

## CHAPTER V

### NITRIC ESTERS

*Nitric esters* or *organic nitrates* contain the nitrate radical,  $\text{—O—NO}_2$ , attached to a carbon atom, or, to express the same idea in a different way, they contain the nitro group,  $\text{—NO}_2$ , attached to an oxygen atom which is attached to a carbon. In *nitro compounds*, strictly so called, the nitro group is attached directly to a carbon; in *nitroamines* or *nitramines* it is attached to an amino nitrogen atom, that is, to a nitrogen which is attached to a carbon. In the nitric esters and in the nitroamines alike, a single atom stands between the nitro group and the carbon atom of the organic molecule. Substances of the two classes are alike in their most characteristic reaction, namely, they are formed by the reversible nitration of alcohols and amines respectively.

During the nitration of glycerin by the action of strong nitric acid or of strong mixed acid upon it, nitro groups are introduced in place of three of the hydrogen atoms of the original molecule. There is therefore a certain propriety in thinking of the product as a nitro compound, and a reasonable warrant for the common practice of calling it by the name of trinitroglycerin or, more commonly, of *nitroglycerin*. The hydrogen atoms which are replaced were attached to oxygen atoms; the product is really a nitric ester, and its proper name is *glyceryl trinitrate*. Similarly, the substances which are commonly called nitroglycol, nitro-starch, nitrosugar, nitrolactose, nitrocotton, etc., are actually nitric esters.

The physical properties of the nitric esters resemble in a general way the physical properties of the alcohols from which they are derived. Thus, methyl and ethyl nitrate, like methyl and ethyl alcohol, are volatile liquids; nitroglycerin is a viscous oil, more viscous and less volatile than glycol dinitrate as glycerin is more viscous and less volatile than glycol. Nitrocellulose from

fibrous cellulose yields a tough and plastic colloid, but nitro-starch remains from the evaporation of its solutions as a mass which is brittle and friable.

### Methyl Nitrate

Methyl nitrate is a powerful explosive although its physical properties are such that it is not of practical use, and it is of interest only because it is the simplest of the nitric esters. Like ethyl and *n*-propyl nitrates, it may be prepared by the careful distillation of the alcohol with concentrated nitric acid (*d.* 1.42) from which, however, the last traces of nitrous acid must first have been removed by the addition of urea. It may also be prepared by adding the alcohol to strong mixed acid at low temperature, stirring, and separating and washing the product without distillation, by a process similar to that which is used for the preparation of nitroglycerin and nitroglycol except that the volatility of the product requires the stirring to be done by mechanical means and not by compressed air. It is a colorless limpid liquid somewhat less viscous than water, boiling point 65–66°, specific gravity 1.2322 at 5°, 1.2167 at 15°, and 1.2032 at 25°. Its vapors have a strongly aromatic odor resembling that of chloroform, and cause headache if they are inhaled. It dissolves collodion nitro-cotton to form a jelly from which the methyl nitrate evaporates readily.

Methyl nitrate has a slightly higher energy content than nitroglycerin and a slightly greater explosive effect. Naoúm<sup>1</sup> reports that 10 grams of methyl nitrate in the Trauzl test with water tamping caused an expansion of 615 cc., while 10 grams of nitroglycerin under the same conditions gave 600 cc. Methyl nitrate is very much more sensitive to initiation than nitroglycerin, a fact which, like its higher velocity of detonation, is probably associated with its lower viscosity. It is less sensitive than nitroglycerin to the mechanical shock of the drop test. In the small lead block test, or lead block compression test, 100 grams of methyl nitrate under slight confinement in a shell of sheet lead 1 mm. thick and tamped with thin cork plates, gave a compres-

<sup>1</sup> Phokion Naoúm, "Nitroglycerine and Nitroglycerine Explosives," trans. E. M. Symmes, Baltimore, The Williams and Wilkins Company, 1928, p. 205.

sion of 24.5 mm. while nitroglycol similarly gave 30 mm. and nitroglycerin 18.5 mm.

Methyl nitrate is easily inflammable and burns in an open dish with a large non-luminous flame. Its vapors explode when heated to about 150°.

Berthelot<sup>2</sup> measured the velocity of detonation of methyl nitrate in tubes of such small diameter that the maximum velocity of detonation was not secured, but he was able to make certain interesting inferences both as to the effect of the envelope and as to the effect of the physical state of the explosive. Some of his results are summarized in the table below. The data indicate

TUBE OF			VELOCITY
	INTERNAL DIAMETER, MILLIMETERS	EXTERNAL DIAMETER, MILLIMETERS	OF DETO- NATION, METERS PER SECOND
Rubber, canvas covered	5	12	1616
Glass	3	12	2482
Glass	3	7	2191
Glass	5	7	1890
Britannia metal	3	12 6	1230
Steel	3	15	2084
Steel	3	15	2094

that with tubes of the same internal diameter the velocity of detonation is greater in those cases in which the rupture of the tube is more difficult; it is greater in the tubes which have thicker walls and in the tubes which are made of the stronger materials. The extent to which the velocity of detonation builds up depends in some measure upon the pressure which builds up before the container is ruptured. By comparing these results with those from other explosive substances, Berthelot was able to make further inductions.

