## Analogs of Tetryl Hexanitrodiphenylaminoethyl Nitrate

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HIS paper presents the results of determinations of the chemical, physical, and explosive properties of hexanitrodiphenylaminoethyl nitrate, more properly and correctly designated as bis [2, 4, 6-trinitrophenyl]aminoethyl nitrate, which is prepared from bis[2, 4-dinitrophenyl]aminoethanol, a byproduct in the preparation of syn-trinitrophenylnitraminoethyl nitrate, a tetryl-like substance (3, 4), which was described in Part I of this series (2) and termed, for purposes of brevity, "pentryl."

These determinations have been carried on in accordance with the continuing policy of the Explosives Division of the Bureau of Mines to

familiarize itself with the chemical, physical, and explosive properties of those substances which are used, which have been proposed for use, or which give promise of use as initiating or base charges in detonators. By such determinations the Explosives Division ascertains the relative ability of various detonants to cause complete detonation of explosives, particularly permissible explosives which are designed to increase safety in underground blasting operations where inflammable gases and/or dusts may be encountered.

Safety in the use of a permissible explosive<sup>1</sup> depends not only upon the explosive itself but also upon its being completely detonated, the fulfilment of which requirement demands use of a suitably powerful detonator (5, 6, 7). Use of low-grade detonators, or detonators that have become phlegmatized because of deterioration of the explosive contents during storage, greatly increases the chance for improper detonation or even failure of the When charge to detonate.

low-grade or defective detonators are used there may be (1) great loss in explosive strength, (2) production of large quanti-

<sup>1</sup> Explosives enumerated on the permissible lists of the United States Bureau of Mines are permissible in use only when employed in accordance with the prescribed conditions set forth in Bureau of Mines' Schedule 17B, "Procedure for Testing Explosives for Permissibility for Use in Coal Mines," 1930. ties of toxic gases, and (3) production of flame which may cause ignition of inflammable gas and/or dust in the mine. Contingent upon the occurrence of either of the two latter conditions, there is apt to be great loss of life or property.

The detonants of the aromatic class of organic substances most commonly used as base charges in commercial detonators are tetryl (trinitrophenylmethylnitramine), picric acid, and trinitrotoluene (TNT). Pentryl has been found quite satisfactory for this use. Results of tests on these commonly used detonants are repeated here to permit comparison with hexanitrodiphenylaminoethyl nitrate.

Preparation of Hexanitrodiphenylaminoethyl Nitrate

The preparation of his[2, 4-dinitrophenyl]aminoethanol, from which hexanitrodiphenylaminoethyl nitrate is prepared, has been discussed at length in a previous publication (2). The reactions involved in these preparations are summarized as follows:



Hexanitrodiphenylaminoethyl nitrate may be prepared as follows:

Thirty grams of bis [2,4-dinitrophenyl]aminoethanol are dissolved in 200 grams of sulfuric acid (specific gravity, 1.84) at a temperature not exceeding 40° C. This solution is then slowly added to 120 grams of nitric acid (specific gravity, 1.49) contained in a 400-cc. beaker resting in a bath of cold water. Dur-



FIGURE 1. TYPE B PENDULUM FRICTION DEVICE MODIFICATION 1

ing the addition of the sulfuric acid solution the temperature is not allowed to exceed 30°. When the addition has been completed, the temperature, during a period of one hour, is increased by 5° increments to 50° C. when nitration is complete. The reaction mixture is drowned in 1000 cc. of ice water and the product is filtered, washed with cold water, and stabilized as usual by washing with dilute sodium bicarbonate solution. The yield is 80 per cent of theoretical. The dried, stabilized product may be purified by dissolving in acetone, from which solution the pure product is precipitated in the form of pale yellow, glistening plates, by the addition of 95 per cent ethanol. The melting point was established at 184° C. (corrected).

#### Physical Properties

Hexanitrodiphenylaminoethyl nitrate, prepared according to the above method, has a true density of 1.69, yet its apparent density when placed in a cylinder and tapped is only 0.39. Pressed in a detonator shell under a reënforcing capsule at a pressure of 3400 pounds per square inch (239.0 kg. per sq. cm.), the apparent density is 1.27.

