used in the U.S.S.R. which contain 6–15% nitroglycerine and nitroglycol. Particularly popular is Detonit M of the composition:

- $\text{NH}_4\text{NO}_3$ mark ZhV 78% (hydrophobic)
- Low freezing nitrate esters 10%
- Collodion cotton 0.3%
- Al 10.7% and Ca or Zn stearate in addition (over 100%) – 1%.

Oxygen balance is +0.18%, lead block expansion 460–500 cm$^3$, rate of detonation in cartridges of
### TABLE 94. Ammonium nitrate explosives in U.S.S.R. [6]

<table>
<thead>
<tr>
<th>Components</th>
<th>Ammonit (rock) No. 6 ZhV</th>
<th>Ammonit (rock) No. 10 ZhV</th>
<th>Ammonal VA-4</th>
<th>Skalayi No. 1</th>
<th>Skalayi No. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃ (hydrophobic)</td>
<td>79</td>
<td>85</td>
<td>80.5</td>
<td>66</td>
<td>72</td>
</tr>
<tr>
<td>TNT</td>
<td>21</td>
<td>8</td>
<td>15</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Wood meal</td>
<td>-</td>
<td>7</td>
<td>-</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>-</td>
<td>4.5</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Cyclonite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>24</td>
<td>15</td>
</tr>
<tr>
<td>Oxygen balance</td>
<td>0.42%</td>
<td>1.53%</td>
<td>40.18</td>
<td>-0.79</td>
<td>-0.78</td>
</tr>
<tr>
<td>Lead block expansion cm³</td>
<td>360–380</td>
<td>300–320</td>
<td>440–460</td>
<td>450–480</td>
<td>470–500</td>
</tr>
<tr>
<td>Rate of detonation m/s</td>
<td>3600–4800</td>
<td>3200–3600</td>
<td>4000–4500</td>
<td>4800–5300</td>
<td>4000–4500</td>
</tr>
<tr>
<td>Critical diameter in open mm</td>
<td>10–13</td>
<td>15–20</td>
<td>12–14</td>
<td>5–6</td>
<td>8–10</td>
</tr>
<tr>
<td>Gap test cm for diameter 32 mm</td>
<td>3–6</td>
<td>2–5</td>
<td>5–8</td>
<td>10–14</td>
<td>8–12</td>
</tr>
</tbody>
</table>

### TABLE 95. Zernogranulits and Grammonals in U.S.S.R. [6]

<table>
<thead>
<tr>
<th>Components</th>
<th>Zernogranulits 50/30–V</th>
<th>Grammonals A-8</th>
<th>A-45</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>79</td>
<td>50/30</td>
<td>40</td>
</tr>
<tr>
<td>TNT</td>
<td>21</td>
<td>50/30</td>
<td>45</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>50/30</td>
<td>15</td>
</tr>
<tr>
<td>Oxygen balance</td>
<td>0.45</td>
<td>-27.15</td>
<td>-45.9</td>
</tr>
<tr>
<td>Lead block expansion cm³</td>
<td>360–370</td>
<td>330–340</td>
<td>420–440</td>
</tr>
<tr>
<td>Rate of detonation m/s</td>
<td>3000–3600</td>
<td>3600–4200</td>
<td>3800–5000</td>
</tr>
<tr>
<td>Critical diameter in open mm</td>
<td>50–60</td>
<td>40–60</td>
<td>30–40</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Components</th>
<th>Ammonit AP-4zhV</th>
<th>Ammonit AP-5zhV</th>
<th>Poliet VP-4</th>
<th>PZHv-20</th>
<th>T-19</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃ ZhV</td>
<td>68</td>
<td>70</td>
<td>65.5</td>
<td>64</td>
<td>61</td>
</tr>
<tr>
<td>TNT</td>
<td>17</td>
<td>18</td>
<td>12</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>Nitrate esters</td>
<td>-</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wood meal</td>
<td>-</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaCl or (KCl)</td>
<td>15</td>
<td>12</td>
<td>12</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Oxygen balance</td>
<td>+0.45</td>
<td>+0.16</td>
<td>+0.48</td>
<td>+0.4</td>
<td>-2.47</td>
</tr>
<tr>
<td>Rate of detonation m/s</td>
<td>3600–4200</td>
<td>3600–4600</td>
<td>3800–4600</td>
<td>3500–4000</td>
<td>3600–4300</td>
</tr>
<tr>
<td>Critical diameter after 1 hr in water</td>
<td>5–10</td>
<td>5–10</td>
<td>6–25</td>
<td>5–10</td>
<td>5–10</td>
</tr>
<tr>
<td>Density</td>
<td>1.0–1.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

They do not ignite methane when 600 g fired with stemming of 1 cm. Class IV: in addition they do not ignite coal dust when 700 g fired without stemming.

### TABLE 97. Permitted, Class V and VI [6]

<table>
<thead>
<tr>
<th>Components</th>
<th>Ugelinit E-6</th>
<th>Class V Selectivit granulated</th>
<th>Ugelinit No. 5</th>
<th>Class VI Ugelinit No. 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃ ZhV</td>
<td>66.5</td>
<td>14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaNO₃ or (KNO₃)</td>
<td>46.2</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Nitrate esters</td>
<td>14.2</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Wood meal</td>
<td>2.5</td>
<td>8.5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>NaCl or (KCl)</td>
<td>16</td>
<td>15</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>29</td>
<td>-</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>Steinates</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diatomite or PCV</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oxygen balance</td>
<td>+0.53</td>
<td>-0.22</td>
<td>+0.13</td>
<td>+4.94</td>
</tr>
<tr>
<td>Lead block expansion cm³</td>
<td>130–170</td>
<td>220–240</td>
<td>60–90</td>
<td>100–120</td>
</tr>
<tr>
<td>Rate of detonation m/s</td>
<td>1900–2200</td>
<td>1800–2000</td>
<td>1750–1900</td>
<td>1600–1800</td>
</tr>
<tr>
<td>Gap test cm diameter 36 mm</td>
<td>5–10</td>
<td>5–7</td>
<td>3–10</td>
<td>3–10</td>
</tr>
</tbody>
</table>

They do not ignite methane when the cartridge of 200 g of Ugelinit E 6 or Selectivit is suspended in experimental gallery.

The same with cartridges of: Ugelinit No. 5 (500 g) and Ugelinit No. 7 (1000 g).
24 mm diameter 3900–4300 m/s
32 mm diameter 4800–5000 m/s.
Critical diameter (in open) 8–10 mm
Gap test: 24 mm diameter 6–12 cm and
32 mm diameter 16–22 cm.

After keeping under water the figures are 4–8 cm and 10–15 cm respectively.

Density 1.1–1.3.

Dynamites which contain a higher proportion of nitrate esters, for example 62% are very little used in U.S.S.R. and form only 0.2–0.3% of the total production of explosives. The main objection is low shelf life and misfiring which have produced a number of accidents.

Permitted in Sulphur Mines and Oil Fields

In sulphur mines Sulphur Ammonit No. 1 ZhV and in oil fields Neftyanoi Ammonit No. 3 are used. Their properties were given in Vol. III, pp. 488–489 and the composition is given below (Table 98).

<table>
<thead>
<tr>
<th>Components</th>
<th>Sulphur Ammonit No. 1 ZhV</th>
<th>Neftyanoi Ammonit No. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃, ZhV</td>
<td>52</td>
<td>52.5</td>
</tr>
<tr>
<td>TNT</td>
<td>11.5</td>
<td>7</td>
</tr>
<tr>
<td>Nitrate esters</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>Wood meal</td>
<td>1.5</td>
<td>–</td>
</tr>
<tr>
<td>KCl</td>
<td>–</td>
<td>30</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>30</td>
<td>–</td>
</tr>
<tr>
<td>Stearates</td>
<td>–</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Oxygen balance %
-1.0
Lead block expansion cm³
200–220
Rate of detonation m/s
2500–3000
Gap test: cm
5–10
after storage in water for 1 hour
3–7
Ignition test in an experimental gallery
400 g in a mortar does not ignite sulfur dust suspension
400 g in a mortar does not ignite methane with petroleum vapor


Recent information about some Japanese mining explosives are given in Tables 99–104.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Sakura dynamite</th>
<th>Tokuguri dynamite</th>
<th>Explosives No. 3 Kiri dynamite</th>
<th>No. 2 Enoki dynamite</th>
<th>Akatsuki dynamite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroglycerine/nitroglycerine mixture 60/40 stabilized with nitrocellulose</td>
<td>48–55</td>
<td>35–54</td>
<td>18–24</td>
<td>20–27</td>
<td>5–20</td>
</tr>
<tr>
<td>Nitro Compounds (DNT, DNX, TNT)</td>
<td>–</td>
<td>–</td>
<td>0–9</td>
<td>2–9</td>
<td>0–10</td>
</tr>
<tr>
<td>NH₄NO₃ and sodium nitrate</td>
<td>34–42</td>
<td>39–60</td>
<td>65–75</td>
<td>50–72</td>
<td>60–85</td>
</tr>
<tr>
<td>Sawdust</td>
<td>8–12</td>
<td>2–8</td>
<td>1–11</td>
<td>4–8</td>
<td>1–5</td>
</tr>
</tbody>
</table>

Properties
Density
1.45–1.55
1.40–1.50
1.30–1.45
1.30–1.45
1.25–1.45
Lead block cm³
320–360
430–480
380–430
270–340
370–430
Detonation velocity m/s
5500–6100
6500–7200
5800–6500
5800–6500
5000–5500
Gap test
as the multiple of charge diameter
5–7
6–8
4–6
4–6
2–6

† For open-pit work

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>No. 1 Toku-Ume dynamite</th>
<th>No. 3 Shiza-Ume dynamite</th>
<th>No. 3 Toku-Shiraume dynamite</th>
<th>EqS Bakuyaku</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate esters</td>
<td>18–23</td>
<td>18.7</td>
<td>18–20</td>
<td>9–12</td>
</tr>
<tr>
<td>(as in Table 99)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Nitro Compounds (as in Table 99)</td>
<td>4–8</td>
<td>3.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Inorganic nitrates (ammonium, sodium potassium)</td>
<td>50–55</td>
<td>49.5</td>
<td>50–46</td>
<td>50–55</td>
</tr>
<tr>
<td>Sawdust</td>
<td>1–3</td>
<td>3.8</td>
<td>2–4</td>
<td>5–10</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>20–26</td>
<td>25.0</td>
<td>25–27</td>
<td>30–34</td>
</tr>
</tbody>
</table>

Properties
Density
1.35
1.40
1.35–1.45
0.95–1.05
Lead block cm³
290–310
280–300
300–320
170–230
Detonation velocity m/s
5500–6000
5500–6000
5500–5800
2700–3300
Gap test (as in Table 99)
5–7
5–7
5–7
3–6
### TABLE 101. Japanese permitted explosives containing less than 7% of or no nitrate esters

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>No. 5 Shouann-Bakuyaku</th>
<th>G Shouann-Bakuyaku</th>
<th>Explosives No. 105 Shouann-Bakuyaku</th>
<th>No. 2 Kurotaka Shouann-Bakuyaku</th>
<th>EqS-1 Bakuyaku</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate esters (as in Table 99)</td>
<td>-</td>
<td>6.2</td>
<td>5-6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nitro compounds (as in Table 99)</td>
<td>5-8</td>
<td>-</td>
<td>-</td>
<td>4-6</td>
<td>5-7</td>
</tr>
<tr>
<td>Inorganic nitrates (as in Table 99)</td>
<td>75-80</td>
<td>69.8</td>
<td>67-73</td>
<td>76-80</td>
<td>63-71</td>
</tr>
<tr>
<td>Sawdust</td>
<td>4-6</td>
<td>9.0</td>
<td>6-11</td>
<td>4-7</td>
<td>10-14</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>11-13</td>
<td>15.0</td>
<td>14-16</td>
<td>4-7</td>
<td>25-30</td>
</tr>
<tr>
<td><strong>Properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>1.0</td>
<td>1.0</td>
<td>0.95-1.05</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Lead block cm³</td>
<td>270-290</td>
<td>280-300</td>
<td>280-300</td>
<td>270-290</td>
<td>205-215</td>
</tr>
<tr>
<td>Detonation velocity m/s</td>
<td>4500-5000</td>
<td>3300-3800</td>
<td>3400-3600</td>
<td>4500-5000</td>
<td>3000-3500</td>
</tr>
<tr>
<td>Gap test (Table 99)</td>
<td>2-4</td>
<td>3-5</td>
<td>3-5</td>
<td>3-5</td>
<td>&gt;2</td>
</tr>
</tbody>
</table>

### TABLE 102. Japanese perchlorate explosives

(Vol. III, p. 474, Table 136)

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>No. 5 Kuro Carlit</th>
<th>Carlit Explosives</th>
<th>Ao Carlit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium perchlorate</td>
<td>73-78</td>
<td>22-27</td>
<td>17-22</td>
</tr>
<tr>
<td>Nitro Compounds</td>
<td>-</td>
<td>2-7</td>
<td>2-7</td>
</tr>
<tr>
<td>Inorganic Nitrates</td>
<td>-</td>
<td>60-70</td>
<td>60-70</td>
</tr>
<tr>
<td>Sawdust</td>
<td>6-11</td>
<td>8-13</td>
<td>8-13</td>
</tr>
<tr>
<td>Pero-Silicon</td>
<td>13-18</td>
<td>2-7</td>
<td>2-7</td>
</tr>
<tr>
<td><strong>Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>1.10-1.15</td>
<td>1.10-1.15</td>
<td>1.05-1.10</td>
</tr>
<tr>
<td>Lead block cm³</td>
<td>440-470</td>
<td>390-440</td>
<td>380-440</td>
</tr>
<tr>
<td>Detonation velocity m/s</td>
<td>4000-4500</td>
<td>4000-4500</td>
<td>3700-4200</td>
</tr>
<tr>
<td>Gap test (Table 99)</td>
<td>4-6</td>
<td>3-5</td>
<td>3-5</td>
</tr>
</tbody>
</table>

* For open pit work.

