

CHAPTER IV

OTHER INITIATING EXPLOSIVES

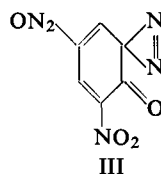
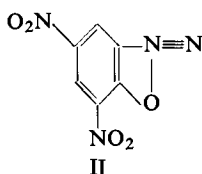
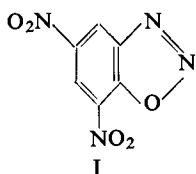
DIAZO COMPOUNDS

BERTHELOT and Vieille [1] examined the explosive properties of diazobenzene nitrate ($\text{C}_6\text{H}_5\text{N}=\text{N})^\oplus\text{NO}_3^\ominus$. Later Wöhler and Matter [2] demonstrated that it is unsuitable for use as an initiator due to its very weak initiating properties and very high sensitivity to friction and impact. Herz [3] suggested the use of *m*-nitrodiazobenzene perchlorate. This, however, is hygroscopic and insufficiently stable (it explodes at 154°C).

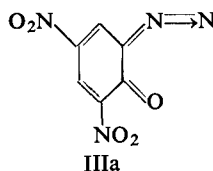
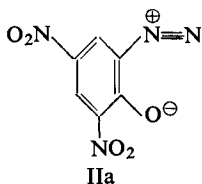
DINITROBENZENEDIAZO-OXIDE (DINITRODIAZOPHENOL)

The only diazo compound of practical value is dinitrobenzenediazo-oxide (dinitrodiazo-oxide, or less correctly dinitrodiazophenol). In technical literature it may be denoted as DDNP or Dinol.

The following formulae have been ascribed to this substance: cyclic (I) (Bamberger [4]), diazonium (II) (Hantzsch and Davidson [5], Klemenc [6]) or quinonoid (III) (Wolff [7]).



In modern transcription formulae (II) and (III) take the forms (IIa) or (IIIa) (Hodgson and Marsden [8], Anderson and Le Fèvre [9]):



Recently from a comparison of the infra-red absorption spectrum of this compound with that of *o*-benzoquinone Głowiak [10] came to the conclusion that dinitrobenzenediazo-oxide has a quinonoid structure. Both substances show the presence of the strong absorption band of the carbonyl group: 1666 cm^{-1} for dinitrobenzenediazo-oxide and 1680 cm^{-1} for *o*-benzoquinone. In addition dinitrobenzenediazo-oxide gives a band with a frequency of 2190 cm^{-1} , characteristic of a double bond between nitrogen atoms. (Some derivatives of this compound may also have the diazo structure (IIa), which is discussed later on.)

This substance was the first diazo compound to be discovered. It was prepared by Griess [11] by diazotizing picramic acid. Its explosive properties attracted the attention of Lenze [12] who found it to be as valuable as mercury fulminate in spite of its higher sensitiveness to impact. This compound is also of interest as being the first initiator containing no heavy metals. It has now been utilized in the United States of America and Japan as a component of initiating charges in detonators and caps.

Physical properties

Dinitrodiazophenol has a specific gravity of 1.63, and occurs as yellow needles which decompose without melting on heating to 188°C .

Its crystalline form is of great importance from the practical point of view.

The needle-like shape of the crystals prevents their being easily poured (into the capsule) making them liable to felt so the aim is to produce short crystals either by a suitable selection of conditions for the reactions of diazotization and precipitation of the product (D. Smoleński and Pluciński [13]) or by the addition of certain substances to the solution from which the product is to be precipitated; Garfield [14], for instance, suggests for this purpose the addition of triphenylmethane dye-stuffs to the solution.

The physical and explosive properties of dinitrodiazophenol were investigated by Clark [15] and by D. Smoleński and Pluciński [13]. The solubility of dinitrodiazophenol at 50°C (in 100 g of solvent) is: 2.45 g in ethyl acetate, 1.25 g in methyl alcohol, 2.43 g in ethyl alcohol, 0.23 g in benzene, 0.11 g in chloroform.