Hexanitrodiphenylaminoethyl nitrate is very soluble in nitrobenzene, 1, 4-dioxan, nitric acid, pyridine, aniline, and hot ethylene glycol; is less soluble in xylene, acetone, and acetic anhydride; and is only slightly soluble in ethanol, ethyl ether, ethylene dichloride, ethyl acetate, amyl acetate, methanol, and benzene.

#### Explosive Properties of Hexanitrodiphenylaminoethyl Nitrate

SENSITIVENESS TO IMPACT AND FRICTION. Sensitiveness to impact was determined on the Bureau of Mines small impact device (6). The following table shows results of these tests, together with results of similar tests on pentryl, tetryl, picric acid, and TNT:

| $Explosive^a$                        | Max. Height of Drop of<br>2000-Gram Weight for<br>"No Explosions" in 5 Trials |
|--------------------------------------|---|
|                                      | Cm.   |
| Hexanitrodiphenylaminoethyl nitrate  | 35  |
| Pentryl                              | 30  |
| Tetryl                               | 27.5  |
| Pieric acid                          | 42.5  |
| TNT                                  | > 100   |
| <sup>a</sup> 0.02-gram charges used. |   |

Hexanitrodiphenylaminoethyl nitrate was not detonated when subjected to friction between the steel anvil and steel shoe of the type B pendulum friction device, modification 1 ( $\beta$ ), shown in Figure 1, with a weight of 5000 grams added to the shoe. Pentryl, tetryl, picric acid, and TNT also fail to detonate under similar conditions of test. A limited quantity of material prevented tests on the type A pendulum friction device ( $\beta$ ).

PREPARATION OF TEST DETONATORS. As in previous investigations (1, 2), after Wöhler and Matter (14), the experimental detonators tested during this investigation have been prepared as follows, unless otherwise specified: A 0.50-gram base charge of the explosive, or explosive composition, to be tested, was weighed into a No. 8 detonator shell, and a priming charge of 0.20 gram of mercury fulminate added. Both base and priming charges were then compressed under a reenforcing capsule at a pressure of 3400 pounds per square inch (239.0 kg. per sq. cm.). This method of loading has been followed to keep results on a basis comparable with those obtained by the writer (1, 2) in previous investigations.

#### SENSITIVITY TO DETONATION BY INITIATING AGENTS

The sensitivity of an explosive to detonation by a given initiating agent is expressed in terms of the minimum weight of the initiating agent which causes complete detonation. Details of this test have been given in previous publications (1, 2, 11, 12).

The following table shows results of tests on hexanitrodiphenylaminoethyl nitrate, compared with results of similar tests on other explosives:

| Explosive  | Minimum<br>DDNP  | DETONATING<br>Mercury<br>fulminate  | CHARGE <sup>a</sup><br>Lead<br>azide   |
|--|--|---|--|
|  | Gram   | Gram  | Gram   |
| Hexanitrodiphenylaminoethyl nitrate<br>Hexanitrodiphenylamine<br>Pentryl<br>Tetryl<br>Picrio acid<br>TNT | $\begin{array}{c} 0.05 \\ 0.075 \\ 0.095 \\ 0.075 \\ 0.115 \\ 0.163 \end{array}$ | $\begin{array}{c} 0.16\\ 0.165\\ 0.150\\ 0.165\\ 0.225\\ 0.240 \end{array}$ | $\begin{array}{c} 0.04 \\ 0.05 \\ 0.025 \\ 0.03 \\ 0.12 \\ 0.16 \end{array}$ |

 $^{\rm a}$  Minimum weight of priming charge which causes complete detonation of base charge.

SAND-CRUSHING STRENGTH (6, 8, 9, 10). To compare the sand-crushing strength of hexanitrodiphenylaminoethyl nitrate with that of other explosives, experimental detonators were prepared and fired in the No. 2 sand test bomb, following the method employed at the Bureau of Mines Explosives Experiment Station (6). Results of these tests are shown in the following table:

|                                     | WEIGHT<br>CRUSHED F                     | OF SAND             | г <u> </u>  |
|-------------------------------------|---|---------------------|---|
| EXPLOSIVE                           | 30-M<br>By total<br>charge <sup>a</sup> | By base<br>charge   | $\begin{array}{l} \text{Relative} \\ \text{Strength} \\ (\text{TNT} = 1) \end{array}$ |
|                                     | Grams                                   | Grams               |   |
| Hexanitrodiphenylaminoethyl nitrate | 62.8                                    | 51.1                | 1.20  |
| Pentryl                             | 67.5                                    | $\frac{46.5}{55.8}$ | 1.28  |
| Tetryl<br>DDNP                      | $65.9 \\ 63.9$                          | 54.2<br>52.2        | $\frac{1.24}{1.20}$   |
| Pierie acid                         | 57.0                                    | 45.3                | 1.04  |
| Tetranitraniline                    | 00.3<br>56.3                            | 43.6                | 1.00  |
| Mercury fulminate                   |   | 18.0                |   |