### TABLE 103. Miscellaneous Japanese commercial explosives

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Urbanite</th>
<th>Explosives Dal Happa yo Bakuyaku</th>
<th>Akatsuki Bakuyaku</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate esters</td>
<td>50-54</td>
<td>5-7</td>
<td>-</td>
</tr>
<tr>
<td>Nitro compounds</td>
<td>2-6</td>
<td>10-15</td>
<td>6-8</td>
</tr>
<tr>
<td>Inorganic nitrates</td>
<td>36-44</td>
<td>75-78</td>
<td>81-84</td>
</tr>
<tr>
<td>Sawdust</td>
<td>2-6</td>
<td>3-6</td>
<td>6-8</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>-</td>
<td>2-4</td>
</tr>
<tr>
<td><strong>Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>1.30-1.40</td>
<td>0.98</td>
<td>1.0</td>
</tr>
<tr>
<td>Lead block cm³</td>
<td>420-470</td>
<td>380-400</td>
<td>380-400</td>
</tr>
<tr>
<td>Detonation velocity m/s</td>
<td>2000-2500</td>
<td>3800-4300</td>
<td>4400-4600</td>
</tr>
<tr>
<td>Gap test (Table 99)</td>
<td>6-8</td>
<td>-</td>
<td>2-3</td>
</tr>
<tr>
<td>Used in</td>
<td>Urban blasting</td>
<td>Large blasting</td>
<td>Open pit</td>
</tr>
</tbody>
</table>

### TABLE 104. Japanese ‘TNT commercial’ explosives

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>No. 2 Kohuzumite</th>
<th>Explosives No. 12 Kohuzumite</th>
<th>No. 31A Kohuzumite*</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>15-30</td>
<td>6-15</td>
<td>100</td>
</tr>
<tr>
<td>RDX</td>
<td>0-10</td>
<td>11-20</td>
<td>-</td>
</tr>
<tr>
<td>Inorganic Nitrates</td>
<td>50-80</td>
<td>43-85</td>
<td>-</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>0-8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>0-5</td>
<td>0-6</td>
<td>-</td>
</tr>
<tr>
<td>Sawdust</td>
<td>0-15</td>
<td>1-3</td>
<td>-</td>
</tr>
<tr>
<td><strong>Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>1.10</td>
<td>1.03</td>
<td>1.12</td>
</tr>
<tr>
<td>Lead block cm³</td>
<td>450-480</td>
<td>380-400</td>
<td>310-350</td>
</tr>
<tr>
<td>Detonation velocity m/s</td>
<td>5300-5500</td>
<td>4800-5000</td>
<td>5500-5600</td>
</tr>
<tr>
<td>Gap test (Table 99)</td>
<td>5-6</td>
<td>4-5</td>
<td>-</td>
</tr>
</tbody>
</table>

* For open pit work.

**Belgium**

The composition of typical permitted explosives made in Belgium are given overleaf (Table 105), according to Goffart and Waterlot [119]. The explosives belong to ion exchange group with potassium or sodium nitrate and ammonium chloride.
## Table 105.

<table>
<thead>
<tr>
<th>Components</th>
<th>Charbrite 418</th>
<th>Explosives Charbrite 4/50</th>
<th>Kemioxide 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroglycerine and</td>
<td>9.5</td>
<td>9.5</td>
<td>12.0</td>
</tr>
<tr>
<td>Nitroglycerol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KNO₃</td>
<td>55.25</td>
<td>55.25</td>
<td></td>
</tr>
<tr>
<td>Na NO₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>30.0</td>
<td>28.0</td>
<td>48.0</td>
</tr>
<tr>
<td>Ammonium Oxalate</td>
<td></td>
<td></td>
<td>30.3</td>
</tr>
<tr>
<td>Hydrophobic compounds</td>
<td>2.25</td>
<td>2.25</td>
<td></td>
</tr>
<tr>
<td>Calcium stearate</td>
<td></td>
<td></td>
<td>0.35</td>
</tr>
<tr>
<td>Gahn</td>
<td></td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Cellulose</td>
<td></td>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td>Oxygen balance %</td>
<td>16%</td>
<td>+5.5%</td>
<td>+4.3%</td>
</tr>
</tbody>
</table>

### WATER—GEL (SLURRY) EXPLOSIVES

The last twenty years have shown a rapid increase in the use of Water—gel (Slurry) Explosives in commercial explosives.

The consumption of 2.5 millions of pounds in 1958 grew to over 460 and 400 millions of pounds in 1979 and 1980 respectively [10] in the U.S.A. They were originally used in metal mining (iron-ore open-pit operations) on a large scale, and until now metal mining, quarrying and non-metal mining remain the main consumers of water—gel explosives.

Two excellent reviews have appeared on the earlier history [72, 73] and recent development of slurry (water—gel) explosives [74].

### History

Abel as early as 1874 [75], Kast [76] and T. Urbaniński et al. [77, 78] proved that the presence of water in high explosives increased the rate of detonation (see Fig. 43 and Tables 50 and 62). This found limited practical application in the use of nitroglycerol with water in demolition cartridges [75, 76]. Streng and Kirshenbaum [79] obtained a patent for an explosive composed of ammonium nitrate aqueous solution with aluminium powder. In Sweden Wetterholm et al. [80] obtained a patent in 1957 which claimed: ‘an oxygen balanced plastic safety explosive characterized by its main ingredients being 20—45% of a high velocity, high brisant explosive, oxygen delivering inorganic salts mixed in a gel of water and a hydropholic colloid with an amount of water between 3—25%’. The explosive 'Securi' contained 34% DITEU (N,N-bis-β, β-trinitroethyl) urea (Chapter VIII, p. 247) 54% NH₄NO₃ and Ca(NO₃)₂, 0.8% rice starch, 5.2% glycol and 6.5% water. The explosive showed the rate of detonation 6100 m/s, gap test of diameter, 25 mm was 4—5 cm, critical diameter in a glass tube was 11 mm. Industrial manufacture was not fulfilled (1950) owing to the introduction of the successful AN—FO explosives.

On the contrary, in the United States the ‘slurry explosives’ developed by Cook [81, 82] and tested in the Iron Ore Co., in Canada in 1957 was quickly accepted in open pit work. The original composition by Cook and Farnam [81] was 25% coarse TNT, 55% NH₄NO₃ or NH₂NO₃ (35—45%) and NaNO₃ (10—20%) 20% H₂O with added guar gum as a thickening agent. The addition of the thickening agent was a considerable improvement as it prevented segregation of the ingredients. Guar gum is a polysaccharide: galacto-mannan [83].

Also another patent appeared at the same time by Harde and Bjork [84] who used aluminium powder as a sensitizer (instead of TNT).

It was soon recognized that the presence of tiny air-bubbles in the slurry was a very good sensitizer. The bubbles adhere to TNT particles or Al powder and help detonation by creating hot spots by adiabatic compression.

Another kind of early slurry was that developed by Gehrig of Atlas Chemical Industries [85]. It consisted of a saturated solution of ammonium nitrate in nitric acid of 60—70% HNO₃ and some organic substances which are not attacked by nitric acid, for example, vinyl polymers. However handling of the solution with nitric acid is difficult and can be dangerous. A fire occurred in a factory in Rourkela (India) in 1972 through spilling nitric acid slurry on wooden boards [86].

The advantages of slurry explosives were summarized by Mahadevan [74] as below:

1. By dissolution, water brings the ingredients into close contact with each other.
2. It provides a continuous medium through which a detonation wave passes.
3. It desensitizes the explosive against fire, sparks, impact and friction thereby decreasing hazards associated with storage and handling.
4. Water is believed to increase the energy of the explosive by taking part in the reaction at the time of explosion especially when Al is present in the composition.
5. It affects the products of detonation and suppresses the formation of toxic gases: carbon monoxide and oxides of nitrogen.
6. It has a pronounced effect on the ‘Coke Oven’ reaction 2 CO → C + CO₂ which is very important in preventing dissociation of energetic products of detonation such as H₂O and CO₂.
7. Low percentage of water presents problems on storage: the explosive becomes hard and grainy due to the crystallization of inorganic oxidizer salts on the contrary a higher percentage of water decreases the sensitivity as well as the strength. According to Cook, 1% increase in water lowers the strength of the slurry by ca. 1.7%. Thus an optimum percentage of water is in the range of 8—20%.
8. Water acts as a coolant and offers a perspective of using water—gel explosives in underground gassy coal mines.
Cross-linking Agents

One of the drawbacks of early compositions was the low viscosity of the solution and hence the ease of segregation and loss of air-bubbles. A deterioration in performance was observed on storage. A significant achievement consisted in increasing the viscosity of guar gum by adding cross-linking gel forming agents.

The first cross-linking agents were borax and other boron compounds, amylopectin compounds, e.g. ammonium pyrroantimonate, potassium antimony tartrate followed by adding a dichromate, that is oxidation of trivalent to pentavalent antimony was found to give an efficient cross-linking agent [74].

Semi-synthetic and synthetic polymers are also used as thickening agents. Such are carboxymethyl cellulose [87, 6] and polyacrylamide [73] respectively.

Surface Active and Emulsifying Agents

Surface active agents (surfactants) improve the dispersion of ingredients and consistency of slurry. According to Hiroshi et al. [88] by adding small amounts of alkali metal salts of alkylphenyl ether disulfonic acid a slurry explosive was obtained which can be initiated with a No. 6 cap without adding sensitizers. Also alkali metal salts of sulphuric acid esters of higher aliphatic alcohols, of aromatic sulphonylic acids are good surfactants and improve the detonability of slurry explosives. Sorbitol monoxide was recommended [74] as the emulsifier.

Oxygen Carriers

In addition ammonium nitrate, sodium nitrate and calcium nitrate are added to slurry explosives. A mixture of calcium nitrate and sulphur [89] seems to be particularly efficient. Calcium nitrate makes slurry more resistant to low temperature and the explosive can withstand the temperature of -12°C. Ammonium perchlorate can also be used [72], but does not seem to get a wider application.

Aluminium

The addition of aluminium powder in a form of foil, flakes or granules can make slurry without nitro compounds. The patent by Davis, Fassnacht, Kirst and Noran [90] gives slurry explosives composed of ammonium and sodium nitrate, aluminium and water. An emulsifier is added to help the presence of air bubbles. The fact that aluminium can react with the strongly oxidizing ingredients of the explosive mixture can be dangerous.

Aluminium in the presence of water in a strongly oxidizing medium can make the explosive deteriorate and also create danger through heating and gassing. To avoid the reaction of aluminium coating is recommended of Al particles, with stearic, palmitic and oleic acids [74]. Flakes and dust of aluminium exposed handling problems as it resists wetting of aqueous medium. Mahadevan and Varadarajan [91] solved the problem by wetting aluminium with ethylene glycol and adding such paste to the mixture.

Alkylamine Nitrates

A number of patents (e.g. by Dunglison [92]) disclosed that by adding alkylamine nitrates to slurries a great increase in sensitivity could be achieved. Particularly efficient is methyamine nitrate, as disclosed by Frederic [93] and at present Du Pont Co. and I.C.I. are using methyamine nitrate as an ingredient of their slurry explosives [74]. Du Pont issued the explosive under the trade name ‘Toxet’ [73]. Methyamine nitrate is made by reacting methyamine with concentrated nitric acid (66%) free of nitrous acid (Vol. II, p. 455). It is important that nitric acid is free of nitric oxides which would give side reactions (e.g. diazotization) of methyamine.

There are no remaining problems in formulating water-gels which will perform well in any construction or mining operations under all climatic conditions. Although water-gels are not cheaper than NG-based explosives, manufacturers and customers prefer to use these explosives because of lesser hazards involved in manufacture, storage, transportation and handling.

The slurries can be ‘tailor made’ to suit individual site conditions, thus enabling maximum burden to be achieved with the best fragmentation resulting in the reduction of the overall cost of mining. Maximum coupling and hence maximum utilization of energy released to break the rock can be achieved by using water-gels especially pourables. At present the only advantage of NG-based explosives is their greater shelf-life as compared to slurries. To a greater or smaller extent, water-gels have replaced NG-based explosives. The present trends indicate that the former may replace the latter.

Compositions of a few slurry explosives in different countries are given in Tables 106–109.

In Germany Wasag Chemie Sythen G.m.b.H. factories are producing Wasagel explosives with 12% or more water. Mark IK is a non-freezing gel.

Dynamit Nobel AG are making Dynagel mark 1, 2, 3, P1 and P2. All the above explosives are with negative oxygen balance and can be used for open-cast work only. For their properties — see Meyer [69].

Slurry explosives for open-cast work in U.S.S.R. comprise also granulated TNT (‘Granulobol’) and a granulated mixture of TNT with 15% Al (‘Alumotol’).

Table 108 gives a comparison of the properties of Granulotol dry and with water.

The heat of detonation of ‘Alumotol’ is by ca. 35% higher than of ‘Granulotol’ and so is lead block expansion.
Japanese slurry explosives are all based on Du Pont, Hercules or IRECO Chemicals.

Sunvex 100A, 200 and 220 contain methylamine nitrate. Energel MA-7 contains ethanamine mononitrate. IRECO explosives are sensitized with Al.

The following are slurry explosives used in Sweden [67]: Reonex A (aluminized and methyl nitrate sensitized), Roomex B (methyl nitrate sensitized) and Reolit C (TNT sensitized) gels. Their oxygen balance is $-0.35, +1.43$ and $-1.75$ respectively, and the rate of detonation 4000–5000 m/s, however no exact com-
cartridges of 'Tovex' explosives with amine nitrate sensitizer and without nitroglycerine.

Although methylamine nitrate was considered to be a relatively safe and — in addition — is present in an aqueous solution precautions should be taken with regards to the problem of safety of handling the solution. The explosion of two tank cars loaded with 86% solution of methylamine nitrate occurred in Potomac River (U.S.A.) in 1976. The explosion was probably due to friction in a pump [86]. An important paper by Persson, Jerberg and Almgren [111] established that methylamine nitrate slurry explosives of the Swedish type of pumpable water-gel (Bulkanomex) could decompose when piston velocity increased above 20 m/s.

Gas Bubbles

The role of gas bubbles in explosives has already been discussed (pp. 298, 547). Goffart [96] described the importance of gas bubbles which increase the cup sensitivity of slurry explosives containing aluminium dust. However, the presence of gas bubbles of course reduces the density and subsequently the rate of detonation, for example a density of 1.33 falls to 0.83 and the rate of detonation from 3600 m/s to 2710 m/s (for a diameter of 36 mm).

The critical diameter of slurry explosives was determined by Michot and Bigourd [97]. The smallest critical diameter (22 mm) is shown by slurry with Al (density 0.95) and with methylamine nitrate (density 1.00). Also the method of determining the critical diameter has been given [98].

Permuted Slurries


Slurries with High Explosives

TNT was a common ingredient of slurry explosives of the 'Tovex' type made by Du Pont of Canada (see Table 107) [73]. PETN and RDX slurries were developed by T. Urbanski [95]. The method consisted in dissolving pentaaethylentetrol and hexamethylene-tetramine in nitric acid (d. 1.50) and neutralizing with ammonia or ammonium carbonate the solution containing some suspended PETN and RDX. A solution of ammonium nitrate in water with suspension of the above explosives resulted.

There is however a tendency to avoid incorporating typical high explosives into slurries owing to their high cost and sensitivity to impact and friction.

Ethylene glycol mononitrate was in use in Canada and an accident occurred in Beloel in 1975 [86]. As glycol mononitrate was considered to be safe to handle no special precautions were taken and it was pumped with two Moyno pumps. The detonation which destroyed the factory probably started through friction in a pump.

Composition of Slurries with Nitroglycerine based Explosives

A comparison was made by Mahadevan [11] of slurries with 'classical' nitroglycerine explosives as follows:

"At present the only advantage of nitroglycerine-based explosives is their greater shelf-life as compared to slurries. To a greater or smaller extent, water-gels have replaced nitroglycerine-based explosives."

FIG. 109. Nobel I-tube (detonating fuse) showing a thin layer of explosive inside the plastic tube (Courtesy Nitro Nobel A.B., Gytorp, Sweden).
NONEL DETONATING FUSE

Among the most important inventions in the field of accessories to mining explosives is the Nonel Detonating Fuse ingeniously invented by P. A. Persson at Nitro Nobel A.B. [113]. It is composed of a thick walled polyethylene tube sprayed inside with a small amount of a highly sensitive and strong explosive such as Octogen (HMX), Cyclonite (RDX) or FETN. It is based on the fact that a shock wave travels along the tube with a higher velocity than the detonation wave. Figure 100 gives a cross-section of the Nonel tube.