The substance is also soluble in concentrated hydrochloric acid, acetone, acetic acid, nitrobenzene, aniline, pyridine, and nitroglycerine, at room temperature. In water its solubility is only 0.08% at 25°C .

Chemical and explosive properties

Dinitrodiazophenol is not decomposed by concentrated acids at room temperature, but on the other hand a dilute (e.g. 0.5%) solution of sodium hydroxide causes its decomposition with the evolution of nitrogen even at room temperature. This property finds application in the destruction of residues.

Dinitrodiazophenol is more stable than mercury fulminate. It may be stored without change at 50°C, in dry condition, for 30 months (under these conditions fulminate is stable only for 9 months) and under water for 12 months.

Vaughan and Phillips [16] investigated the decomposition of dinitrodiazophenol at temperatures between 111 and 120°C *in vacuo*. The gaseous products of decomposition contain: 61.5% of N₂, 3% of NO, 4.0% of NO₂, 2.5% of CO, 28% of CO₂. This is evidence of the fact that decomposition consists not only in the loss of diazo group nitrogen, but also in the decomposition of the benzene ring.

Smoleński and Pluciński [13] examined the effect of sunlight and found that signs of decomposition are perceptible after only 40 hr of irradiation. A sample so irradiated shows a somewhat lower ignition temperature.

Kaufman [17] found that γ -radiation produces gas evolution from dinitrodiazophenol. Partial decomposition occurred after 45 days of irradiation (on average 10⁵ r per hour) and the explosive power of the irradiated substance was reduced and irregular.

Dinitrodiazophenol explodes [13] on a metal plate at 180°C after 10 sec; at 185°C after 5 sec; at 190°C after 2.5 sec; at 200°C after 1 sec.

In spite of its high specific gravity the apparent density of the needle-shaped crystals, according to Clark [15], is only 0.27; under a pressure of 240 kg/cm² it is 0.86. The crystals may be obtained in the form of pellets whose apparent density is about 0.8. The effect of the conditions of preparation have been thoroughly examined by Smoleński and Pluciński [13]. They found that at a diazotization temperature as recommended by Clark, i.e. 15°C, the product pours with difficulty. Conversely, diazotization at a higher temperature (25–45°C) results in formation of a product with a density of about 0.82.

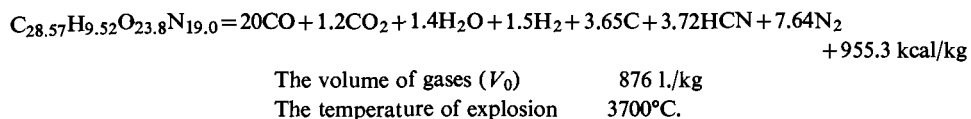
Smoleński and Pluciński prepared dinitrodiazophenol in the form of free-flowing crystals by applying the following reaction conditions:

A solution of 320 g of sodium nitrite in 2 l. of water is added to a suspension of 1000 g of the sodium salt of picramic acid in 8 l. of water. Next, 6 l. of 5.5% hydrochloric acid is added dropwise for 2 hr, stirring continuously. The initial temperature of 20°C rises to 25°C. Completion of the reaction is determined by means of starch–iodide paper. The product is filtered off, washed with cold water and dried at 35–40°C. Its yield amounts to 80% of the theoretical.

T. Urbański, Szyć-Lewańska *et al.* [18] have recently found that dinitrobenzene-diazo-oxide can be prepared by oxidation of picramic acid with chromium trioxide in the presence of sulphuric acid at 55–60°C. One part of picramic acid is fully oxidized by chromic acid to yield gaseous products: CO, CO₂, NO₂, NH₃ and H₂O. Nitrogen dioxide acts further as a diazotizing agent on undecomposed picramic acid to yield the diazo compound. The yield of this reaction does not exceed 31% of theoretical calculated on the picramic acid used.