 $^a$  Total charge consisting of a base charge of 0.50 gram of the explosive under test and a priming charge of 0.30 gram of mercury fulminate.

Results of these tests show the sand-crushing strength of hexanitrodiphenylaminoethyl nitrate to be 20 per cent greater than that of TNT, about 15 per cent greater than that of picric acid, about 7 per cent less than that of pentryl, about 3 per cent less than that of tetryl, and equal to that of DDNP.

For complete combustion of hexanitrodiphenylaminoethyl nitrate to carbon dioxide, nitrogen, and water, 2 molecules of the explosive require 17 molecules of oxygen:

$$\begin{array}{ccc} 2C_{14}O_{15}H_{3}N_{8} + 17O_{2} \longrightarrow 28CO_{2} + 8N_{2} + 8H_{2}O \\ 1056.13 & 554 \end{array}$$

It follows, then, that the oxygen value per gram of hexanitrodiphenylaminoethyl nitrate, or the oxygen ratio, is

In view of this large deficiency of oxygen, it is to be expected that the explosive strength of hexanitrodiphenylaminoethyl nitrate can be increased by the addition of an oxidant such as potassium chlorate. Accordingly, mixtures in various proportions of the explosive and potassium chlorate were prepared. Detonators containing the mixtures were prepared and fired in the No. 2 sand test bomb:

| Base Charge<br>Hexanitrodiphenyl-<br>aminoethyl nitrate | KClO3                     | WEIGHT OF SAND<br>THAN 30<br>By total<br>charge <sup>a</sup> | CRUSHED FINER<br>D-MESH<br>By base<br>charge |
|---|---------------------------|--|--|
| %   | %                         | Grams  | Grams  |
| 100<br>90<br>80<br>70<br>60                             | 0<br>10<br>20<br>30<br>40 | 58.6<br>55.9<br>56.1<br>56.6<br>56.1                         | 52.149.449.651.549.6                         |

 $^a$  Total charge consisting of a base charge of 0.50 gram of the mixture under test and a priming charge of 0.20 gram of mercury fulminate.

It is apparent from these results that the sand-crushing strength of hexanitrodiphenylaminoethyl nitrate is enhanced by the addition of an oxidizing salt.



Hexanitrodiphenylaminoethyl nitrate





Pieric acid

Trinitrotoluene FIGURE 2. LEAD PLATE TESTS OF HEXANITRODIPHENYLAMINO-ETHYL NITRATE COMPARED WITH OTHER EXPLOSIVES

#### STRENGTH IN THE SMALL TRAUZL BLOCK

Experimental detonators were prepared and tested in the small Trauzl block, after the Bureau of Mines method (6), to ascertain the disrupture power of hexanitrodiphenylaminoethyl nitrate and to compare this value with that of other explosives previously tested:

| Explosive                           | Expansion of<br>Cavity in Block<br>Cc. | Relative<br>Strength<br>(TNT = 1) |
|-------------------------------------|--|-----------------------------------|
| Hexanitrodiphenylaminoethyl nitrate | 16.3                                   | 1.34                              |
| Hexanitrodiphenylamine              | 13.3                                   | 1.09                              |
| Pentryl                             | 15.8                                   | 1.30                              |
| Tetryl                              | 13.8                                   | 1,13                              |
| TNŤ                                 | 12.2                                   | 1.00                              |
| Pieric acid                         | 12.4                                   | 1.02                              |
| DDNP                                | 13.4                                   | 1.10                              |
| Mercury fulminate                   | 8.1                                    | ••                                |

These data show the disruptive power of hexanitrodiphenylaminoethyl nitrate to be 23 per cent greater than that of hexanitrodiphenylamine, 3 per cent greater than that of pentryl, 19 per cent greater than that of tetryl, 34 per cent greater than that of TNT, 31 per cent greater than that of pieric acid, and 22 per cent greater than that of DDNP.

LEAD PLATE TESTS. Figure 2 shows results of lead plate tests. It is apparent that hexanitrodiphenylaminoethyl nitrate produces a good type of lead plate. Under similar conditions of test the plates produced by pentryl, tetryl, or picric acid are somewhat superior and that produced by TNT somewhat inferior to that produced by hexanitrodiphenylaminoethyl nitrate. The degree of fineness of the striations on the plates in Figure 2 indicates that hexanitrodiphenylaminoethyl nitrate possesses a high degree of brisance, comparing favorably in this respect with the other explosives tested.<sup>2</sup>

SURVEILLANCE TESTS. Hexanitrodiphenylaminoethyl nitrate has been stored in the dry state in the laboratory for 6 months without developing any discoloration or otherwise showing decomposition.

\* For a detailed discussion of the significance of the lead plate test see Grotta, Bennet, Chem. & Met. Eng., 26, 1126 (1922).



Tetrvl

The explosive has been subjected for 48 hours to the International 75° C. (167° F.) heat test with no discoloration or loss in weight. To ascertain the effect of higher temperatures, the material used for the International heat test was subjected to a temperature of 100° C. (212°F.) for 48 hours. At the expiration of this period, no loss in weight had occurred, although a slight discoloration was evident.

IGNITION TEMPERATURE. Ignition temperature of hexanitrodiphenylaminoethyl nitrate was determined by dropping 0.02-gram portions on a molten metal bath and noting the time interval between the moment of contact of the explosive with the molten mass and the moment of explosion or ignition. Results of these tests are as follows:

| TEMP. <sup>6</sup> OF METAL BATH   | TIME TO IGNITION   |
|--|--|
| ° C.   | Seconds  |
| $ \begin{array}{r} 450 \\ 440 \\ 430 \\ 420 \\ 400 \\ 390 \\ \end{array} $ | Instantaneously<br>0.25-0.5<br>0.5<br>1-1.5<br>1.5-2<br>Failed to ignite in 5 trials |

<sup>a</sup> Temperature measurements were made with a chromel-alumel couple.

#### SUMMARY

1. Hexanitrodiphenylaminoethyl nitrate may be prepared by nitration in mixed acids of bis[2, 4-dinitrophenyl]aminoethanol, a by-product in the preparation of pentryl.

2. The sensitiveness of hexanitrodiphenylaminoethyl nitrate to impact is slightly less than that of pentryl or tetryl. It is somewhat more sensitive to impact than picric acid, and much more sensitive than TNT.

3. The sensitiveness of hexanitrodiphenylaminoethyl nitrate to detonation by such initiating agents as mercury fulminate, lead oxide, or DDNP is of the same order as that of pentryl, tetryl, or hexanitrodiphenylamine.

4. The sand-crushing strength of hexanitrodiphenylaminoethyl nitrate is equal to that of DDNP, 20 per cent greater than that of TNT, 15 per cent greater than that of picric acid, 7 per cent less than that of pentryl, and 3 per cent less than that of tetryl.

5. The addition of an oxygen-bearing salt, such as potassium chlorate, to hexanitrodiphenylaminoethyl nitrate greatly enhances its explosive strength and is therefore recommended as being of economic advantage.

6. The disruptive power of hexanitrodiphenylaminoethyl nitrate as measured in the small Trauzl block is 34 per cent greater than that of TNT, 3 per cent greater than that of pentryl, 19 per cent greater than that of tetryl, 22 per cent greater than that of DDNP, and 31 per cent greater than that of picric acid.

7. Hexanitrodiphenylaminoethyl nitrate produces a lead plate somewhat superior in character to that produced by TNT and somewhat inferior to that produced by pentryl, tetryl, or picric acid.

8. When rapidly heated, hexanitrodiphenylaminoethyl nitrate ignites at 390° to 400° C.

#### Acknowledgment

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# Explosive Properties of Divinyl Ether

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IVINYL ETHER.  $C_2H_3OC_2H_3$ , a combustible liquid having a boiling point of 28.3° C. (82.9° F.), is now being produced in commercial quantities, and studies are under way to determine its value as an anesthetic. In anesthesia it will be used in various concentrations with air and oxygen. In this connection it is important for the explosive properties of this material to be known. The explosive properties are also of interest because it has the same molecular formula as crotonaldehyde. The two compounds, however, differ in molecular structure and afford a means of studying the effect of structure on the explosive properties of combustible liquids.

The physical and chemical properties, methods of preparation, and reactions of divinyl ether have been investigated

by Ruigh and Major (14) whose work should be consulted for details, and by others (2, 4, 5, 9, 15).

#### LIMITS OF INFLAMMABILITY OF DIVINYL ETHER-AIR MIXTURES

The limits of inflammability of divinyl ether (containing 0.01 per cent phenyl- $\alpha$ -naphthylamine) in air were determined in an upright closed metal bomb, 4 inches (10.2 cm.) in inside diameter and 38 inches (96.5 cm.) in length. The bomb was mounted upright. It had three quartz windows along one side so that the right. It had three quartz windows along one side so that the progress of the flame within the bomb could be followed. A Bureau of Mines manometer (1, 13) was attached at the middle position. Provision was made for registering the time of ignition on the sensitized paper in the manometer. A tuning fork having a period of 49.07 vibrations per second was operated when the test was made, and these vibrations were recorded on the sensitized paper in the manometer, thus giving the rate at which the drum revolved.

The mixtures were prepared and the concentrations determined by the method described by Jones, Harris, and Miller (6). The values obtained in the bomb for limits of inflammability, pressures developed when the mixtures were exploded, and speed of the flame are given in Table I. The lower inflammability limit was established at 1.70 per cent by volume. The upper limit was erratic and ranged from

Organic combustible substances, that a few years ago were laboratory curiosities, have through recent investigations become of industrial importance. One of these compounds, divinyl ether, has been found to have certain advantages as an anesthetic. Other uses may be found for this compound in the future. It is important to know the explosive properties in connection with its manufacture, transportation, and use.

In this report the inflammable limits and ignition temperatures of divinyl ether when mixed with air and with oxygen are determined. Some information is obtained on the pressures developed when divinyl ether-air mixtures are ignited in a closed bomb. Similar tests are also made with mixtures containing 96.5 per cent divinyl ether and 3.5 per cent ethanol by volume.

The conclusion is that divinyl ether and divinyl ether-ethanol mixtures are more hazardous than methyl formate, acetone, or dioxan, and offer about the same hazards as ethyl ether.

22.5 to 27.9 per cent, depending on the intensity of the spark used for igniting the mixtures. The mixtures which propagated flame near the upper limit also gave heavy deposits of carbon on the walls of the bomb, and it was found necessary to remove the head after each test and clean the bomb with compressed air.

Because of the erratic upperlimit values obtained in the bomb, the tests were supplemented with tests in a 2-inch (5.1-cm.) glass tube 6 feet (183 cm.) long, de-scribed in a previous paper (7). The tube was mounted upright and completely evacuated, and divinyl ether was vaporized directly into the explosion tube. The amount introduced was determined by the rise in pressure on the mercury manometer. Dry air was then admitted until the pressure became atmospheric. The tube was then dismounted and the contents thoroughly mixed. Before evacuation several

large glass beads were placed inside the tube to assist in mixing the contents. The mixing was accomplished by lowering one end of the tube, thus allowing the beads to run to that end. After about a minute the other end was lowered and the process continued 30 minutes. After mixing, the tube was replaced in its upright position, the room darkened, the ground glass plate at the bottom of the tube removed, and the flame from an alcohol lamp brought across the open end.

Mixtures near the upper limit always showed copious burning at the bottom of the tube; then some seconds afterward a pale blue flame traveled slowly to the top. The pale blue flames were present only for mixtures containing 20 per cent or more divinyl ether. An upper limit of  $26.5 \pm 0.3$ per cent was found by this method.

When both the closed-bomb and 2-inch glass-tube results for the upper limit are considered, the upper inflammable limit of divinyl ether in air may be given as  $27.0 \pm 1.0$  per cent.

#### PRESSURES DEVELOPED IN A CLOSED BOMB

The pressures developed by divinyl ether-air mixtures and divinyl ether (96.5 per cent)-ethanol (3.5 per cent)-air mixtures ignited in a closed bomb are given in Table I and shown graphically in Figure 1. The maximum pressures are de-