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13. COST 9736-64.
22. E. BURLOT, Mèm. d'Artillerie Francaise 9, 793 (1930).
COMMERCIAL (MINING) EXPLOSIVES


APPENDIX

METHODS OF DETERMINING THE ABILITY OF EXPLOSIVES TO DEFLAGRATE

Methods of determining the ability of explosives to deflagrate were introduced in 1934 by Audibert and Delmas [1]. It consisted determining whether an explosive can be subjected to burning or exploding under the flame produced by ignition charges.

A general scheme was developed in different countries which consists in the following method: an explosive is confined in a steel tube of different dimensions, viz.:

- length: 200-1370 mm
- diameter: 38-90 mm
- wall thickness: 3-20 mm

The tube is closed on both sides. One of the closing plates is provided with a nozzle of different diameters, e.g. from 1 to 20 mm. Another one is covered inside by an inert substance, such as sand. The initiation of the explosive is usually made by black powder or an explosive mixed with coal-dust.

The minimum diameter of the nozzle which produces a deflagration is determined and serves as a measure of the ability of the explosive to deflagrate.

Another criterion is the proportion of coal-dust added to the examined explosive. In Poland the explosive is mixed with coal-dust (up to 55%). The minimum addition of coal-dust which gives a deflagration is 17-28%. Pure ammonium nitrate explosives do not deflagrate.

Further description of the methods of determining a deflagration is outside the scope of this book. They are fully described by Charewicz [2].

REFERENCES

CHAPTER 20

THE MANUFACTURE OF COMMERCIAL (MINING) EXPLOSIVES

(Vol. III, p. 498)

Little can be added to first steps of manufacturing mining explosives, such as drying, milling and mixing of ingredients of mining explosives (Vol. III, pp. 498–503). Disk mixers (Vol. III, p. 504, Fig. 167), edge runners (Vol. III, p. 350, Figs 93, 94) and Werner-Pfleiderer kneaders (Vol. III, pp. 586–7, Figs 206–209) are still in use for mixing ammonium nitrate explosives without nitroglycerine.

Those with a small amount of nitroglycerine (4–6%) can be mixed in Werner-Pfleiderer and in Drais kneaders (Vol. III, pp. 512–514, Figs. 173–175). The latter are particularly suitable for making explosives with a higher content of nitroglycerine.

PLANETARY MIXERS

The typical planetary mixer is a Drais kneader the most commonly used type is with two bowls pivoting around an axle. While one of the bowls is being emptied or filled, the other one is under the stirrers. The capacity of the bowl is of about 500 kg of dynamite. More recently Drais has built a machine of 500 l useful capacity consisting of four instead of two pillars (Fig. 101).

Another kind of planetary mixer of a smaller capacity (250 kg) was developed by Bazzi S.A., Vevey (Fig. 102) [1]. The main characteristics are the light structure of aluminium, the particular disposition of blades which makes it possible to avoid a foreign body being caught into the mass and wedged between the blades and the interior of the bowl.

The stirrers revolve one around the other at 17 rpm and rotate around their own axis at 45 rpm. The speed can be changed and the mixing time can be kept between 4 and 8 min. At a lower speed the danger of explosion is smaller. The stirring can be clockwise or anticlockwise. The machine is stopped and the stirrers are raised automatically by means of a timing device.

FIG. 101. New design for a Drais Planetary Mixer (Courtesy Draiswerke Maschinenfabrik G.m.b.H., Mannheim-Waldorf, FRG).
Although the design of planetary mixers excludes friction, a few explosions have occurred [2]. Most of them were due to the presence of foreign bodies in the bowl, and a few accidents were due to hand stirring the mixtures, contrary to instructions.

Also a few accidents with Werner-Pfleiderer mixers have been described [2] mostly due to the accidental presence of foreign bodies.

Another kind of explosives mixer 'Tellex Mixer' has recently been developed by Fr. Niepman, G.m.b.H., Gevelsberg, FRG [3]. The mixing bowl is of steel alloy and consists of two troughs in which mixing can be made of powder, semi-gelatinous and gelatinous explosives, as well as AN-FO and slurry mixtures. The capacity of the troughs is 180-700 kg.

Two spiral stirrers guarantee good mixing (Figs. 103a, b).

Mixing lasts 8-10 min and remote control assures the safety of personnel (Fig. 104).

FIG. 103. Tellex explosives mixer by Niepman (Courtesy Niepman A.G., Maschinenfabrik, Wadwil/ZG, Switzerland) (a) View from above; (b) Diagram of functioning of stirrers.

CARTRIDGING

Maschinenfabrik Fr. Niepman G.m.b.H. & Co., Gevelsberg, FRG specializes in making cartridge making machines for explosives. A diagram of an early version of a cartridge making machine is given in Vol. III, pp. 517-8, Fig. 179. Two modern Niepman cartridge making machines will be described here.

Figure 105 depicts 'Cartex' for cartridge powder-explosives, a cartridge machine which makes 9 cartridges (there are also models making 12 cartridges) [4].

The explosive is fed by screws into the open end of the paper tubes. When shells have been filled, the screws stop automatically, then a brief reverse rotation prevents a surplus feed. The filled tubes travel to the folding machinery where they are closed before being conveyed to the paraffining station, if necessary. The operation is controlled at two points: by manual control inside the cartridge making room and by a remote control panel in the control room.

Machines of this type can make cartridges of 20-40 mm diameter and 90-254 mm length, with a yield of 100-180 cartridges per minute.
Figure 106 depicts a cartridge filling machine LD-Ex 701 for gelatinous explosives [5]. Large diameter cartridges can be made: 50–125 mm diameter and 300–800 mm length. The hopper is loaded with an explosive. Feed rollers and transfer screws convey the material to the filling station. Plastic film from a supply reel is formed into tube, and the longitudinal seam is sealed. The explosive is fed into the casing until a desired length has been reached. The filling screw is stopped, the tube is pulled away and wire clips are applied to close the cartridge and the film is cut between the two clips. Cartridge length is adjustable. The machine can make 10–15 cartridges/minute.

Although the Niepmann machines are safe to handle, an accident occurred as described by Biasutti [2] in Rego da Amorita, Portugal. As is usual in such accidents, it was due to the presence of a foreign metal object in gelatinous explosive with 33% nitroglycerine.

AN–FO

The methods of making AN–FO mixtures were described in Vol. III, pp. 508–510. In the early stages of AN–FO manufacture no necessary precautions were taken AN–FO being erroneously considered to be a safe mixture. A huge accident at Norton, Virginia, U.S.A. (Vol. III, p. 508) compelled the authorities to issue instructions on the manufacture and handling of AN–FO, a detailed description of the accident can be found in the book by Biasutti [2]. The accident started when the mixture caught fire, probably from welders working in the premises. The fire was followed by several explosions which produced extensive damage. Since then AN–FO has been recognized as a conventional explosive and all regulations valid for explosives, should be applied as regards manufacture, handling, transportation and storage of AN–FO.

The methods for making and applying AN–FO for blasting have been given by Schiele [6].

Two modern methods developed by Nitro Nobel in Sweden are depicted in Figs 107 and 108. Portanol (Fig. 107) is a pneumatic ejector developed for the efficient charging of AN–FO made from ammonium nitrate prills. It is based on the ejector principle, that is, the blasting agent is sucked from the container and blown through a hose into the bore-hole.

Anol (Fig. 108) is a compressed air unit for charging AN–FO into shot-holes of 25–150 mm diameter.
FIG. 106. Explosives packing machine for large diameter cartridges (Courtesy Maschinenfabrik Fr. Niepmann G.m.b.H. and Co., D-582 Gevelsberg, FRG).

FIG. 107. 'Portanol' ejector charger for prilled AN–FO (Courtesy Dr J. Hanson and Mr Bengt Ljung of Nitro Nobel Mee. Stockholm).
It is important that the vital parts of the apparatus are made of stainless steel owing to the fact that AN–FO is highly corrosive. The charging hose is anti-static and electrically semi-conductive to avoid charging with static electricity.

REFERENCES
1. Planetary Mixer, M. Biauzzi S.A., Vevey, Switzerland.
3. Tellex Explosives Mixer, Niepmann A.G., Walkwill/ZG, Switzerland.
4. Cartex 9412, Niepmann GmbH & Co., Gevelsberg, FRG.
5. LD-Ex 701, Niepmann GmbH & Co., Gevelsberg, FRG.

FIG. 108. 'Aaeol' for charging AN-FO (Courtesy Dr Jan Hamson and Mr Bengt Ljung of Nitro Nobel Mee, Stockholm)
CHAPTER 21
LIQUID EXPLOSIVES

LIQUID OXYGEN EXPLOSIVES (OXYLIQUITS) (LOX) (Vol. III, p. 491)

Liquid oxygen explosives were widely used in Germany during World War I owing to a shortage of nitric acid and hence – aromatic nitro compounds. Shortly after World War I (Vol. III, p. 493) their use was limited. This was partly due to a number of fatal accidents, these explosives are little used today in most countries [1]. The use of LOX declined because of the introduction of AN–FO and Slurry explosives [2].

LIQUID ROCKET PROPPELLANTS—PROPERGOLS (Vol. III, p. 291)

A few monographs and collective volumes have been published and should be consulted for further information on this expanding and very wide subject [3–9, 35]. The history of liquid propellants is given by Roth [7] based on the description by Malina and Truax in a collective volume [8]. The scope of the science of Liquid Propellants is not limited to rocket propulsion but also embraces jet propulsion of engines and their design. This is outside the scope of this book. Subsequently the information strictly connected with rocket propulsion will be given here.

Mono- and Bipropellants

a. Monopropellants are composed of substances which contain in one molecule both combustible and oxidizer moiety and possess explosive properties. Such are: nitromethane, methyl nitrate described already in Vol. I and II respectively and in Chapters VIII, X (this volume). They will not be discussed here.

b. Bipropellants are composed of two components: a fuel and a liquid oxidizer. Separately neither of them is explosive, but their mixture possesses burning and explosive properties. The liquids can be individual compounds or mixtures, and usually belong to hypergolic mixtures (Vol. III, p. 291), that is, they react spontaneously after a short induction period followed by mixing. The term ‘hypergolicity’ is now in use for ‘self-ignitability’. Non-hypergolic systems are not currently much in use [9].

LIQUID EXPLOSIVES

The following were groups of compounds used as fuels: hydrocarbons, amines, hydrazines, boranes and as oxidizers: nitric acid, nitrogen oxides, hydrogen peroxide, liquid oxygen, halogens.

A few requirements are posed with regard to the stability of the components, their toxicity, ease of handling and cost of manufacture. From that point of view some ingredients originally suggested could not be accepted, such as liquid ozone which proved to be too sensitive to handle.

Cryogenic and Storable Components

Liquid hydrogen is a typical cryogenic fuel and oxygen and fluorine are cryogenic oxidizers. The latter is a more energetic oxidizing agent than oxygen and also oxidizers containing active fluorine atoms. Thus oxygen difluoride (OF₂) and chlorine trifluoride (ClF₃) (Vol. III, p. 312) are more energetic and reactive than oxygen containing oxidizers such as nitric acid, hydrogen peroxide (68%), dinitrogen tetroxide.

The energetic advantages of cryogenic fuel and oxidizers are visible from their performance in terms of specific impulse Iₛ as compared with storable components:

<table>
<thead>
<tr>
<th></th>
<th>Iₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryogenic</td>
<td>410</td>
</tr>
<tr>
<td>hydrogen and fluoride</td>
<td>391</td>
</tr>
<tr>
<td>hydrogen and oxygen</td>
<td></td>
</tr>
<tr>
<td>Storable</td>
<td></td>
</tr>
<tr>
<td>hydrazine and nitrogen tetroxide</td>
<td>292</td>
</tr>
<tr>
<td>methylhydrazine and chlorine trifluoride</td>
<td>284</td>
</tr>
</tbody>
</table>

Storable liquid propellants now receive greater attention than cryogenics. Storability refers to a liquid which can be kept for a long time at ambient temperature in standard containers without any significant loss of material.

The following are requirements applied to storable liquids [10]:

1. the freezing point should be sufficiently low to assure the liquid state under different climatic conditions. Also they should possess:
2. high density,
3. low vapour pressure,
4. relatively low viscosity.

They should not be excessively toxic, corrosive, reactive with air or thermally unstable. Their performance should be as high as possible and this is obviously limited to particular chemical structures. Subsequently blends were introduced for example, 50/50 hydrazine/unsym-dimethylhydrazine (UDMH), or UDMH with acetone triazole and diethyleneetriamine (DETA). On UDMH see Vol. III, p. 308.

Most storable energetic oxidizers are very reactive, toxic and not very stable
Hypergolic Systems

The above described systems with compounds containing amino groups are hypergolic systems.

Kulkarni [11] gave a list of various compounds hypergolic with WFNA and their induction period according to [12] (Table 110).

The data for hydrazine [13] and UDMH [14] are given in Table 111.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Induction period sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylenediamine</td>
<td>0.09</td>
</tr>
<tr>
<td>Tripropylamine</td>
<td>0.05</td>
</tr>
<tr>
<td>Triethylenetriamine</td>
<td>0.04</td>
</tr>
<tr>
<td>Triethylenetramine</td>
<td>0.07</td>
</tr>
<tr>
<td>Di-isopropylamine</td>
<td>0.15</td>
</tr>
<tr>
<td>Dipropylamine</td>
<td>0.17</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>0.63</td>
</tr>
<tr>
<td>Diethyleneamine</td>
<td>0.45</td>
</tr>
<tr>
<td>sec-Butyamine</td>
<td>0.94</td>
</tr>
<tr>
<td>Propylamine</td>
<td>1.73</td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>2.03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Induction period sec</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrazine</td>
<td>0.003</td>
<td>[13]</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>0.005</td>
<td>[13]</td>
</tr>
<tr>
<td>UDMH</td>
<td>0.012</td>
<td>[14]</td>
</tr>
</tbody>
</table>

Capener [9] and other sources [7, 24] give a wide list of hypergolic systems which can be summarized as follows:


There is currently a tendency to use oxygen fluorine and its compounds more widely.

- Fuels: Diethylenetriamine (DETA), (NH₂C₂H₄)₂NH, Hydrazine, Monomethyldihydrazine (NMM), Unsymmetrically Dimethylhydrazine (UDMH, Vol. III, p. 308), Terpenes, also non-hypergolic fuels JP-4 and JP-5 are in use.

Other composite fuels which are in use are:

MAF 1 a mixture of 50% DETA, 40% UDMH and 10% Acetonitrile, MAF 3: 20% UDMH and 80% DETA, MAF 4 (Hydrazine or U-DETA): 60% UDMH + 40% DETA, N₂H₄-UDMH: a mixture 50/50 of two components. Hydrazine V: 75% hydrazine and 25% MMH, JP-X: 60% JP-4 and 40% UDMH.

Practical applications have been found for most of these compounds with some exceptions such as: liquid ozone as it is considered to be too difficult to handle, the only probable form of ozone safe enough is its mixture with oxygen (Vol. III, p. 309).

Intensive research is still being carried out to find the best oxidizer and fuel. Capener [9] gives a few examples of the most promising systems, they are collected in Tables 112–116. Roth [7] reported the most commonly used liquid propellants – Table 117.