Clark confirmed that dinitrodiazophenol does not become “dead pressed” even under a pressure of 9140 kg/cm² which is a great advantage in an initiating material. Smoleński and Pluciński quote the following figures which are characteristic of its

explosive properties. The substance is endothermic. Its heat of formation is about 365 kcal/kg. The reaction proceeds according to the following equation:



Owing to the great volume of gases, high heat of formation and high explosion temperature this substance is a much stronger explosive than those initiators which contain metal in the molecule.

According to Clark [15] 1 g of dinitrodiazophenol on being pressed at a pressure of 240 kg/cm² into a copper capsule gives an expansion of 25 cm³ in a small lead block (mercury fulminate 8 cm³, lead azide 7 cm³). Using 0.75 g of the substance, Smoleński and Pluciński obtained a lead block expansion of 17–23 cm³.

Clark found dinitrodiazophenol less sensitive to impact than mercury fulminate, lead azide or lead styphnate; it is exploded by a drop of 375 g weight from a height of 22.5 cm, whereas mercury fulminate is exploded by a drop of 15 cm.

Smoleński and Pluciński also disclosed that a fine crystalline product is more sensitive (15 cm drop) and coarse crystalline less sensitive (30 cm drop).

A. Belayev and A. Belayeva [19] found its linear rate of burning to be 2.15 cm/sec.

The initiating properties of dinitrodiazophenol were investigated by Clark [15] and Smoleński and Pluciński [13]. According to Clark the initiating power of the substance is approximately twice as great as that of mercury fulminate, but a little less than that of lead azide.

Thus to initiate picric acid the following quantities of priming explosives are required:

0.115 g of dinitrodiazophenol
0.225 g of mercury fulminate
0.12 g of lead azide

For trinitrotoluene the corresponding figures are as follows:

0.163 g, 0.240 g, 0.16 g

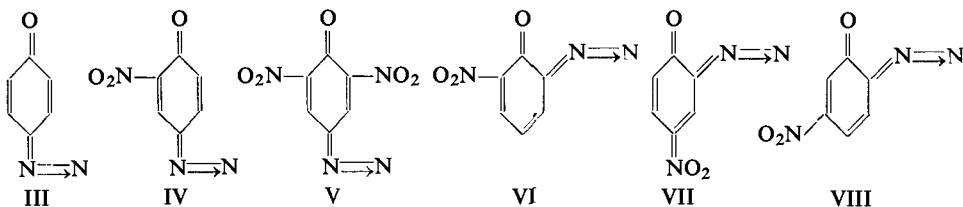
and for tetryl:

0.075 g, 0.165 g, 0.03 g.

In Smoleński and Pluciński's opinion dinitrodiazophenol alone is not suitable as an initiating material for detonators since it requires too long a path for burning to change into detonation, hence it is necessary to add another initiating substance e.g. lead azide. Nevertheless it is suitable for filling caps.

The properties of benzenediazo-oxides

Vaughan and Phillips [16] studied the decomposition of 4-diazo-1-oxide (III) and nitro derivatives of this compound (IV, V) and of the nitro derivatives of 2-diazo-1-oxide (VI, VII, VIII).



Their experiments showed that the nitro derivatives of 4-diazo-1-oxide are more stable than the corresponding derivatives of 2-diazo-1-oxide.

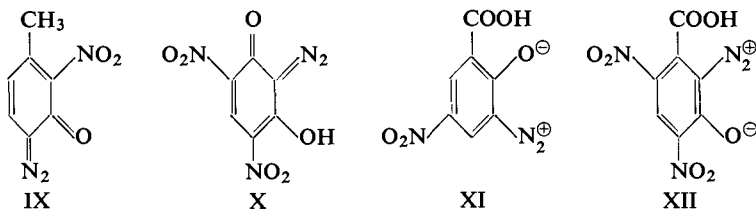
The introduction of a nitro group at the *ortho*-position to the oxygen atom in 4-diazo-1-oxide (IV) increases the stability. Great stability is also demonstrated by the *o*- and *p*-substituted nitro derivatives of 2-diazo-1-oxide (VI and VII). On the other hand, the *m*-substituted compound (VIII) has a lower stability than compounds (VI) and (VII). Dinitro substituted derivatives, *ortho-ortho* (V) and *ortho-para* (IIa), are distinguished by a higher stability than the mononitro derivatives of the same oxides (IV) or (VI) and (VII).

