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Synthesis of 4,4'-Dimethyl-3, 3' 5, 5' -Tetranitroazoxybenzene by Selective Reduction of Trinitrotoluene

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ABSTRACT

Selective reduction of trinitrotoluene in dioxane solution by H_2S/NH_3 yields a mixture containing 4-amino-2,6-dinitrotoluene, 4-hydroxylamino-2,6-dinitrotoluene and 4,4'-dimethyl-3,3',5,5'-tetranitroazoxybenzene. Treatment of crude mixture with KI/HCl converts 4-hydroxylamino-2,6-dinitrotoluene into 4-amino-2,6-dinitrotoluene as well as increases the percentage of 4,4'-dimethyl-3,3',5,5'-tetranitroazoxybenzene. The resulting compound 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) was isolated and characterised by IR, NMR and elemental analysis. Its thermal decomposition as well as explosive properties have been studied. The data indicate that TATB is stable up to 294 °C and is also insensitive to impact and friction.

1. INTRODUCTION

The compound 1,3,5-triamino-2,4,6-trinitro benzene (TATB) is known for several decades. However, interest in TATB as an explosive increased during the sixties because of its excellent thermal stability, impact and friction insensitivity.

TATB was first synthesised in 1887[1]. It has also been prepared on laboratory scale from 3,5-dinitrobenzoic acid 2,3 and3,4-dichloroanisole[4] as starting materials. Another procedure for its laboratory scale preparation involves selective[5] reduction of trinitrotoluene (TNT) followed by nitration of the intermediate to pentanitroaniline, which on ammonolysis yields TATB. The procedure used for large scale preparation of TATB uses 1,3,5-trichlorobenzene as starting material[6].

Cathodic reduction of TNT in alkaline, acidic and neutral media was studied by Brand[7], *et al.* The reduction of TNT in alkaline solution yielded an unanalysable product, whereas its reduction in acidic solution produced 2-amino-4, 6-dinitrotoluene. On the other hand, reduction of TNT in neutral solution resulted in the formation of 4-hydroxylamino-2, 6-dinitrotoluene which formed 4,4'-dimethyl-3,3',5,5'-tetranitroazoxy benzene on heating with concentrated HCl for 2-3 hr.

The selective reduction of TNT with H_2S in different reaction conditions was also studied [8-14] These selective reductions resulted in a mixture of aminodinitrotoluenes and hydroxylaminodinitrotoluenes. On reproducing the work of Atkin[14], *et al.* with some modifications to obtain 4-amino-2,6-dinitrotoluene, the formation of 4,4'-dimethyl-3,3',5,5'-tetranitroazoxybenzene along with 4-amino-2,6-dinitrotoluene and 4-hydroxylamino-2,6-dinitrotoluene was observed. During selective reduction of TNT, the formation of

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4,4'-dimethyl-3,3',5,5'-tetranitroazoxybenzene has not been reported so far. In the present study, the procedure described by Atkin[14], *et al.* was modified for selective reduction of TNT that resulted in the synthesis of 4-amino-2,6-dinitrotoluene and 4,4'-dimethyl-3,3',5,5'-tetranitroazoxybenzene. The paper describes the process of reduction of TNT, isolation, characterisation and evaluation of the explosive and the thermal properties of DMTNAB.

EXPERIMENTAL SETUP

2.1 Materials

The chemicals used, viz., dioxane, methanol, ether, concentrated NH_4OH and KI were of LR grade. TNT of high purity with set point 80.8 °C was used. H_2S was generated from FeS and dilute HCl in Kipp's apparatus, washed with aqueous sodium hydrogen sulphide ($NaHS.\ H_2O$) and dried over $CaCl_2$.

2.2 Synthesis

TNT (20 g) was dissolved in dioxane (50 ml) and 4 to 5 drops of concentrated NH_3 solution were added. Dry and acid-free H_2S was bubbled through the mechanically-stirred solution at a moderate rate. After 30 min induction period, the temperature of the reaction mixture started rising, and sulphur started precipitating at about 35 °C. The temperature of the reaction mixture was not allowed to exceed 40 °C. Further, 4 to 5 drops of NH_3 solution were added to bring down the temperature to ambient after about 90 min, and bubbling of H_2S continued. In the subsequent 90 min, the temperature of reaction mixture dropped to ambient. At this stage, the temperature of reaction mixture did not rise on addition of NH_3 solution, thereby indicating the completion of the reaction. Sulphur (6.52 g) was filtered and washed with a mixture of dioxane and ether. The filtrate was dried and weighed to give 16.1 g of product (m.p. =115-130 °C).

Solution of KI (19.2 g) in methanol (115 ml) and concentrated HCl (16.6 ml) were added to crude material dissolved in methanol (167 ml) and the mixture was allowed to reflux for 90 min. The solution was then cooled and poured into ice-cold water. The yellow precipitate thus formed was washed with water to yield 13 g of product (m.p.=134-158 °C).

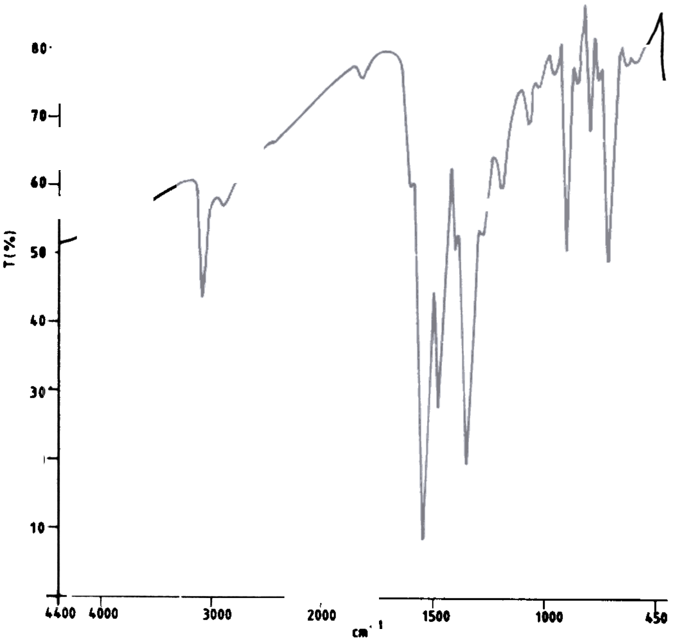


Figure 1. FTIR spectrum of 4, 4'- dimethyl - 3,3',5,5'-tetranitroazoxybenzene.

The suspension of this product in methanol (240 ml) was stirred at room temperature for about 30 min and then filtered to give a white residue. The filtrate obtained was poured into ice-cold water to yield a yellow precipitate of impure 4-amino-2,6-dinitrotoluene, weighing 8.5 g (recrystallised from methanol, m.p.=168-169 °C). The white residue was washed with methanol (20 ml) and dried to yield 4.0 g of 4,4'-dimethyl-3,3',5,5'-tetranitroazoxybenzene (recrystallised from ethyl acetate, m.p. = 215 °C).

2.3 Characterisation

The IR spectrum was recorded at room temperature by KBr disc method using Perkin-Elmer IR spectrophotometer (Model-683). The ^{1}HNMR spectrum was recorded with 9 BRUKER 90 MHz instrument (Model-WG-90) using DMSO-d6 as a solvent with tetramethylsilane as an internal standard. The elemental analysis was

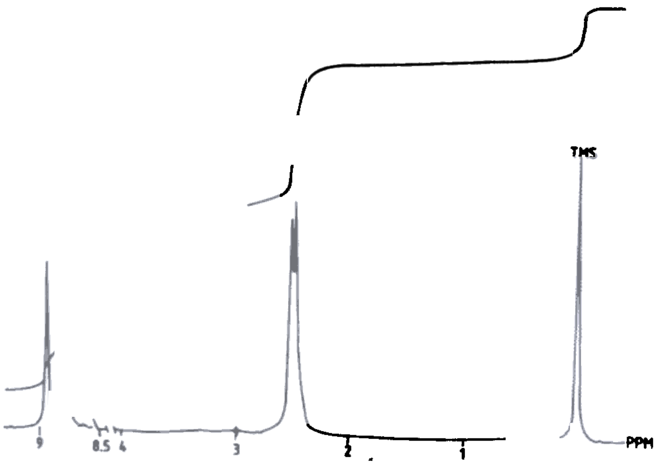


Figure 2. ^{1}HNMR of 4,4'-dimethyl-3,3',5,5'-tetranitroazoxybenzene.

performed on elemental analyser Model EA-1108, Carlo Erber Instruments.

2.4 Explosive & Thermal Properties

Impact sensivitiy[15] of 4,4'-dimethyl-3,3',5,5'-tetranitroazoxybenzene was determined by Fall Hammer method using 2 kg drop weight. Its friction sensitivity was determined on Julius Peter apparatus. Deflagration temperature was determined by heating 0.02 g of sample in a glass tube using Wood's metal bath, at a rate of 5 °C/min and the temperature at which the sample got ignited, was recorded. Differential thermal analysis (DTA) was recorded on locally fabricated DTA apparatus heating 10 mg sample at a rate of 10 °C/min, in the presence of static air.

Table 1. Explosive and thermal properties of 4,4'-dimethyl-3,3',5,5'-tetranitroazoxybenzene

Impact sensitivity, 20 % explosion height (cm)	170
Friction sensitivity (kg)	Insensitive up to 36
Deflagrationtemperature (°C)	286
Differential thermal analysis (°C)	
Endotherm	215
Exotherm	294
Velocity of detonation (calculated) (m/s)	6145

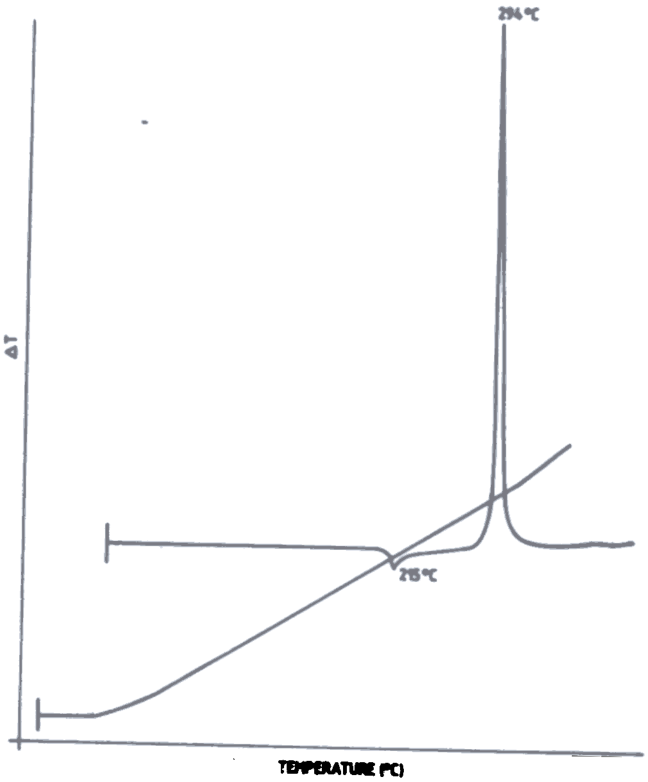


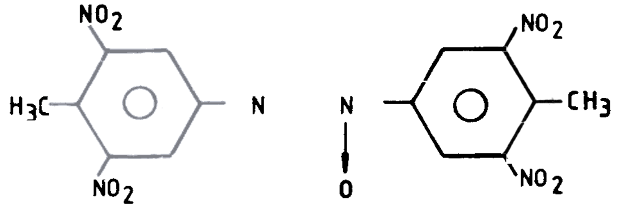
Figure 3. DTA curve of 4,4'-dimethyl-3,3',5,5'-tetranitroazoxybenzene.

3. RESULTS & DISCUSSION

For selective reduction of TNT with H_2S, NH_3 acts as a catalyst and its quantity and mode of addition are important. When liquor NH_3 was added in large quantity (1 ml of concentrated NH_4OH solution for 25 g TNT), as recommended by Atkin[14], *et al.*, large quantity of TNT remained unreacted. However, when NH_3 was added in small quantity and that too in small increments, very less quantity of TNT remained unreacted, and 4-amino-2,6-dinitrotoluene,4-hydroxylamino-2,6-dinitrotoluene and 4,4'-dimethyl-3,3',5,5'-tetranitroazoxybenzene were formed. As revealed by HPLC, DMTNAB is formed up to an extent of 10 per cent. The treatment of crude mixture with KI/HCl converts $-NHOH$ group of 4-hydroxylamino-2,6-dinitrotoluene to $-NH_2$ group, thus effectively increasing the overall yield of 4-amino-2,6-dinitrotoluene to approx. 65-70 per cent. However, it is observed that there is an increase in the percentage of azoxy compound up to

30 per cent after *KI/HCl* treatment. This is because hydroxylamino group may be simultaneously oxidised in the acidic environment resulting in the formation of DMTNAB.

The IR spectrum (Fig. 1) of DMTNAB shows major bands at 3094 (*Ar-H*), 2914 (CH_3), 1546, 1350 ($-NO_2$), and 1478 cm^{-1} (azoxy). In ^{1}HNMR spectrum (Fig. 2), the protons of $-CH_3$ group on phenyl ring attached to the oxidised nitrogen appear at 2.54 ppm, whereas those on the other ring appear at 2.50 ppm. The aromatic protons appearing at 8.98 ppm belong to the phenyl ring attached to the oxidised nitrogen, whereas those appearing at 8.8 ppm belong to the other ring. IR and NMR data suggest the following structure:



The above structure is supported by elemental analysis of DMTNAB, ($C_{14}H_{10}N_6O_9$) $C = 41.56$ per cent, $H = 2.71$ per cent and $N = 20.77$ per cent. The experimental values are comparable with the calculated values, $C = 41.39$ per cent, $H = 2.48$ per cent and $N = 20.68$ per cent. The study on explosive properties of DMTNAB indicates that it is very insensitive to impact and friction. Its deflagration temperature is 286 °C and peak temperature for exothermic decomposition on DTA is 294 °C (Fig. 3), thereby indicating that the compound has good thermal stability coupled with calculated[18] velocity of detonation (VOD) of 6145 m/s (Table 1).

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Dr JP Agrawal, Joint Director, HEMRAL has a background of brilliant academic career and valuable professional experience. He obtained his PhD for his work on explosive nature of metal picrates and picramates' from Gorakhpur University in 1971. His areas of interest are cost-effective polymeric materials, such as unsaturated polyesters, chloropolyesters, epoxy resins, epoxy flexibilizers, silicons and polyurethanes which find applications as inhibitors for rocket propellants and binders for explosives/pyrotechnics etc. At present, He is active in the field of thermally stable explosives, high performance explosives, insensitive explosives and energetic additives for explosives/propellants and has contributed immensely in this area. He has made significant contributions in the field of inhibition of rocket proellants. The development of filament winding technology and inhibitor sleeve technology are some of his major achievements for inhibition of composite rocket propellants. He was given *DRDO Cash Award* and Commendation Certificate for his significant contributions to the integrated guided missile development programme. He also given '*DRDO Technology Award* (1996) for the development of mine antipersonnal inflammable (MAPI).