Further information has been presented by Silverman and Constantine [24], who have described non-hypergolic mixtures of liquid oxygen with RP-1 (a hydrocarbon blend), hydrogen, ammonia, alcohol, hydrogen peroxide with hydrocarbons JP-4 and JP-5; IRFNA with JP-4. They also described hypergolic mixtures, such as: IRFNA with JP-X, UDMH, MAF-1, -3 and -4, nitrohex, furfurol; JWFN with terpentine; N₂O₄ and hydrazine with UDMH, MMH, hydrazine with MMH, MON with MMH and UDMH.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidizer wt %</th>
<th>Specific impulse sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂H₆</td>
<td>77</td>
<td>298</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>60</td>
<td>278</td>
</tr>
<tr>
<td>MMH</td>
<td>71</td>
<td>278</td>
</tr>
<tr>
<td>UDMH</td>
<td>76</td>
<td>272</td>
</tr>
</tbody>
</table>
TABLE 113. Propellants with N₂O₄

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidizer wt %</th>
<th>Specific Impulse Iₚ (max) sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>84</td>
<td>342</td>
</tr>
<tr>
<td>B₃H₉</td>
<td>77</td>
<td>306</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>57</td>
<td>291</td>
</tr>
<tr>
<td>MMH</td>
<td>68.5</td>
<td>288</td>
</tr>
<tr>
<td>UDMH</td>
<td>72</td>
<td>286</td>
</tr>
<tr>
<td>DETA</td>
<td>74</td>
<td>278</td>
</tr>
</tbody>
</table>

TABLE 114. Propellants with H₂O₂ (100%)  

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidizer wt %</th>
<th>Specific Impulse Iₚ (max) sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>88</td>
<td>322</td>
</tr>
<tr>
<td>B₃H₉</td>
<td>73</td>
<td>316</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>67</td>
<td>286</td>
</tr>
<tr>
<td>UDMH</td>
<td>81</td>
<td>283</td>
</tr>
</tbody>
</table>

TABLE 115. Propellants with fluorine

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidizer wt %</th>
<th>Specific Impulse Iₚ (max) sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>89</td>
<td>410</td>
</tr>
<tr>
<td>B₃H₉</td>
<td>82</td>
<td>360</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>69</td>
<td>365</td>
</tr>
<tr>
<td>UDMH</td>
<td>71</td>
<td>344</td>
</tr>
<tr>
<td>NH₃</td>
<td>72</td>
<td>357</td>
</tr>
</tbody>
</table>

LIQUID EXPLOSIVES

TABLE 116. Chlorine trifluoride

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidizer wt %</th>
<th>Specific Impulse Iₚ (max) sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>92</td>
<td>318</td>
</tr>
<tr>
<td>B₃H₉</td>
<td>88</td>
<td>290</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>75</td>
<td>293</td>
</tr>
<tr>
<td>MMH</td>
<td>74</td>
<td>283</td>
</tr>
<tr>
<td>UDMH</td>
<td>75</td>
<td>280</td>
</tr>
<tr>
<td>DETA</td>
<td>75</td>
<td>267</td>
</tr>
</tbody>
</table>

TABLE 117. Most commonly used liquid propellants  
(according to Roth [17])

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>Fuel</th>
<th>Oxidizer: Fuel ratio</th>
<th>Specific-Impulse Iₚ sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>99%H₂O₂</td>
<td>Hydrazine</td>
<td>1.0</td>
<td>245</td>
</tr>
<tr>
<td>LOX</td>
<td>Ethanol</td>
<td>1.5</td>
<td>242</td>
</tr>
<tr>
<td>LOX</td>
<td>JP-4</td>
<td>2.2</td>
<td>248</td>
</tr>
<tr>
<td>Fluorine</td>
<td>NH₃</td>
<td>2.6</td>
<td>288</td>
</tr>
<tr>
<td>Fluorine</td>
<td>Diborane</td>
<td>(B₂H₆)</td>
<td>5.0</td>
</tr>
<tr>
<td>Fluorine</td>
<td>Methanol</td>
<td>2.37</td>
<td>296</td>
</tr>
<tr>
<td>Fluorine</td>
<td>Hydrazine</td>
<td>1.98</td>
<td>2.98</td>
</tr>
</tbody>
</table>

Although considered as being storable, oxidizers such as N₂O₄ and CIF₃ are less in use owing to their low boiling points: 21⁰C and 113⁰C respectively and hence difficulty in handling.

Novel Trends in Liquid Rocket Fuel

In the search for efficient hypergolic fuel various derivatives of furfuryl alcohol have been suggested [14–16]. Some of them have an induction period of the order of 0.020–0.025 sec with 98.3% nitric acid.

Among the fuels reacting with RFINA the following showed hypergolic properties: Schiff’s bases [17], furfurylidene aniline and furfuramide [18], Δ⁵-carene [19]. Particularly important are the findings of Panda and Kulkarni [20] who described aliphatic, alicyclic and aromatic furfurylidene ketones which are hypergolic with RFINA. The latter had the following composition: 76% HNO₃, 21% N₂O₄, 1% H₃PO₄, 0.3–0.5% HF and 1.7% H₂O.
OXIDIZERS

Oxygen Difluoride (OF₂)

As previously mentioned, oxygen fluorine and fluorine compounds are infrequently used as oxidizers. Oxygen difluoride is a particularly attractive oxidizer. It is denser than the stoichiometric mixture O₂/F₂ and consequently should give a better performance. It was first identified as a product of electrolysis of wet HF as early as 1927 [26]. A detailed description is given by Donohue, Nevitt and Zletz [21] with a yield of 45%, although a yield of 60% was also claimed [27]. Donohue et al. found that the yield varies with concentration.

The reaction [21] can be represented by the diagrammatic equation:

\[ \text{HF} + \text{H}_2\text{O} \rightarrow \text{OF}_2 + \text{O}_2 + \text{H}_2 \]  

(1)

According to Donohue et al. the conversion of HF to OF₂ is 100%.

Oxygen difluoride is a colourless gas of m.p. -224°C, b.p. -145°C [28, 25]. Its density is 1.52 at -145°C [25]. Bisbee, Hamilton, Rushworth, Haeuser and Gerhauser [23] determined thermochemical parameters of the compounds: the standard \(-\Delta H_f^\circ\) was found to be 4.06 kcal/mol and of O-F bond energy -50.7 kcal/mol.

EPR spectrum of OF₂ was also examined [22].

Nitrogen Fluorides

Four nitrogen fluorides are known: NF₃, N₂F₄, N₂F₅ and N₃F, but only NF₃ and N₂F₄ [25, 29] are of real interest in rocket propulsion. They are both cryogenic with b.p. -126° and -73°C respectively. They are relatively resistant to the hydrolytic action of water. So far there is little prospect of practical use owing to the high cost and the yield of toxic decomposition products.

Multicomponent Fuel

Multicomponent systems usually contain aluminium as a component which increases the combustion energy. The stabilization of the system with an insoluble component and aluminium requires that insoluble phases (an insoluble combustible and metal) are uniformly suspended through the liquid phase. According to Beiglhey, Fish and Anderson [25] two methods were promising:

(1) by forming an emulsion,
(2) by forming a gel.

The latter method proved to be more successful. Two types of gelling agents were in use:

(a) silica and acetylene black,
(b) natural and synthetic hydrophilic polymers.

There is an increasing demand for hydrazine as an excellent fuel. It is commercially made by the Raschig method and has been known since 1907. Its main drawback consists in yielding dilute (2%) solution. The monograph by Audneith and Ogg (Vol. III, p. 307) is also dedicated to the problem of concentrating the solution. The problem still exists although the classical method was improved by Bayer in Germany. There are environmental problems in disposing of large quantities of by-products and a consumption of large quantities of energy.

According to the Encyclopedia [2] Usine Kuhlmann in France developed a new method which consists in a sequence of reactions: ammonia, hydrogen peroxide and carbonyl compounds (e.g. propene) react in the presence of an amide and a catalytic quantity of phosphate to form an azide intermediate:

\[ \text{C} \equiv \text{N} \rightarrow \text{N} \equiv \text{C} \]

The latter hydrolysed quantitatively to hydrazine and carbonyl compound which is recycled. A yield of 75% was claimed.

For gelling hydrazine, MMH, UDMH and their mixtures were used: natural gums, guar gum (applied extensively in slurry explosions - Chapter XIX), gum arabic, locust bean gum, alginates, gelatin, carboxymethyl- and hydroxymethyl cellulose, polynvinyl alcohol, polynvinyl pyrrolidone etc. The solid phase should be of course, compatible with the carrier fuel.

The rheological properties of such gels are of importance [10, 25].

The methods of examining the chemical and mechanical stability of propellant systems are described by Tannenbaum and Beardell [10].

POLYMERIZATION OF HYPERGOLIC FUEL

Trent and Zucrow [30] (while studying the hypergolicity of bicyclo-pentadiene with WFNA) advanced a hypothesis of polymerization reaction of the diene as a pre-ignition reaction. This was substantiated by Panda and Kulkarni [20, 31] through their experiments on self-ignition of several fururylindone ketones and amines with RFINA. The same authors discovered hypergolicity of unsaturated phenols with RFINA and N₂O₅ [32]. The phenols are able to polymerize. In a series of recent papers Panda and Kulkarni [33] supported their hypothesis experimentally.

ANALYSIS

The analysis of liquid rocket propellants has been described in a monograph by Malone [34]. This is however outside the scope of the present book.
CHAPTER 22

SMOKELESS POWDER
(Vol. III, p. 528)

Little can be added to the general description of smokeless powder given in Vol. III, although its use is wider than originally described and is not limited to firearms but is extensively used for rocket propulsion.

From the point of view of composition three kinds of smokeless powder can be described: single, double and triple-base powders.

The general characteristics of these groups of powder are summarized in Tables 118–120, according to Roth and Capener [1]. Potassium salts are added (Tables 118 and 119) as flash reducing agents. Lead salts (Table 119) are decomposition ‘moderators’ which play a role in producing low temperature coefficients of burning propellants and a low exponent \( n \) in the expression

\[ \nu = k \cdot p^n, \]

where
- \( \nu \) is the rate of burning
- \( k \) is a coefficient
- \( p \) is pressure under which the propellant is burning.

A low exponent \( n \) assures a ‘plateau’ burning, that is, there is little change in the rate \( \nu \) with pressure (Freckel [39]).

STABILITY OF SMOKELESS POWDER (Vol. III, p. 559)

The stability of smokeless powder remains one of the major problems connected with the storage of propellants containing nitrate esters. It also forms the main subject matter of an International Symposium which has been organized in Sweden by J. Hansson for over ten years [2].

Tranchant [3] points out that three types of stability can be considered:

(a) chemical stability
(b) mechanical stability
(c) ballistic stability

However (b) and (c) depend on the chemical stability. The same author [4] suggested that the term ‘Chemical Stability’ should be replaced by a more pre-

577
TABLE 118. Typical single-base powder in U.S.A. [1]

<table>
<thead>
<tr>
<th>Nitrocellulose (13.15% N)</th>
<th>M6</th>
<th>MIO</th>
<th>IMR</th>
<th>EC–NACO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Celulose</td>
<td>87</td>
<td>98</td>
<td>100</td>
<td>91.4</td>
</tr>
<tr>
<td>Basic Lead Carbonate</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.8</td>
</tr>
<tr>
<td>Volatile (ethanol + dibutyl ether)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.0</td>
</tr>
<tr>
<td>K2SO4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.8</td>
</tr>
<tr>
<td>Diphenylamine (DPA)</td>
<td>1</td>
<td>1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>DNT</td>
<td>10</td>
<td>—</td>
<td>8 (coating*)</td>
<td>—</td>
</tr>
<tr>
<td>Dibutyl Phthalate</td>
<td>3</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* See Vol. III, p. 627.


<table>
<thead>
<tr>
<th>Nitrocellulose (13.25%)</th>
<th>M2</th>
<th>M5</th>
<th>M8</th>
<th>M21</th>
<th>N5</th>
<th>MDM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroglycerine</td>
<td>77</td>
<td>81</td>
<td>52</td>
<td>53</td>
<td>50</td>
<td>48.6</td>
</tr>
<tr>
<td>KNO3</td>
<td>19</td>
<td>15</td>
<td>43</td>
<td>31</td>
<td>34</td>
<td>27.0</td>
</tr>
<tr>
<td>Ethyl Celulose</td>
<td>2.1</td>
<td>2.1</td>
<td>1.25</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.6</td>
<td>0.6</td>
<td>0.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Trissicin</td>
<td>0.3</td>
<td>0.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Lead Salleylate</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>11</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Lead Stearate</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>2.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Diethyl Phthalate</td>
<td>—</td>
<td>3</td>
<td>—</td>
<td>0.03</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2-Dinitrophenylamine</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>10.5</td>
<td>—</td>
</tr>
<tr>
<td>Lead Salts*</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>2.0</td>
<td>—</td>
</tr>
<tr>
<td>Candelilla Wax</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>2.4</td>
<td>—</td>
</tr>
</tbody>
</table>

* Composition undisclosed.

TABLE 120. Triple-base propellants in U.S.A. [1]

<table>
<thead>
<tr>
<th>Nitrocellulose (13.15%)</th>
<th>M15</th>
<th>M17</th>
<th>M31</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroglycerine</td>
<td>20</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>Nitroguanidine</td>
<td>19</td>
<td>21</td>
<td>19</td>
</tr>
<tr>
<td>Ethyl Celulose</td>
<td>54.7</td>
<td>54.7</td>
<td>54.7</td>
</tr>
<tr>
<td>Sodium Aluminium Fluoride</td>
<td>6.0</td>
<td>1.5</td>
<td>—</td>
</tr>
<tr>
<td>Dibutyl Phthalate</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>2-Dinitrophenylamine</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

TABLE 121. French smokeless powders [38]

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Calorimetric value cal/g</th>
<th>Gas volume cm³/g</th>
<th>Force f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poudre B Épaisse</td>
<td>Nitrocellulose 12.8% N</td>
<td>98</td>
<td>925</td>
<td>10 500</td>
</tr>
<tr>
<td></td>
<td>Diphenylamine</td>
<td>2</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Poudre SD Épaisse</td>
<td>Nitrocellulose 11.7% N</td>
<td>66</td>
<td>762</td>
<td>1012</td>
</tr>
<tr>
<td></td>
<td>Nitroglycerin 25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Celulite 9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Balistite CI</td>
<td>Nitrocellulose 12.5% N</td>
<td>58</td>
<td>1243</td>
<td>833</td>
</tr>
<tr>
<td></td>
<td>Nitroglycerin 42</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Celulite (to add) 1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The term 'Chemical Stability' will be used for short.

The stability of smokeless powder depends not only on the purity of the used nitrate esters, or the presence of a stabilizer, but also on the web thickness of powder grains (Vol. III, p. 55).

Currently the stability tests are directed towards the determination of changes of the stabilizers present in the propellant. The most important methods currently used to evaluate the change of the stabilizer are chromatographic methods.

The pioneering work of Schroeder (Vol. III, p. 563) and [5, 6] should be mentioned.

With the progress of chromatography techniques various methods were used, such as thin-layer chromatography (TLC) which started in 1962 by Hansson and Alm [7] followed by other papers [8, 9] including those on high velocity chromatography [10, 11].

Current research on stability and changes of stabilizers are published in volumes of Symposia [2].