Głowiak [20] examined the properties of the diazotization products of numerous nitro derivatives of *o*-aminophenol, viz.:

2,6-dinitro-4-amino-*m*-cresol
 4,6-dinitro-2-amino resorcinol
 5-nitro-3-aminosalicylic acid
 4,6-dinitro-2-amino-*m*-hydroxybenzoic acid.

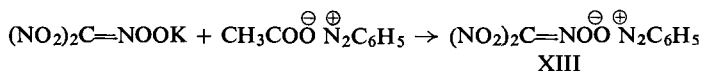
From them he prepared the diazo compounds (IX), (X), (XI), and (XII).

From their infra-red absorption spectra he ascribes a quinonoid structure to the first two compounds and a diazo structure to the last two and to their plumbous salts:



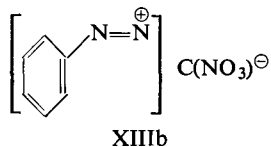
The compounds with a quinonoid structure differ from those with a diazo structure by their darker colour and lower chemical stability. They are for example easily decomposed by light and concentrated acids; they are less resistant to heat and show a higher sensitiveness to impact, friction and flame than compounds with a diazo structure.

Phenyldiazonium nitroformate. Nitroform derivative (XIII) is of particular interest among derivative diazonium salts. It was prepared by Ponzio [21] who reacted the potassium salt of trinitromethane (nitroform) with an aqueous solution of phenyldiazonium acetate:



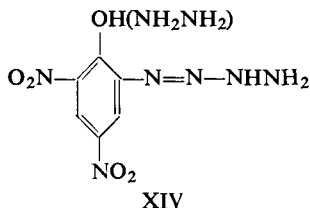
Quilico [22] questioned the formula (XII), assuming the substance to be an azo compound with the structure $(\text{NO}_2)_3\text{C}-\text{N}=\text{NAr}$, but in a later paper Ponzio [23] insists that in principle his formula is correct, while modifying it into $(\text{NO}_2)_3\text{CN}_2\text{C}_6\text{H}_5$ (XIIIa).

On the basis of its infra-red absorption spectrum Głowiak [20] deduced an ionic structure (XIIIb), confirming, in principle, the formula (XIIIa):



According to Głowiak's researches this substance has the following properties. Its ignition temperature with an induction period of 1 sec is 124°C . To initiate 0.5 g of tetryl, compressed under a pressure of 500 kg/cm^2 , the minimum charge of the phenyl diazotate of nitroform, loosely poured or compressed under a pressure of 100 kg/cm^2 , is 0.3 g. When compressed at higher pressure (300 kg/cm^2) the charge must be increased to 0.5 g.

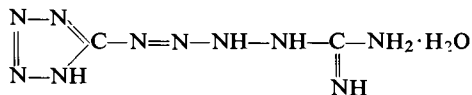
Dinitrobenzene diazo-oxide reacts with hydrazine hydrate to yield 2,4-dinitro-6-[tetrazene-(1)]-phenolhydrazine salt (XIV)



The product (XIV) can form metal salts. Some of them (e.g. potassium salt) possess initiating properties [24].

THE DERIVATIVES OF AMINOGUANIDINE

TETRAZENE



Tetrazene or tetrazolylguanyltetrazene hydrate was first prepared by Hoffmann and Roth [25], by the action of a neutral solution of sodium nitrite on aminoguanidine salts (without an excess of inorganic acid). According to these authors the reaction proceeds as follows:

