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NAVORD REPORT 2498

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THE PREPARATION OF 2,2,2-TRINITROETHYL
4,4-DINITROPENTANOATE

3 July 1952



U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

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THE PREPARATION OF 2,2,2-TRINITROETHYL 4,4-DINITROPENTANOATE

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ABSTRACT: 2,2,2-Trinitroethyl 4,4-dinitropentanoate has been made by the addition of 1,1-dinitroethane to methyl acrylate, hydrolysis of the methyl ester and esterification of the resulting acid with trinitroethanol. The compound is a castable high explosive, m.p. 92.5°C; crystal density 1.60; impact sensitivity 70 cm; hot bar ignition temperature 297°C; vacuum stability 1.1 cc of gas/g/48 hours at 100°C.

Explosives Research Department
U. S. NAVAL ORDNANCE LABORATORY
White Oak, Maryland

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3 July 1952

This report is a description of the preparation and some of the properties of 2,2,2-trinitroethyl 4,4-dinitropentanoate. The work was done in this laboratory under Task NOL-Re2c-19-1-52. The reliability of the work and the validity of the conclusions are the responsibility of the author and of the Chemistry Division, Explosives Research Department, Naval Ordnance Laboratory. This report is for information only.

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By direction

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THE PREPARATION OF 2,2,2-TRINITROETHYL 4,4-DINITROPENTANOATE

INTRODUCTION

Trinitroethyl 4,4,4-trinitrobutyrate, TNETB, has many of the properties (1,2) desired in a high explosive of improved performance over TNT as a casting medium for use in mixtures like composition B and HBX, except for its excessive sensitivity. As this sensitivity is shared by many other compounds containing the trinitromethyl group (1), several compounds have been prepared in which a methyl has replaced one of the nitro groups of the trinitromethyl. These compounds are readily prepared by using 1,1-dinitroethane in place of the nitroform used in the synthesis of the prototype compound.

This substitution of dinitroethyl for trinitromethyl groups in high explosive compounds has generally caused a marked reduction in impact sensitivity, although at the cost of reduced crystal density and oxygen content. A comparison of the compounds studied so far is given by Hill (3).

Hill (3) observed that the 2,2-dinitropropyl ester of 4,4,4-trinitrobutyric acid had substantially the same melting point as the trinitroethyl ester, TNETB, and that mixed melting points gave no depression. He concluded that the dinitropropyl ester was isomorphous with the high temperature form (2) of TNETB, and that mixed crystals were formed. This is not unexpected, as a methyl group is not greatly different in size from a nitro group, but this isomorphism is apparently not general.

Some interest was therefore aroused in the physical, chemical and explosive properties of the compound related to the above esters by the substitution of a methyl for a nitro group at the other, the acid, end of the TNETB molecule. As shown below, its properties are similar to those of the dinitropropyl ester, but it is more sensitive.

RESULTS AND DISCUSSION

The preparation of the 2,2,2-trinitroethyl ester of 4,4-dinitropentanoic acid presented no difficulties. The acid has been prepared previously (4), and its chloride reacted readily with trinitroethanol in the presence of aluminum chloride (5). The gradation of properties of the three related esters, trinitroethyl 4,4,4-trinitrobutyrate, TNETB; trinitroethyl 4,4-dinitropentanoate, TNDP, and 2,2-dinitropropyl 4,4,4-trinitrobutyrate, DNPTB, is interesting.

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Compound	M.P.	Crystal Density	Impact Sensitivity	100°/48hr. Stability	Ignition Temperature
$(\text{O}_2\text{N})_3\text{CCH}_2\text{OCOCH}_2\text{CH}_2\text{C}(\text{NO}_2)_3$	93°	1.78	20 cm	0.6	225°
$(\text{O}_2\text{N})_3\text{CCH}_2\text{OCOCH}_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{CH}_3$	92.5°	1.60	70	1.1	297°
$\text{CH}_3(\text{O}_2\text{N})_2\text{CCH}_2\text{OCOCH}_2\text{CH}_2\text{C}(\text{NO}_2)_3$	95°	1.66	151	0.5	300°

The similarity of the melting points of the three compounds is unusual. The present compound, like DNPTB, also forms mixed crystals with the high temperature form (2) of TNETB, and mixed melting points of any of the three compounds shows no depression. While the crystal densities of the two methyl substituted compounds, which are apparently isomorphous and possess only one crystal form, might be expected to be more nearly alike, their difference of 4% is not unreasonable. The large difference in sensitivity caused by the introduction and by changing the position of the methyl group is unexpected.

The new compound is probably sufficiently stable for use as a casting medium, although its density is fairly low and less sensitivity would be desirable.

EXPERIMENTAL

The preparation of the trinitroethanol ester of 4,4-dinitropentanoic acid was accomplished in four steps: (1) and (2) the addition of dinitroethane to methyl acrylate and hydrolysis of the ester to 4,4-dinitropentanoic acid; (3) and (4) the preparation of the acid chloride and its reaction with trinitroethanol.

1,1-Dinitroethane. - A quite pure product was prepared from purified 1-chloro-1-nitroethane by the ter Meer reaction (5).

Methyl Acrylate. - A commercial product was distilled before use.

4,4-Dinitropentanoic Acid. - The procedure of Schechter (4) was followed without isolation of the methyl ester. The product melting at 98-99° was obtained in 62% yield as compared to the 37% reported by Schechter, possibly because of the use of purer starting materials.

2,2,2-Trinitroethyl 4,4-Dinitropentanoate. - The acid (0.02 mole) was converted to the chloride by treatment with phosphorus pentachloride (0.02 mole) for 1-2 hours at 60-70°C. After the HCl and POCl₃ were removed from the reaction flask by reduced pressure distillation (40-49 mm, 60-70°C water bath), trinitroethanol (0.02 mole) was added. Reaction started without catalyst at room temperature, but was completed by adding anhydrous aluminum chloride (0.06 mole), the procedure developed in this laboratory by Hill (6), and warming to 70°C until no more HCl was evolved. The resulting solid product was washed with water, dissolved in 75 ml of chloroform and dried over anhydrous calcium sulfate. After filtering and warming the chloroform solution, 100 ml of n-hexane were added. Upon cooling,

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the product began to separate as an oil but soon crystallized into colorless crystals with a melting point of 92-93°C. Yield; 83%.

Analysis. Calculated for $C_7H_9N_5O_{12}$: C, 23.67; H, 2.55; N, 19.72. Found: C, 24.28, 24.14; H, 2.69, 2.68; N, 19.25, 19.24.

ACKNOWLEDGMENT

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