Thus thin layer chromatography (TLC) was extensively used by Volk [12]. TLC and liquid chromatography by Ammann and co-workers [13], gas-chromatography (GC), TLC and high pressure chromatography (HPLC) by Ammann [14]. HPLC was introduced by Lebert, Stephen and Zeller [15], Brook, Kelso, Neil and MacLeod [16], Lindblom [17], Sopranetti and Reich [18], Volk [19]. Gas chromatography was used by Sopranetti and Reich [20]. To obtain different retention times for derivatives of diphenylamine, they N-acylated the products with heptafluorobutyric anhydride and obtained a high resolution.

Microrcalorimetry was also tried as a method of determining the beginning of decomposition of propellants [21–26]. It should be recalled that the first experiments on measuring the heat evolved during the decomposition of nitro-
cellulose powder were carried out by W. Świętołaski, T. Urbaniński and co-workers [27] (Vol. III, p. 552, 555).

Brook et al. [16] summarized the widely-used stability tests in Table 122 (see also Vol. III, p. 558).

<table>
<thead>
<tr>
<th>Test</th>
<th>Temperature °C</th>
<th>Time of Test</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abel &amp; Heat</td>
<td>65.5</td>
<td>10-30 min</td>
<td>KI starch paper</td>
</tr>
<tr>
<td>Methyl Violet</td>
<td>120</td>
<td>40 min</td>
<td>Methyl Violet paper</td>
</tr>
<tr>
<td>Dutch</td>
<td>105</td>
<td>72 hrs</td>
<td>Decomposition monitored by weight loss of sample</td>
</tr>
<tr>
<td>Surveillance</td>
<td>80</td>
<td>150 hrs</td>
<td>Decomposition by weight loss of sample</td>
</tr>
<tr>
<td>Small Vessel</td>
<td>100</td>
<td>5 days</td>
<td>Decomposition by weight loss of sample</td>
</tr>
<tr>
<td>NATO</td>
<td>65.5</td>
<td>60 days</td>
<td>Loss in stabilizer determined spectroscopically</td>
</tr>
<tr>
<td>Woolwich</td>
<td>80</td>
<td>3 weeks</td>
<td>Loss in stabilizer determined by gas-liquid chromatography</td>
</tr>
</tbody>
</table>

In France and U.S.S.R. the stability test of Vieille is widely used. It consists in heating the samples at 110° or 106.5°C in the presence of litmus paper for a minimum of 70 hours (Vol. III, p. 558).

As pointed out in Vol. III quantitative methods such as Bergmann and Junk, pH measurement of heated samples, Taliani (Vol. II, pp. 26–28) are rarely used for control in magazines.

Volk [12] reported the results of his examination of the products of the changes in diphenylamine (DPA) and ethylcentralite during the storage of single and double base propellants respectively at temperatures between 60 and 95°C until the moment that NO₂ appears (a temperature 65.5°C for 60 days has been approved by NATO [3, 16]). According to Volk the nitrogen dioxide was evolved after more than 800 days.

He established the presence of 28 derivatives of DPA as follows:

2-nitro-, N-nitroso-, N₄,₄-dinitroso-, N-nitroso-4-nitro-, 3-nitro-, 2,6-dinitro-, 2,4-dinitro-, N-nitroso-2,4-dinitro-, 2,2-dinitro-, 2,4,6-trinitro-, 2,4',3'-dinitro-, N-nitroso-2,3'-dinitro-, N-nitroso-4,4'-dinitro-, 4-nitroso-2-nitro-, 4-nitro-, 2,2',4', 4'-tetratinitro-, N-nitroso-2,2',4'-dinitro-, N-nitroso-2,2',4',6'-dinitro-, N-nitroso-2,3',4'-trinitro-, 2,4,4',6'-trinitro-, 2,4,4',6'-tetranitro-, 2,2',4',6'-pentanitro-, 4-nitroso-, 4,4'-dinitro-, 2,2',4',4',6,6'-hexanitro-diphenylamine, and picric acid.

Similar results were obtained by Brook et al. [16]. Ethylcentralite gave 24 products as follows:

**SMOKELESS POWDER**

Nitro-, 1,3-dinitro-, 1,3,5-trinitro-benzene; ethyl-, 2-nitroethyl-, 4-nitroethyl-, 2,4-dinitroethvl-, 2,4,6-trinitroethyl-, N₂,2,4,6-tetranitroethyl-, N-nitrosoethyl-, N-nitroso-2-nitroethyl-, N-nitroso-4-nitroethyl-aniline; 2-nitro-, 4-nitro-, 2,4-dinitro-, 4,4-dinitro-2,2,4,4'-tetratinitro-ethylcentralite; 4-nitro-, 2,4-dinitro-, 2,6-dinitro-phenol and picric acid.

It is important to note which compounds were formed in single and double base powders during long storage at normal storage temperature.

In 1976, Ammann [14] examined nitrocellulose powder manufactured in 1927 and found derivatives of diphenylamine as follows by TLC: 2-nitro-, 2,2', 2,4', 4,4'-dinitro-, 2,2',4', 2,4',4'-trinitro and tetranitrodiphenylamine. Also trace quantities of N-nitroso-4-nitro and N-nitroso-4,4'-dinitrodiphenylamine were detected.

In a 15-year-old single base powder, Brook et al. [16] found 0.77% DPA, 0.23% N-nitroso-DPA, 0.02% 2-nitro, and 0.04% 4-nitrodiphenylamine. Similar products in much the same quantities were found in nitrocellulose powder subjected to heating at 105°C (Dutch Test) for ca. 24 hours and at 65.5°C (NATO Test) for ca. 24 days.

**FREE RADICALS IN THE CHANGE OF DIPHENYLAMINE**

A new and original approach has been given by Mrzewiński [28] to the problem of the change of diphenylamine in single-base powder. He applied ESR technique to follow the transformation of the stabilizer and came to the conclusion that the charge-transfer phenomenon occurs in the first instance at room temperature between nitrocellulose (acceptor) and diphenylamine (donor) in agreement with the finding of T. Urbaniński et al. [29] that nitrate ester give charge-transfer with amines.

The ESR signal was recorded in nitrocellulose powder at room temperature. The intensity of the signal increased at 106.5°C (Vieille test) and reached a maximum after 20 hours.

According to Mrzewiński [30] this was due to the formation of a free radical of diphenylamine (I) a transient free radical of diphenylamine N-oxide (II). Free radical I is known to the literature [31]. It yielded N-nitrosodiphenyamine (which, as is known possesses stabilizing properties), N-nitrosodinitro-, dinitro- and higher nitrated diphenylamines. According to Mrzewiński free radical I is
the active species of the formation of nitroso and nitro derivatives of diphenylamine when single base powder is heated. Short lived free radical II also participated in the formation of nitro compounds, but its role is much less pronounced.

![Graph](a)

![Graph](b)

FIG. 109 (a) ESR signal in single-base propellant. 1 — broad line of metal impurities (Mn, Ni, Fe in quantity of ca. 10−4%), 2 — narrow line of radical species [28, 30]. (b) Intensity of ESR signal against time (hours) of heating single base powder and Nitrocellulose with Diphenylamine at 106.5°C, according to Mrzewski [28, 30].

**STABILIZERS**

It is well known that diphenylamine (DPA) is too basic as a stabilizer of nitroglycerine and DEGDN (diethylene glycol dinitrate) containing powder. To reduce the basicity of DPA, 2-nitrodiphenylamine (2-NDPA) was introduced into propellants, particularly double base powders, as a successful stabilizer.

A similar action shows p-nitro-N-methylaniline (pNMA).

**SMOKELESS POWDER**

Centralites I and II (Vol. III, p. 645). Centralite III were successful as both stabilizers and 'non-volatile solvents' of nitrocellulose along with urethanes which seem now to be less used. Unsymmetrically substituted urea: unsym-diphenylurea (Vol. III, p. 645) named Acardite I is currently employed as also are its homologues—diphenylmethyl and diphenylethyl urea: Acardite II and Acardite III respectively.

![Centralite III](mp. 60.5°C)

![Acardite II](mp. 171°C)

![Acardite III](mp. 73°C)

More recently a use has been found for resorcinol as a stabilizer. It readily reacts with nitrogen dioxide to yield nitroso- and nitroresorcinol which can further react with resorcinol molecules yielding various heterocyclics among them resorfin.

The action of this stabilizer was extensively discussed by Blay [32] and Volk [33].

Soliman [42] recently suggested a new stabilizer for double base propellants. This is 5,6,7-trihydro-5,7-diphenyl-thiurazole-3,2-bis-triazin-3(2H)-one (III)

![Resorcinol](OH)

![III](C₆H₆)

It gave good results when incorporated, in proportion of 3%, into a double base powder containing 56% nitroglycerine (12.0% N), 27% nitroglycerine, 9% dinitrotoluene, 4% dibutyl phthalate and 1% mineral oil.

When the propellant was kept for 12 days at 100°C, compound III was transformed in mononitro- and dinitrophenyl derivatives of III.

The substance was found to be unsuitable for stabilizing simple base powder due to its insolubility in ether or ether—ethanol.
Volk [33] also described the stabilising action of a number of compounds. Some lead salts such as lead salicylate and stearate appear to possess good ‘moderating’ properties, that is, moderating the decomposition process. As mentioned previously lead salts improve the ballistic properties of propellants lowering the temperature coefficient of burning propellants and helping a ‘plateau’ burning.

**Kinetics of Decomposition**

The kinetics of decomposition of single base powder have been studied by Mayet and Lucotte [34]. They found the activation energy $E = 27.5 - 36.3$ kcal/mol for the temperature range 80–100°C.

The kinetics of decomposition have also been examined by Mrzewinski [28] who rationalized it on the basis of the change of diphenylamine. He came to the conclusion that free radical II does not play a role in the kinetics of the decomposition of powder.

**Electric Susceptibility of Single Base Powder**

Mrzewinski [28] examined the electric susceptibility of a single base powder to detect whether decomposition of nitrocellulose and changes of diphenylamine of ionic character. First the change of dielectric constant with temperature was examined. It showed a trend presented in Fig. 110, typical for dielectric polymers. There is an abrupt increase of the dielectric constant with the increase of temperature around $-12^\circ$C. The change in the dielectric constant with the age of the powder is given in Fig. 111. A similar trend was observed with laboratory ageing of powder at 106.5°C: there is a slight fall of the dielectric constant with a minimum after ca. 24 hours of keeping at this temperature. This is probably connected with the change of rational movements of fragments of functional groups.

**Erosiveness of Smokeless Powder** (Vol. III, 531, 548)

Lowering of the erosiveness of smokeless powder can be achieved by lowering its calorific value. Such is nitroguanidine containing powder (Vol. III, Tables 187, 191). Recently the addition of titanium dioxide and silicon dioxide were suggested as erosion reducing agents [47].

**MANUFACTURE OF POWDER**

**Single Base Powder**


On the other hand great progress can be seen in the manufacture of double base powder, particularly for rocket propulsion.

**Double Base Powder** (Vol. III, p. 641)

A few monographic descriptions exist, such as that by Sarner [35], collective volume [36], Encyclopedia [1] and [37], Tavernier [38].

**Traditional Double Base Powder**

Little can be added to the description of the manufacture of traditional double base powder of the ballistic type (Vol. III, pp. 647–651) where hot roll-
ing is the essential operation for manufacture (Vol. III, Figs 259, 260). Hot rolling is also the central part of the manufacture of solventless powder (Vol. III, p. 654) prior to pressing. Hot rolling in the Kemira factory (Finland) is depicted in Fig. 112.

FIG. 112. Hot rolling of double-base powder in Kemira factory (Courtesy of Kemira OY, Vihtavuori, Finland).

Rocket Double Base Powder

Monographs [36, 37] and Encyclopedia [1] are mainly dedicated to double base rocket propellants. One of the trends of making large ‘grains’ of rocket propellant charges consists in making charges by casting. The principles of the methods were given in Vol. III, pp. 675–682.

During World War II the Germans used TNT/nitrocellulose cast propellant (Vol. III, p. 681). A similar propellant was developed by T. Urbański [41] in Great Britain during World War II. It was composed of TNT, low viscosity nitrocellulose, potassium nitrate and aluminium.

As previously mentioned (Vol. III, p. 675) two methods of making cast propellants charges are known:

(1) Cast propellant,
(2) Slurry cast propellant.

CAST PROPELLANTS

Some information based on the description by Steinberger and Drechsel [40] is given here. They give the composition of single base, double base and composite cast propellants in Table 123.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Single Base</th>
<th>Double Base</th>
<th>Composite propellant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Casting powder</td>
<td>Finished propellant</td>
<td>Casting powder</td>
</tr>
<tr>
<td>Nitrocellulose</td>
<td>88</td>
<td>59</td>
<td>75</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td></td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>5</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Lead salts</td>
<td>5</td>
<td>3.4</td>
<td>6</td>
</tr>
<tr>
<td>(e.g. lead stearate)*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄ClO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stabilizer</td>
<td>2</td>
<td>1.6</td>
<td>2</td>
</tr>
</tbody>
</table>

* 'Ballistic Additives'.

Method of Manufacture

Casting powder is composed of small cylinders of ca. 1 mm diameter and length. The manufacture of casting powder consists in the operations as follows typical for smokeless powder [40]:

1. Mixing in the presence of solvents (alcohol/ether),
2. Extrusion by cutting the threads,
3. Drying to remove the volatile solvent at 60°C,
4. Finishing by polishing and covering with graphite, screening.

Propellant manufacture from casting powder and solvent consists of the following steps:

1. Filling a mould with casting powder, to occupy ca. 68% of the volume,
2. Evacuation by reducing the pressure below 10 mmHg,
3. Casting to fill the interstitial space with casting solvent – a mixture of nitrocellulose and plasticizers (Vol. III, p. 677, Fig. 270).

The casting solvent may be introduced from the top, from the bottom or radically from perforated cores.

Some types of casting powder are best cast in vacuo, and some under atmospheric pressure.
4. Curing under pressure: the solvent is introduced under pressure ca. 4 kg/cm² and a pressure of ca. 14 kg/cm² with a piston is applied on the solid (Fig. 113).

![Diagram of casting, curing, and applying ram and solvent pressure of double-base rocket propellant]

Finished propellant grain has different shapes assuring the best ballistic performance – Fig. 114, according to Steinberger and Drechsel [40]. (See also Fig. 130 in Chapter XXIII).

There is however a problem of the migration of nitroglycerine into the lining which is an inhibitor of combustion. It is usually made of polyesters (Vol. III, p. 677, Fig. 270 and Fig. 115 this volume). Caire-Maurisier and Tranchant [43] examined modifications of the composition of lining and came to the conclusion that by introducing electron accepting groups into the composition of the lining migration could be inhibited. The electron accepting groups would repel the electron acceptor which is nitroglycerine. Practically all polymers were effective in containing chlorine, for example, polymers with units of octochlorodiphenyl. On the migration of nitroglycerine in ballistite propellants – see also Vol. III, p. 651.

**SLURRY-CAST PROPELLANTS (PLASTISOL PROPELLANTS)**

(Vol. III, p. 677)

A new description of slurry-cast propellants (‘Plastisol Propellants’) has been given by Camp [44]. Fine particle spheroidal nitrocellulose is the base of the slurry-cast propellant. Olin Mathieson ball powders of various sizes (Vol. III, pp. 632–639) form a good basis for slurry cast propellants. They have been known and used for this purpose since 1947. A novel method of producing spherical nitrocellulose with an average particle size of ca. 10 μ was developed in 1959 by Naval Ordnance research units. The method consists in complete solution of nitrocellulose in nitromethane and dispersion in water with the aid of a colloid mill and an emulsifying agent.

A typical composition of the propellant is as follows [45]:

- Spheroidal nitrocellulose (12.2 or 12.6% N)
- Nitrate esters (nitroglycerine, DEGDN etc.)
- Desensitizing plasticizers (e.g. dibutyl phthalate)
- Stabilizers (centralite or 2-nitrodiphenylamine)
- Oxidizers (NH₄CLO₄, RDX)
- Metallic fuel (Al, Be)

5–20%
25–40%
0–10%
0.5–2.0%
40–50%
0–20%
Screw-extrusion Process

The worm screw extrusion process (Vol. III, p. 659) is a new and original method for the production of double-base powders developed in Germany at Dynamit Nobel A.G. A detailed description appeared recently [46]. The main part of the apparatus is a twin screw extrusion apparatus with two shafts rotating in the same direction — see the monograph by Jansen [46] — Fig. 115.

![Diagram of twin extrusion process]

**FIG. 115. Twin extrusion, according to Jansen [46].**

This is a perfection of the original single screw extrusion apparatus (Vol. III, p. 658, Fig. 266).

The paper by Homburg and Brachert [45] describes the steps as follows:

1. Mixing of ingredients under water.
2. Dehydration to 15–20% water and gelatinizing the propellant charge by kneading.
3. Granulation of the kneaded material for further dehydration and gelatinization in the granulating plant (I).
4. Blending of the granulate.
5. Second granulation in granulation plant (II).
6. Drying the granulate in the drying plant.
7. Shaping of the pellets into the raw grain, in the extrusion plant.

Kneading is a double-disc screw, that is, an eccentric disc mounted on two shafts rotating in the same direction, the screws are water cooled. Feeding of kneader is continuous. The water is thus separated from the material.

Granulation consists of steps: granulation (I) of lumpy material which returns to the mixing unit and back to granulation and to a twin-screw extruder.

Granulate I passes to the blending unit and then to granulation unit II. The material is dried and shaped in the extrusion plant with a twin-screw extrusion extruder with two shafts rotating in the same direction.

The propellant is plasticized in the twin-screw extruder and the final shape is eventually given.

The propellant is composed of nitrocellulose, nitroglycerine, plasticizer and stabilizers. The method is used to make tubes or cigarette burning cylinders.

The advantage of the described process is in it being continuous, with minimum personnel at a remote control.

Figure 117 shows a roller conveyor of the finished tubular product [45].

Bofors Nobel Chematur [48] have recently described a novel method of making a double-base powder as depicted in Fig. 118. Nitrocellulose, nitroglycerine and additives (e.g. centralite and a solvent) is to pelletize the powder paste, this is done in batches. All the ingredients are charged in the form of a slurry together with a solvent, to a pelletizer (1). The slurry is heated and the solvent makes the nitrocellulose fibres stick together in pellets of about 1 mm size. The heating continues until all the solvent is driven off and recovered. The upper and lower parts of the pelletizer are shown in Figs 119 and 120 respectively. The slurry in the pelletizer is cooled and pumped to a storage tank (2), where the pellets are settled in water. The water in that tank is used for the next pellet batch.

The pelletized material is transported as a water suspension to a screw extruder (3). The extruder drains the pellets, kneads them to a homogeneous material and extrudes through a slotted tube of propellant. The slotted tube is cut into granules (Fig. 121) by a rotating knife and stored under water in another storage tank (4). When enough material has been produced the granulate is agitated to form a uniform mixture and transferred to the second tank (5).

In an extrusion the granulate of the second storage tank is transformed into the finishing propellant by the same type of extruder as in the first extrusion step. The propellant tubes, single or multiperforated are extruded through the dies (60 directly into flowing water which transports them to a cutter. They are
FIG. 116. Twin-extrusion process of manufacturing double-base rocket propellant, according to Homburg and Brücher [45].


FIG. 119. Pelletizer of a double-base powder, upper part (courtesy Bofors Nobel Chematur).

FIG. 120. Pelletizer of a double-base powder lower part (courtesy Bofors Nobel Chematur).
cooled by water which reduces the evaporation of nitroglycerine from the cut propellants.

The propellant with a low water content constitutes a risk of explosion if ignited. For that reason the extruders are placed in a separate room. Figure 122 gives a view from inside the room for final extrusion and Fig. 123 – the cutters. The mean production is 50 kg/hr per extruder.

The factory of Bofors has experienced a few explosions caused by ignition in the extruders. The ignition was by a foreign object produced in the extruded material. The remote control operation gives a higher safety level. This new method reduces the manual work and the exposure to nitroglycerine and increases the safety of the manufacture.

**Classical Extrusion Method**

The modernized classical extrusion method of double base powder by means of a heated hydraulic press Werner and Pfeiderer is shown in Fig. 124.

**HIGHER ENERGY SMOKELESS PROPELLANTS** (Vol. III, p. 670)

The attempts to increase the energy of smokeless powder by adding a considerable amount of PETN did not pass beyond large-scale experiments. Also the use of polymers containing nitro groups (Chapter XIV) does not seem to have a practical application for propellants.
Nevertheless there are continuing attempts to introduce such compounds as RDX and HMX into smokeless powder. Thus Sumi and Kubota [49] described double base powder containing up to 27% HMX. The propellant was characterised by a low exponent $n$ even at low pressure: $n = 0.3$ at 20 atm.

The addition of RDX or HMX into composite propellants is also known — see Chapter XXIII.

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INTRODUCTION

Roth and Capener [1] formulate composite propellants as follows:

'Composite propellants which are used almost entirely in rocket propulsion normally contain a solid phase oxidizer combined with a polymeric fuel binder, with a \(-\text{CH}_2-\text{CH}_2\) structure. Practically speaking ammonium perchlorate is the only oxidizer which has achieved high volume production, although ammonium nitrate (AN) has limited special uses such as in gas generators. Other oxidizers which have been studied more or less as curiosities include hydrazinium nitrate, nitronium perchlorate, lithium perchlorate, lithium nitrate, potassium perchlorate and others. Among binders, the most used are: polyurethanes, polybutadiene/acrylonitrile/acrylic acid terpolymers and hydroxy-terminated polybutadienes.'

According to recent information [2], the space shuttle's orbiter Columbia was powered by two solid rocket motors with a propellant which consists of:

- ca. 70% Ammonium Perchlorate (AP),
- 16% Al powder,
- 12% polybutadiene-acrylic acid-acrylonitrile (PBAN) terpolymer (a combustible binder),
- 2% liquid epoxy resin (a curing agent), and in addition
- 0.17% iron oxide powder (as a catalyst).

Each rocket motor is loaded with more than one million pounds (ca. 454,000 kg) of solid propellants.

The problems of Composite Propellants is a fast developing branch of propellants chemistry and technology. The following are monographs (in addition to those mentioned in Vol. III) dedicated to composite propellants: [3–8, 27]. The Encyclopedia of Kaye [1] and collective volume [6] are particularly important sources of information.

A vast amount of work is being done and continuing progress now merits a special modern monograph. Only the principles of the formulation of composite propellants and their manufacture will be given here. The description will be based on different polymeric binders mainly with ammonium perchlorate. Some data on the thermal decomposition of ammonium perchlorate will be given here to complete the information in Chapter XVI.

An important feature of ammonium perchlorate propellants is their decomposition at high temperature. Differential thermal analysis of NH₄ClO₄ is given in Fig. 125, according to Sarnar [4]. It can be seen that appreciable decomposition occurs at temperatures lower than the main exotherm.

![FIG. 125. Differential thermal analysis of NH₄ClO₄ from Propellant Chemistry by Stanley Sarnar [4]. Copyright © 1966 by Van Nostrand Reinhold Company. Reprinted by permission of the publisher.](image)

The ammonium perchlorate crystal size is of great importance.

Baldwin and Reed [24] give figures for the rate of burning of ammonium perchlorate composite propellant depending on the size of crystals of the salt as:

<table>
<thead>
<tr>
<th>Particle size of NH₄ClO₄</th>
<th>Rate of burning cm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 (\mu)</td>
<td>5.1</td>
</tr>
<tr>
<td>35 (\mu)</td>
<td>6.1</td>
</tr>
<tr>
<td>15 (\mu)</td>
<td>7.6</td>
</tr>
<tr>
<td>5 (\mu)</td>
<td>9.2</td>
</tr>
</tbody>
</table>
POLYURETHANE BINDERS

As is known, urethanes are formed by reacting isocyanates with hydroxyl carrying compounds:

$$RHCN + R'OH \rightarrow R_{2}NCOOR'$$  \hspace{1cm} (1)

With di- or polyfunctional isocyanates and dihydroxylic compounds a rubbery polymer is obtained and with tri-hydroxylic alcohols cross-linked polymers are formed.

The most common polyurethane binders are from 2,4-toluene diisocyanate (TDI) obtained from 2,4-dinitrotoluene by the sequence of reactions (2):

$$\text{and long chain glycols with primary and secondary alcoholic groups. According to Oberth and Bruenner [9] among the glycols are those with: (a) an ester function, e.g. I:}$$

$$(b) \text{and ether function as poly (1,2-oxypropylene)dial (PPG) of } M = \text{ca. 2000.}$$

$$(c) \text{polybutadiene chain.}$$

Binder (b) and (c) are more advantageous than (a).

Binders (b) are more readily available, show a low viscosity, good rate of cure and good ageing stability. Their disadvantage is ease of absorbing oxygen to form peroxides, but the addition of aromatic amine antioxidants removes this disadvantage. They withstand prolonged storage (several years) at temperatures of 65–82°C without the loss of mechanical properties.

TABLE 124. Polyurethane resin propellants JPL XS900

<table>
<thead>
<tr>
<th>Components</th>
<th>70%</th>
<th>80% Oxidizer</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄ClO₄</td>
<td>21.0</td>
<td>24.0</td>
</tr>
<tr>
<td>unground*</td>
<td>49.0</td>
<td>56.0</td>
</tr>
<tr>
<td>Polypropylene glycol</td>
<td>23.9</td>
<td>15.9</td>
</tr>
<tr>
<td>Toluene Diisocyanate (TDI)</td>
<td>4.8</td>
<td>3.2</td>
</tr>
<tr>
<td>1,2,6-Hexanetriol (HT)</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Ferric acetyl acetone</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

* A trimodal oxidizer system is used, consisting of 30% ground and 70% unground ammonium perchlorate.

The propellant shows good mechanical properties (tensile strength, elongation and initial modulus) at temperatures from –40° to +70°C.

By the addition of aluminium (and beryllium) higher energy propellants are formed. Figure 126 gives, according to Oberth and Bruenner [9], the calculated specific impulse of ammonium perchlorate–aluminium–polyurethane (poly-ether) binder (max. $I = 247$ s).

POLYBUTADIENE BINDERS WITH CARBOXYLIC FUNCTION

The polybutadiene polymers containing carboxyl functional groups appear to be the most important group of binders in composite propellants. The following are co-polymers used in this type of propellant, according to Mastroll and Klager [11]:

1. butadiene and acrylic acid (PBAA).
2. terpolymer of butadiene, acrylic acid and acrylonitrile (PBAN).
3. the carboxyl terminate polybutadiene (CTPB).

Here is a brief description from the same source [11]:

1. PBAA was the first butadiene polymer to be used in rockets. It was made by free radical emulsion polymerization to an average $M = 3000$. It was a random mixture of polymers of different molecular weights and functionality.
and therefore did not possess proper mechanical properties. The use of such polymers was eventually discontinued.

(2) PBAN was also made by emulsion polymerization. Mechanical properties of polymer were improved through steric action by introducing acrylonitrile. Also acrylonitrile reduced deteriorating action of oxygen on double bonds of the polymer as known to be suppressed in nitrile rubber.

The following are data for the physical properties of PBAN:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>3000–4500</td>
</tr>
<tr>
<td>Viscosity at 25°C</td>
<td>300–350 poise</td>
</tr>
<tr>
<td>Density</td>
<td>0.93–0.94</td>
</tr>
</tbody>
</table>

The composition of propellants with PBAN and of increased energy through the addition of Al is kept within the limits in wt. %:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄ClO₄</td>
<td>60–84</td>
</tr>
<tr>
<td>PBAN</td>
<td>12–16</td>
</tr>
<tr>
<td>Al</td>
<td>2–20</td>
</tr>
<tr>
<td>Stabilizer</td>
<td>0–1</td>
</tr>
<tr>
<td>Curing agents</td>
<td>0.2–1.0</td>
</tr>
</tbody>
</table>

The resistance against the action of oxygen can be seen from the effect of keeping the propellant in oxygen atmosphere at 105°C at 96 hours.
Here is an example of the composition of a CTPB propellant according to [28]:

- Ammonium perchlorate: 80.0–80.9%
- Al powder: 5%
- CTPB: 14
- Ferric oxide: 0.1–1.0

HYDROXYTERMINATED POLYBUTADIENE BINDER (HTPB)

An example of a composite propellant with hydroxyterminated polybutadiene binder is given here [28]:

- Ammonium perchlorate: 77.6–76.0%
- Al powder: 10
- HTPB: 11.6
- Ferric oxide: 0.4–2.0

CURING BUTADIENE POLYMERS

Carboxyl terminated polybutadiene polymers require curing in order to form a tridimensional network. Polyfunctional epoxides and aziridines are used for cross-linking.

When making propellants with ammonium perchlorate the oxidizing properties of the latter produce side reactions interfering with the action of the curing agent. This involves the formation of a less complete three-dimensional structure.

The structure of a few epoxide and aziridine curing agents are given (II–VIII).

Epoxy compound IV exhibits a minimum of side reactions in the presence of ammonium perchlorate. Epoxy curing agent II shows a high reaction rate but side reactions dominate in the presence of ammonium perchlorate. The compound BITA (V) can be subjected to various transformations shown in scheme (6). They also possess similar properties as V but are less active. Zirconium...
acetylacetone is an effective polymerization catalyst and can be added in quantity 0.5 wt. %. Propellants made with MAPO (VII) possess good properties but a problem arises with ageing, probably due to the presence of P–N bond. A mixed curing agent made of VII and II gave more satisfactory results.

The fact that a variety of reactions given by different curing agents led to developing mixed curing agents composed of both epoxy- and aziridine compounds. This is still a developing side of problems of composite propellants—a specialized problem—connected with polymer chemistry and technology and outside the scope of the present book.

Figure 127 gives theoretical specific impulse for ammonium perchlorate-Al-polybutadiene propellants. The maximum specific impulse was calculated as high as \( I_s = 266 \) [11].

**POLY (VINYL CHLORIDE) PLASTISOL PROPELLANT (PVC)**

According to the description by Rumbel [12] PVC plastisol propellant consists of ammonium perchlorate, uniformly dispersed and cured PVC plastisol. A number of propellants have been developed by the Atlantic Research Corporation under the name Arcite.

Standard Arcite has the composition in wt. %:

- \( \text{NH}_4\text{ClO}_4 \) (equal parts of coarser and finer passing through mesh 62 \( \mu \)) 75.0
- PVC 12.5
- Plasticizer (dibutyl sebacate) 12.5
- Stabilizer (undisclosed compound) added 0.4

The influence of adding aluminium (or magnesium) to increase the specific impulse \( I_s \) up to 242 s is given in Fig. 128. One of the aluminized propellants Arcite 373 D has the composition in wt. %:

- \( \text{NH}_4\text{ClO}_4 \) 58.9
- Al 21.1
COMPOSITE PROPELLANTS

HIGH ENERGY COMPOSITE PROPELLANTS WITH HMX (OCTOGENE)

Attempts have been made to introduce HMX into composite propellants. According to Sayles [13] propellant ‘D’ is composed of:

- Ammonium perchlorate 19.2 wt. %
- Butanetriol trinitrate 25.7
- HMX 48.5
- Ethyl acrylate-acrylic and co-polymer (EA/AA, 95/5) 4.6
- Diepoxydicyclohexyl carboxylate (curing agent) 1.5
- Carbon black 0.5
- Specific impulse $I_p = 262.4$
- RDX can be substituted for HMX.

Some other composite propellants were suggested with nitrogen difluoride groups, for example 1,2,3-tris[1,2-bis(difluoroamino)ethoxy propane] but high cost of the compound did not seem to encourage its use [1].

ROLE OF INGREDIENTS ON PROPERTIES OF COMPOSITE PROPELLANTS

This problem is discussed in detail by Fluke [14] and here is a brief description of his paper.

Ammonium perchlorate of various fineness is used to give a better ‘packing’. Particle size distribution is of great importance to density, rheological properties of the viscous mass, mechanical properties and burning of the propellant. Rheological properties obviously depend on polymer binder which is of course the combustible ingredient in propellants.

Here are some of the outlines given by Fluke on this particular matter:

1) **Formula optimization.** In the formulation of new propellants, it may be desirable to optimize certain rheological characteristics.

2) **Formulation characterization.** Prior to using a new propellant formulation, the material should be fully characterized and analyzed rheologically. Processability predictions may be extrapolated.

In quality control it is necessary to check rheological properties of propellant samples.

In addition to the above, the following are remarks on some components of composite propellants according to the existing literature.

Plasticizers have a very important effect on physical properties of the cured propellants and on the variation of these properties with temperature. Long chain aliphatic plasticizers improve low temperature flexibility. An increase in plasticizer viscosity obviously leads to an increase in viscosity of the mixed pro-

---

**Figure 128.** Increase of specific impulse of PVC Plastisol Propellants by adding Al and Mg according to Rumble et al in [12].

A stabilizer is added to retard the decomposition of PVC during curing, which is carried out at 150–175°C. Because of low thermal conductivity, several hours are required to raise the central portion of the propellant grain to curing temperature. The portions of the grain close to the source of heating may show a tendency to decompose and stabilizers are added to inhibit the decomposition. It is advisable that the stabilizer should be able to bind the hydrogen chloride which would decompose the polymer. However propellants with aluminium powder show better thermal conductivity and hence the time of cure can be reduced.

This is of course related to all composite propellants with aluminium.
CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

The burning rate is little changed by changing plasticizers.

Attention should be paid to preventing the formation of cracks and voids during cure [15], which are caused by shrinkage during solidification of the propellant. Specific processing conditions are required for each propellant formulation and rocket size according to Arendale [15].

Wetting agents in propellant compositions facilitate mixing ingredients and reduce the viscosity so that they are cast more readily.

Metals

Aluminium should be used in spheroidal shaped particles [12]. It gives a better pourability of the compositions [16].

A very important observation was recently made by Rumble [12]. This is the incorporation of fine metal wires into a propellant, which increase the rate of burning as recorded originally in PVC plastisol propellants [12] but seems to be now a general practice in composite propellants. Metal wires are introduced into the composition before cure. When the propellant is burned the wires extend from the unburned propellants into the flame zone. They provide paths for rapid heat transfer and thus burning along the wire is faster than outside the wire. Particularly efficient are silver and copper wire, as described by Rumble — for PVC plastisol propellants (Table 125).

<table>
<thead>
<tr>
<th>Wire</th>
<th>Burning rate along wire cm/s</th>
<th>Ratio of burning rate along the wire standard</th>
<th>Properties of metal melting temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>6.76</td>
<td>5.3</td>
<td>960</td>
</tr>
<tr>
<td>Copper</td>
<td>5.92</td>
<td>4.6</td>
<td>1083</td>
</tr>
<tr>
<td>Aluminium</td>
<td>2.96</td>
<td>2.3</td>
<td>660</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2.45</td>
<td>1.9</td>
<td>651</td>
</tr>
<tr>
<td>Steel</td>
<td>2.04</td>
<td>1.6</td>
<td>ca. 1460</td>
</tr>
</tbody>
</table>

Also aluminium staple was suggested [17] together with aluminium powder in composite propellant containing MAPO (VII) curing agent.

Catalysts (Vol. III, pp. 369, 394)

The role of catalysts on burning ammonium perchlorate and other salts, such as ammonium nitrate, potassium perchlorate etc. is widely described in the monograph by Glazkova [18].

Cohen Nir [19] described the catalytic action of Cu₂O and powdered metals — Al, B, Mg — on steady burning of ammonium perchlorate under low pressure.

The catalytic action of iron oxides (mainly ferrous oxide) was described by Bakhman and co-workers [20]. They also reviewed the literature on the catalytic action of Fe, Fe₂O₃, Fe₃O₄, organo-iron compounds, CO₂O₃, NiO, Cu, Cu₂O, CuO, Cu chromite, Cu chlorides, Cr₂O₃, salts of chromic acid, MnO₂, K₂Mn₄O₁₀, V₂O₅, SiO₂, TiO₂.

Iron oxide catalyst mentioned in the description of the space shuttle's orbiter Columbia [2] was probably ferric oxide or a mixture of various iron oxides.

BURNING COMPOSITE PROPELLANTS CONTAINING AMMONIUM PERCHLORATE

It has been shown that perchloric acid is liberated from the solid fuel and reacted further. Gilbert and Jacobs [21] found that the major products of decomposition of perchloric acid are oxygen and chlorine which further react with organic compounds to yield CO, HCl, H₂ and chlorinated short chain hydrocarbons. The mechanism of burning comprises the depolymerization of the organic solid phase to give gaseous fuel fragments which react further [22].

Stein and Summerfield [23] reviewed existing theories on burning ammonium perchlorate under pressure between one and 100 atm, and built a schematic presentation of the mechanism. In the first stage the dissociation occurs of NH₄ClO₄ into NH₃ and HClO₄ (A/PA) and reacted with oxidant/fuel (O/F) zone.

The pressure exponent n around 100 atm for ammonium perchlorate propellants is ca. 0.3.

Pepekin, Apin and co-workers [28] attempted to rationalize the rate of burning of composite propellants with ammonium perchlorate as a function of the combustible ingredient. They came to the important conclusion that the rate of burning did not depend on the heat of burning, but on the strength of the chemical bond in the combustible substance. A striking example was given by a system with ferrocene. On the basis of the enthalpy of the bond C—Fe (which is 75.0 kcal/mol) it should be expected that the burning rate would be similar to that of ammonium perchlorate with amines. The latter have the enthalpy of the bond C—N equal to 73 kcal/mol. However experiments show that the rate of burning of mixtures of ammonium perchlorate with ferrocene are nearly three times higher than that of ammonium perchlorate with amines.

The authors found an empirical equation:

\[ u = 0.9 - 0.005E \text{ cm/s}, \]

where

\[ u \] — the rate of burning of the mixture,
\[ E \] — the energy of the weakest bond of the combustible material.

The bond C—Fe in ferrocene is very weak and ferrocene readily dissociates according to the equation:
owing to such disadvantages as high hygroscopicity, relatively difficult ignitability and polymorphism at different temperatures combined with a change of density (see Chapter XVI).

Potassium perchlorate shows a high exponent \( n = ca. 0.8 \) in equation rate of burning/pressure. It also gives high temperature of burning which can readily produce corrosion of the nozzle.

The other perchlorates, such as hydrazinium, hydroxylaminium and nitronium perchlorates etc. are at present of theoretical interest only. Some of them (e.g. hydrazinium perchlorate) shows poor chemical stability and high sensitivity to mechanical shock.

Also hydrazinium nitrate does not seem to be a promising oxidizer.

MECHANICAL PROPERTIES

The mechanical properties of solid propellants are discussed by Kelly [25]. In the U.S.A. the methods are based on instructions worked out by a Joint Army-Navy-Air Force (JANAF) Physical Properties Panel and include uniaxial and multiaxial measurements of mechanical strength.

They also include examination of the uniformity of the structure, detection of voids and cracks by X-ray examination.

The problems of testing mechanical properties are outside the chemical problems and are therefore not included in the present book.

MANUFACTURE OF COMPOSITE PROPELLANTS (Vol. III, p. 373)

The principles of the manufacture of composite propellants outlined in Vol. III are still valid. They are also described by Fluke [14] who gave a few schematic presentations for preparing the mixtures.

In principle they consist of:

(a) preparation of oxidizer (grinding, screening, mixing),
(b) binder and fuel preparation (polymerization),
(c) chamber insulation and lining,
(d) mixing of the propellant, casting into the chamber and lining,
(e) extraction of the grain from the chamber.

Mixing should be carried out in a kneading apparatus of the type shown in Figs 102 and 103. It should be done in a well defined sequence [16]. It is advisable to add ammonium perchlorate at the end after aluminium has been added. This is for safety reasons, as finely ground aluminium with ammonium perchlorate can form a dangerous dust when suspended in air.

Curing should not be carried out at a temperature above 80°C. After curing the extraction of the grains from the chamber can easily be done because of the shrinkage of the propellant mass.
Pneumatic mixing of ingredients developed by the Naval Propellant Plant was depicted in Vol. III, p. 390, Fig. 125.

As an illustration of mixing large charges, the following description can be given for preparing propellant for the shuttle's orbiter "Columbia".

The formula is prepared in 7000 lb (ca. 3170 kg) batches at a remote complex in Utah operated by Thiokol Corp. The giant mixing bowl is of 2270 l capacity. Mixing consists of the following steps: aluminium powder, PBAN (polybutadiene acrylic acid-acrylonitrile) polymer and ferric oxide powder are mixed. Then the epoxy curing agent is added without mixing so as to delay the start of the curing reaction. The bowl containing this premix is transported by trailer to another building where ammonium perchlorate is added and blended by remote control for explosive properties of ammonium perchlorate and the operation should be considered as dangerous.

The mixing bowl is transferred to another site where the propellant is poured into casting segments. Each booster is built from four such segments assembled in a reusable steel casing. It takes 20 hours to fill one casting segment. The mixture is then cured at 57°C for four days and takes on the consistency of hard rubber.

**SHAPES OF THE PROPELLANT GRAINS (Vol. III, p. 366)**

A full description of possible shapes of grains and the pressure developed with time of burning has been given in a monograph [3] and is partly reproduced here — Fig. 130.

The most advantageous are shapes (2-cigarette burning), (3) and others (7-10) giving a constant or nearly constant pressure. Tube without inhibiting layers (4) and plain (1) are used when a high initial thrust is needed. Shape (5) and particularly (6) are much appreciated when a high thrust at the later stage of burning is required.

**EXPLOSIVE PROPERTIES OF COMPOSITE PROPELLANTS (Vol. III, p. 393)**

As mentioned in Vol. III, composite propellant detonate with difficulty because of their non-porous texture and very high density.

When in powdered form they behave as most explosives: sensitive to friction and impact and detonate readily when in low density.

According to information given in the Encyclopedia [1] the standard propellant made of ammonium perchlorate, PBAN and aluminium can detonate when RDX is added. Thus with 4.75, 7.1 and 9.2% the critical diameters were found to be: 28.2, 13.2 and 6.9 cm respectively. No rate of detonation was given.

Bernecker and Price [26] determined the rates of detonation of mixtures of ammonium perchlorate and wax (Table 126).

---

<table>
<thead>
<tr>
<th>Shaped</th>
<th>Image 1</th>
<th>Image 2</th>
<th>Diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Plain cylinder</td>
<td><img src="image1" alt="1 Plain cylinder" /></td>
<td><img src="image2" alt="1 Plain cylinder" /></td>
<td><img src="diagram" alt="1 Plain cylinder" /></td>
</tr>
<tr>
<td>2 Plain cylinder inhibited on perimeter &quot;Cigarette burning&quot;</td>
<td><img src="image1" alt="2 Plain cylinder inhibited on perimeter &quot;Cigarette burning&quot;" /></td>
<td><img src="image2" alt="2 Plain cylinder inhibited on perimeter &quot;Cigarette burning&quot;" /></td>
<td><img src="diagram" alt="2 Plain cylinder inhibited on perimeter &quot;Cigarette burning&quot;" /></td>
</tr>
<tr>
<td>3 Tube inhibited on the side of the perimeter</td>
<td><img src="image1" alt="3 Tube inhibited on the side of the perimeter" /></td>
<td><img src="image2" alt="3 Tube inhibited on the side of the perimeter" /></td>
<td><img src="diagram" alt="3 Tube inhibited on the side of the perimeter" /></td>
</tr>
<tr>
<td>4 Tube without an inhibitor</td>
<td><img src="image1" alt="4 Tube without an inhibitor" /></td>
<td><img src="image2" alt="4 Tube without an inhibitor" /></td>
<td><img src="diagram" alt="4 Tube without an inhibitor" /></td>
</tr>
<tr>
<td>5 Tube inhibited on the perimeter</td>
<td><img src="image1" alt="5 Tube inhibited on the perimeter" /></td>
<td><img src="image2" alt="5 Tube inhibited on the perimeter" /></td>
<td><img src="diagram" alt="5 Tube inhibited on the perimeter" /></td>
</tr>
<tr>
<td>6 Cross section shape, inhibited on ends of the perimeter</td>
<td><img src="image1" alt="6 Cross section shape, inhibited on ends of the perimeter" /></td>
<td><img src="image2" alt="6 Cross section shape, inhibited on ends of the perimeter" /></td>
<td><img src="diagram" alt="6 Cross section shape, inhibited on ends of the perimeter" /></td>
</tr>
<tr>
<td>7 Ring forming tube, inhibited on perimeter and ends</td>
<td><img src="image1" alt="7 Ring forming tube, inhibited on perimeter and ends" /></td>
<td><img src="image2" alt="7 Ring forming tube, inhibited on perimeter and ends" /></td>
<td><img src="diagram" alt="7 Ring forming tube, inhibited on perimeter and ends" /></td>
</tr>
<tr>
<td>8 Star shaped channel, inhibited on the perimeter and sides</td>
<td><img src="image1" alt="8 Star shaped channel, inhibited on the perimeter and sides" /></td>
<td><img src="image2" alt="8 Star shaped channel, inhibited on the perimeter and sides" /></td>
<td><img src="diagram" alt="8 Star shaped channel, inhibited on the perimeter and sides" /></td>
</tr>
<tr>
<td>9 Multichannel tube, inhibited on the perimeter</td>
<td><img src="image1" alt="9 Multichannel tube, inhibited on the perimeter" /></td>
<td><img src="image2" alt="9 Multichannel tube, inhibited on the perimeter" /></td>
<td><img src="diagram" alt="9 Multichannel tube, inhibited on the perimeter" /></td>
</tr>
<tr>
<td>10 Wire shaped channel, Tube inhibited on the perimeter</td>
<td><img src="image1" alt="10 Wire shaped channel, Tube inhibited on the perimeter" /></td>
<td><img src="image2" alt="10 Wire shaped channel, Tube inhibited on the perimeter" /></td>
<td><img src="diagram" alt="10 Wire shaped channel, Tube inhibited on the perimeter" /></td>
</tr>
</tbody>
</table>

**FIG. 130. Shapes of grains and pressure against time of burning according to Krowicki and Syczewski [3].**
## CHEMISTRY AND TECHNOLOGY OF EXPLOSIVES

### TABLE 126. Rates of detonation of ammonium perchlorate–wax mixtures [26]

<table>
<thead>
<tr>
<th>Composition</th>
<th>Density</th>
<th>Diameter cm</th>
<th>Critical diameter cm</th>
<th>Rate of detonation m/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄ClO₄</td>
<td>Wax</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>0.93</td>
<td>7.62</td>
<td>0.65–0.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.20</td>
<td>7.62</td>
<td>0.65–0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.52</td>
<td></td>
<td>ca. 5</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>0.91</td>
<td>7.62</td>
<td>0.65–0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.10</td>
<td>7.62</td>
<td>0.65–1.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.40</td>
<td></td>
<td>ca. 5</td>
</tr>
</tbody>
</table>

The above figures can give an approximate idea of the rates of detonation of ammonium perchlorate, PBAN and aluminium.