In fact, nitroglycerin in lead tubes 3 mm. internal diameter gave velocities in the neighborhood of 1300 meters per second, while dynamite in similar metallic tubes attained 2700 meters per second. This sets in evidence the influence of the structure of the explosive substance upon the velocity of propagation of the explosion, pure nitroglycerin, a viscous liquid, transmitting the shock which determines the detonation much more irregularly than the silica impregnated in

<sup>2</sup> *Mém. poudres*, 4, 13 (1891); *Ann. chim. phys.*, 23, 485 (1901).

a uniform manner with the same liquid. Mica dynamite according to my observations produces effects which are still more considerable, a fact which could be foreseen from the crystalline structure of the mica, a substance which is less deformable than amorphous silica.

This last induction is confirmed by observations on nitromannite, a crystalline solid which appears by reason of this circumstance better suited than liquid methyl nitrate for transmitting detonation. It has in fact given practically constant velocities of 7700 meters per second in lead tubes of 1.9 mm. internal diameter at a density of loading of 1.9. Likewise picric acid, also crystalline, 6500 meters per second. . . .

The influence of the structure of the explosive substance on the course of the detonation being thus made evident, let us cite new facts which show the effect due to the containing envelope. . . . Compressed guncotton at such densities of loading as 1.0 and 1.27 in lead tubes 3.15 mm. internal diameter gave velocities of 5400 meters per second, while at a density of loading of practically one-half less (0.73) in a lead tube 3.77 mm. internal diameter, a velocity of 3800 meters per second was observed—a difference which is evidently due to the reduced continuity of the material. In *supple cordeau*, slightly resistant, formed by a single strand or braid, with a density of loading of 0.65, the velocity falls even to 2400 meters per second. But the feeble resistance of the envelope may be compensated by the mass of the explosive which opposes itself, especially in the central portion of the mass, to the instantaneous escape of the gas. Abel, in fact, with cartridges of compressed guncotton, of ten times the diameter of the above-mentioned *cordeau*, placed end to end, in the open air, has observed velocities of 5300 to 6000 meters per second.<sup>3</sup>

### Other Alkyl Nitrates

Ethyl nitrate is a colorless liquid of agreeable odor, boiling point 87°, specific gravity (15°/15°) 1.1159 at 15°, and 1.1044 (25°/25°) at 25°. It has a less favorable oxygen balance than methyl nitrate, and is much less sensitive to initiation than the latter substance. It has only about 48% of the energy content of nitroglycerin, but its lower viscosity tends to give it a higher initial velocity of detonation than nitroglycerin and it performs about 58% as well as nitroglycerin in the sand test.<sup>4</sup> A No. 8

<sup>3</sup> *Mém. poudres*, 4, 18-19 (1891).

<sup>4</sup> *Naoúm, op. cit.*, p. 207.

blasting cap will not detonate ethyl nitrate unless the explosive is tamped or confined. Mixed with fuller's earth in the proportion 70/30 or 60/40, it yields a brisant explosive which may be detonated without confinement.

*n*-Propyl nitrate, like ethyl nitrate, can be prepared by mixing the alcohol with nitric acid of density 1.42 or thereabouts, and carefully distilling the mixture. Ethyl alcohol and *n*-propyl alcohol, which contain the methylene group, are easily oxidized; if they are added to nitric acid of greater strength than density 1.42, or if they are added to strong mixed acid, they are likely to react with explosive violence and the abundant production of nitrous fumes, no matter how efficient the cooling. *n*-Propyl nitrate has a pleasant ethereal odor, boiling point  $110.5^{\circ}$ , specific gravity ( $15^{\circ}/15^{\circ}$ ) 1.0631 at  $15^{\circ}$ , and ( $25^{\circ}/25^{\circ}$ ) 1.0531 at  $25^{\circ}$ . It is less sensitive to detonation than ethyl nitrate. Ten grams in a Trauzl block, with water tamping and with a No. 8 blasting cap, detonated only partially and gave an expansion of 45 cc., or 15 cc. more than the cap alone, but 10 grams of it, mixed with 4 grams of fuller's earth to form a moist powder and exploded with a No. 8 cap, gave a sharp explosion and a net expansion of 230 cc.<sup>5</sup>

*Isopropyl nitrate*, b.p.  $101-102^{\circ}$ , specific gravity 1.054 at  $0^{\circ}$ , 1.036 at  $19^{\circ}$ , is prepared by the interaction of isopropyl iodide and silver nitrate. The hydrogen atom which is attached in isopropyl alcohol to the carbon atom carrying the hydroxyl group is so easily oxidized that it is not feasible to prepare the compound by the action of nitric acid on the alcohol.

### Nitroglycerin (Glyceryl trinitrate, NG)

Nitroglycerin was first prepared late in the year 1846 or early in 1847 by the Italian chemist, Ascanio Sobrero (1812-1888), who was at the time professor of applied chemistry at the University of Torino. Sobrero had studied medicine in the same city, and in 1834 had been authorized to practice as a physician. After that he studied with Pelouze in Paris and served as his assistant in his private laboratory from 1840 to 1843. In 1843 he left Paris, studied for several months with Liebig at Giessen, and returned to Torino where he took up the duties of a teacher and in 1845

<sup>5</sup> *Ibid.*, p. 209.