## REFERENCES

9. A. E. OBERTH and R. S. BRUENNER, in [6], p. 84.
12. K. E. RUMBEL, in [6], p. 36.
15. W. F. ARENDALE, in [6], p. 67.
23. J. A. STEINZ and M. SUMMERFIELD, in [6], p. 252 and references therein.
25. F. M. KELLY, in [6], p. 188 and references therein.

## CHAPTER 24

### PROBLEMS OF SAFETY IN THE MANUFACTURE AND HANDLING OF EXPLOSIVES

The fact that explosive molecules are designed in such a way that they should burn, explode or detonate requires of course that their manufacture, handling and transportation should be carried out with special precautions.

Wide monographs recently appeared on problems of hazards and safety with explosives [14, 15].

### MANUFACTURE

Precautions which are necessary in the processes of manufacturing explosives were described in the texts dedicated to their manufacture. However, there are a few principles common to all processes. These are:

Remote control of the functioning of production apparatus which should be provided with the elements connected to the remote control. The following are the most dangerous to manufacture:

(a) black powder,
(b) nitroglycerine and similar O-nitro compounds,
(c) initiating explosives and their mixtures.

Remote control ensures that not a single person is present in the proximity of the production apparatus.

There is however a danger when automation is not functioning correctly and has ceased to be reliable. This may lead to a disaster (e.g. an accident in Biazzini nitroglycerine plant in Bhandara, India in 1975) [1]. In this case automation became dangerous. There is always a need for human control in the functioning of automation.

The remote control of temperature is needed in the course of nitration as described in Chapters VI, VIII, XI, XII and in making initiating explosives and their mixing, mixing of commercial explosives (Chapter XX), making smokeless powder (Chapter XXII).
SAFETY IN MANUFACTURE AND HANDLING OF EXPLOSIVES

STATIC ELECTRICITY

A great danger exists wherever there is friction and this is through charging with static electricity which on discharging may produce ignition. There are dangerous parts of the manufacture of explosives from that point of view, such as mixing and kneading apparatus, rollers of double and treble-base powder, rotating drums (Vol. III, p. 625), in flowing flammable liquids through the pipes (Vol. III, p. 589) and air with flammable vapours (Vol. III, p. 607), compression of air containing flammable vapours in the course of extrusion of smokeless powder with a volatile solvent (Vol. III, p. 595), friction between the stream of air and the grains of propellants (Vol. III, p. 603), cutting, screening and blending of propellants.

A few monographs have appeared on static electricity and the danger connected with the discharge of it producing explosions of gas mixtures, inflammable dust or even inflammable liquids or solids. These are monographs by Freytag [2] and Haase [3]. Also a book by Gugan should be consulted [4].

The principal method of avoiding the danger of the discharge of the static electricity is to earth all parts of machinery which are subjected to friction.

A general method of avoiding an accumulation of static electricity incorporating substances conducting electricity into the explosive on condition that the manufacturing apparatus is earthed. Relatively high humidity of the atmosphere (wherever it is not harmful to the production [8], ionization of the atmosphere by irradiation with γ- or X-rays are other factors which help in avoiding the accumulation of static electricity [9].

The addition of conducting substances to explosives is a general method of preventing the charging of explosives with static electricity. The conducting substances comprise graphite (a particularly frequent component of smokeless powder Vol. III, p. 625), aluminium powder wherever it can be included in the composition of explosives without creating a new danger (it is known that the addition of aluminium to black powder gives dangerous compositions). Where neither of these substances can be included into the formulation of explosives, some organic conductors, usually CT-complexes (Charge–Transfer complexes) or ionic surface active agents can be added in a small proportion (below 0.5%).

Addition of such surface active agents was recently recommended in a patent by Wielgus, Zdrojek and co-workers [10]. Surface active agents were earlier recommended [11] in the textile industry where the problem of static electricity is particularly important (through friction).

The recent facts on new conducting polymers [13] should be used to examine its action against the accumulation of static electricity, provided they are not harmful to the stability of the powder. Particularly interesting seem to be polyacetylene or poly-p-phenylene arsenic pentafluoride.

Conductive rubber (with graphite or Al dust) is highly recommended and often compulsory for the soles of workers' shoes, and conductive mats and car-

pets where certain explosives are handled.

The charging of smokeless powder was described in detail by Uetake and Sato [12]. See also Vol. III, pp. 542–543, 682, 684.

For one exceptional sensitivity of lead stypnate to static electricity and danger of discharge see Vol. III, pp. 217–218.

FOREIGN BODIES IN MIXING MACHINES

Foreign bodies present by accident or carelessness in mixing machines, such as kneaders have frequently been responsible for accidents. The otherwise safe kneaders of Drais, Biazzi, Werner and Pileiderer can become a source of danger. A few accidents of this type have been described by Biasuti [1].

CONSTRUCTION OF EXPLOSIVE FACTORIES

There is currently a tendency to construct buildings for the manufacture and storage of explosives which could prevent the propagation of a shock wave and thus reduce the area of destruction. Such were heavy underground buildings for some time favoured in Germany (e.g. Vol. II, p. 122, Figs 62, 63).

According to Kaye [5] currently much in use are laced concrete walls (Fig. 131) forming a shock wave barrier, but more modern designs are those of 'suppressive structures'. They are made of new 'suppressive structures' of several layers of louvered and perforated plates of angle iron and 'z' bars. This allows controlled release of blast effects from a detonation within the structure. Subsequently a controlled release of blast effects occurs.

DETECTION OF HIDDEN EXPLOSIVES IN LUGGAGE

The increasing number of acts of terrorism particularly dangerous in airflights have made it necessary to find methods of detecting explosives hidden in luggage. Helf [6] gave a detailed description of the existing method, which consists in irradiating the luggage or suspect package with fast neutrons followed by the measurement of γ-irradiation from the activated explosive if present in the examined package. It is based on the assumption that most explosives contain nitrogen — usually greater than in items present in luggage.

Here is a description of the process as given by Helf: 'when an explosive is irradiated with fast neutrons a 14N nucleus captures the incident fast neutron and ejects two slow neutrons. The resulting nucleus 13N is radioactive and decays with a 10 min half-life to stable 13C. In this last transition a positron β+ is emitted. Because of its opposite charge, the β+ is strongly attracted by the nearby electron; in the resulting collision, both the positron and electron are annihilated and in that process the masses of colliding particles are converted into two 0.511 MeV quanta of electromagnetic radiation.'
These γ-rays are what are detected to indicate the possible presence of an explosive.

Figure 132 gives a scheme of the functioning of the apparatus worked out by North American Rockwell Corp. (Los Angeles) "A conveyor belt transports the luggage first past a neutron generator and then past a detector. The radiation detected is amplified, analysed and compared with a preset threshold. If the detected radiation surpasses the threshold, a visual alarm is activated."

Both generator and detector should be heavily shielded by concrete and lead to protect the environment from the harmful radiation.

The drawback of this system is in the fact that harmless substances containing nitrogen, such as wool and synthetic fibres can give a signal similar to that of explosives.

Picatinny Arsenal [6] developed a method of activating both nitrogen and oxygen considering that explosives contain a characteristic ratio N/O and thus lower the proportion of false alarms.

FIG. 132. Fast neutron activation system for the inspection of airline luggage for the presence of hidden explosives, according to Helf [61].

TAGGING OF COMMERCIAL EXPLOSIVES

It is now required in the United States that commercial explosives should be "tagged" in such a way that the detection and post-detonation identification of explosives should be possible. Materials added to explosives for these purposes are called taggants.

The information on taggants was given by Boyars [7]. They are tiny coded particles added to explosives during their manufacture that can survive detonation in sufficient quantity to be recovered and decoded and, through distribution records, allow the explosives to be traced back to the last legal possessor. They are incorporated in quantities of 0.05% or less by the explosives manufacturers.

They are made of a laminated melaminealdehyde core encapsulated in polyethylene wax. The core is colour coded by the inclusion of pigments. One of the layers contains iron particles to make the taggant magnet-sensitive and one or both exterior layers contain fluorescent compounds which respond to ultraviolet radiation.

Obviously they should not increase the sensitivity to impact, friction and chemical (thermal) stability.
GENERAL DESCRIPTION OF SAFETY

A general description of safety in the manufacture, handling and storage of reactive chemicals and mainly of explosives is described in a Japanese book [14]. It contains chapters on:

1. Fire and explosion hazards from reactive chemicals
2. Estimation of energy hazards
3. Computational prediction of explosion, deflagration and exothermic decomposition
4. Standard tests for reactive chemicals
5. Screening tests
6. Comprehensive evaluation
7. Activities of safety organization in various countries
8. Emergency response system for hazardous material
9. Earthquake countermeasures.

REFERENCES


CHAPTER 25

TOXICITY OF EXPLOSIVES

The toxicity of explosives was described in Vols I—III and more information has appeared recently as a result of the progress of toxicology and hygiene. Thus the former information needs some additions. An excellent review of the toxic properties of more important explosives was recently given by Rosenblatt [1]. Some information from this and other sources will be given below.

AROMATIC NITRO COMPOUNDS

m-Dinitrobenzene

The toxicity of this compound is of a great importance because of its intensity and also because of the importance of the substance as an intermediate in organic industry. The toxicity of m-DNB was described in Vol. I, pp. 240–242 and also in this volume: Chapter VI, refs [8, 82, 83]. Many fatal accidents have been attributed to poisoning by TNT were caused in fact by the impurities of TNT produced by the presence of small proportions of m-DNB. Rosenblatt [1] reported that 24,000 cases of poisoning with TNT were recorded during World War I and out of this 580 were fatal. During World War II the number of fatalities was only 22.

This should be attributed not only to better hygiene (as pointed out by Rosenblatt) but also to the higher purity of TNT, because of a higher purity of toluene used for the nitration.

As already pointed out (Vol. I, p. 240) dinitrobenzene affects haemoglobin and damages the liver.

2,4-Dinitrotoluene

This compound – an intermediate in the formation of TNT, can also be an impurity of TNT. The symptoms of poisoning are similar to poisoning with other nitro compounds the chief clinical findings are [1]: pallor, cyanosis and anaemia in which the blood cells are of normal size and contain normal amounts of haemoglobin. Patients recover from DNT poisoning after being treated in a DNT free atmosphere.
Chemistry and Technology of Explosives

The lethal dose in rats (LD₅₀) was found to be 568–650 mg/kg. Dogs showed high sensitivity: doses 20–25 mg/kg/day were toxic in subchronic test which lasted 90 days, and in some cases were lethal. It was also found that 2,4-DNT is carcinogenic in mammalian animals.

2,4,6-Trinitrotoluene

TNT exposures can occur by inhalation of the dust, through ingestion and via skin absorption [1]. The action of TNT produces changes in blood: the red blood cells count and haemoglobin content decreases on longer exposure because the activity of the bone marrow is lowered. Another type of symptoms are due to atrophy of the liver. No carcinogenic effect has been recorded in men or animals.

The maximum permissible inhalation level in U.S.S.R. is 1.0 mg/m³ and in the U.S.A. Army 0.5 mg/m³.

The lethal dose by oral administration (LD₅₀) in rats is 820–1010 mg/kg.

Among metabolites in humans the following were identified: 4-amino- and 6-amino-dinitrotoluene, tetranitrozoxotoluene, 2-hydroxydiamino-4,6-dinitrotoluene, 2,4-diamino-6-nitro- and 2,6-diamino-4-nitrotoluene, 2,4,6-trinitrobenzoic acid. A former finding that TNT is toxic to fish has been confirmed.

'Red water' from the treatment of TNT with sodium sulphite is more toxic than TNT, this is mainly due to the presence of dinitrotoluene derivatives.

Aliphatic Nitro Compounds

2-Nitropropane

2-Nitropropane is being used extensively in the U.S.A. as a solvent. It was recently reported that prolonged exposure of rats to the action of 2-nitropropane can produce cancer [2].

Tetranitromethane

Experiments with animals show that inhalation of tetranitromethane can produce respiratory tract irritation and severe pneumonia but no methaemoglobin-saemia [1].

Nitrates Esters

Methyl Nitrate [1]

The action is similar to nitroglycerine, but much weaker. Oral LD₅₀ in rats was 344 mg/kg. Inhalation of 117 mg by humans induce headache.

Nitroglycerine [1]

It is known in medicine as a vasodilator and there is an extensive literature on its biochemical and clinical aspects. The most common dose is ca. 0.01 mg/kg. Chronic human exposure to NG produces a methaemoglobinemia and the development of tolerance to the drug. Withdrawal from frequent exposure to NG may cause severe headaches. The LD₅₀ in rats is 822–884 mg/kg by oral administration. It is toxic to fish, e.g. LD₅₀ 1.38 mg/l.

Nitrocelulose

Owing to the insolubility of nitrocellulose, no toxic effect has been found to experimental animals including fish.

Nitramines

Nitroglycolidine

It is of very low toxicity. LD₅₀ in rats was found to be 4640 mg/kg. [1].

Cyclonite (RDX, Hexogene)

More information has been collected on the toxicity of Cyclonite. Experiments with animals confirmed earlier findings on convulsions caused by Cyclonite. Important observations with humans were: the same effects were caused by inhaling the dust of Cyclonite and one fatal accident was recorded [3]. Rosenblatt [1] described acute intoxication of soldiers either chewing a plastic explosive C–4 containing 91% RDX or using it for cooking and inhaling the fumes. RDX intoxication involves gastrointestinal, central nervous system and renal effects. No liver involvement has been recorded and the cerebrospinal fluid was normal.

Acute toxicity in rats (LD₅₀) was determined: by oral administration 200 mg/kg and by intravenous and intraperitoneal administration: 18 mg/kg and 10 mg/kg respectively. Chronic toxicity by oral administration to rats gave variable results: in one series of experiments 10 mg/kg daily in rats for two years showed no toxic symptoms except a retarded weight in females. No carcinogenic effect was found.

In fish LD₅₀ was found to be ca. 3.6 mg/l.

Octogen (HMX)

Very low solubility of HMX (as compared with RDX) makes experiments on toxicity of the compounds less conclusive than with RDX. So far it appears that HMX is less toxic than RDX [1].
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### Chapter VII. Smokeless Powder

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