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CONTINUOUS TRINITROTOLUENE PROCESS STUDIES

IV. IDENTIFICATION AND DETERMINATION OF PURIFICATION BYPRODUCTS

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SUMMARY

The first paper of this series[1] reported the formation of two purification byproducts in the manufacture of trinitrotoluene by the continuous process. One of these compounds was identified as hexanitrobibenzyl and the other was thought to be an azoxy compound. This paper describes the identification of the second compound as 3-methyl-2',4,4',6,6'-pentanitrodiphenylmethane as verified by nuclear magnetic resonance analysis, infrared, and thin-layer chromatographic techniques. The 3-methyl-2',4,4',6,6'-pentanitrodiphenylmethane results from the coupling of 2,4,6-trinitrotoluene with the *meta* position of 2,4,5-trinitrotoluene during purification.

In addition to the identification of 3-methyl-2',4,4',6,6'-pentanitrodiphenylmethane, a rapid liquid chromatographic method was developed for the quantitative determination of hexanitrobibenzyl and 3-methyl-2',4,4',6,6'-pentanitrodiphenylmethane using a microbore column with an ultraviolet detector. Analyses of trinitrotoluene manufactured by the batch process show that hexanitrobibenzyl and 3-methyl-2',4,4',6,6'-pentanitrodiphenylmethane are produced in only trace quantities, while in the continuous process they are present in the final product in the concentration range of 0.1 to 0.5%.

INTRODUCTION

The principal purification process for removal of asymmetrical isomers from 2,4,6-trinitrotoluene (2,4,6-TNT) utilizes an aqueous sodium sulfite (sellite) treatment[2] in an alkaline medium. The nucleophilic attack of sulfite ion on the reactive *meta* position provides removal by formation of water soluble sodium sulfonates. Under these conditions, two major impurities are formed; *viz.* 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB)[1,3] and a compound reported to be 2,2'-dimethyl-3,3',5,5'-tetranitroazoxy benzene[1]. The first is known to be a coupling product of 2,4,6-TNT, the coupling occurring through the methyl groups[4]. Attempts to synthesize the suspected azoxy compound from 2,4,6-TNT alone gave only HNBB; however, a compound

having the same infrared and nuclear magnetic resonance (NMR) spectra, melting point, and thin-layer chromatography (TLC) R_F value as the suspected azoxy compound was synthesized by reacting equal quantities of 2,4,5-TNT and 2,4,6-TNT. This compound was identified as 3-methyl-2',4,4',6,6'-pentanitrodiphenylmethane (MPDM).

Since the presence of these byproducts adversely affects the quality of the finished TNT, a quantitative method of analysis was needed for measuring the concentrations of these compounds. A sensitive and rapid liquid chromatographic method was developed for HNBB and MPDM using a 2 m × 2 mm Porasil A column. The solvent for this analysis is dichloromethane. The method has been used for the analysis of TNT samples to help in determining the cause of low quality TNT as measured by freezing point.

EXPERIMENTAL

Apparatus

NMR spectra were obtained on a Varian A-60 NMR Spectrometer using deuterated dimethylsulfoxide as the solvent. TLC separations were as described previously[1]. A liquid chromatograph was constructed utilizing a Milton Roy Instrument Minipump Model 196-57 and a Laboratory Data Control UV Detector Model 1285, operating at 254 nm. The analytical column was a 2 m × 2 mm stainless-steel column packed with 37/75-μ Porasil A (Waters Associates, Inc.). The Porasil A was dried in an oven for 2 h at 110° and packed dry into the column with tapping. In order to maintain the desired resolution, the eluting solvent, dichloromethane, was dried over molecular sieves. A Hamilton HP 305 high pressure syringe was used for injection.

Reagents

The HNBB was prepared by two methods; the first utilizing the reaction between sodium hypochlorite and 2,4,6-TNT[4], and the second was by adding a 5% sodium hydroxide solution dropwise to a tetrahydrofuran solution of 2,4,6-TNT. The product was subsequently purified by the same procedure used for the sodium hypochlorite–TNT reaction product.

The MPDM was synthesized by adding dropwise, over a 30-min period, 60 ml of a 1% sodium hydroxide solution to 40 ml of tetrahydrofuran containing 2 g of 2,4,6-TNT and 2 g of 2,4,5-TNT. The temperature of the reaction solution increased about 10° upon addition of the sodium hydroxide. The solution was agitated for an additional 30 min and excess base neutralized with sulfuric acid–water (1:1). The intense purple color of the solution became colorless upon neutralization. The tetrahydrofuran was removed in an air stream and the brown precipitate slurried in methanol, filtered, and recrystallized several times from benzene with the aid of decolorizing carbon. This procedure gave yellow crystals having an uncorrected melting point of 224–225°.

The 3-methyl-2,2',4',6,6'-pentanitrodiphenylmethane was prepared by the same method as presented above with the exception of the reactants which, in this case, were 2,4,6-TNT and 2,3,4-TNT. The reaction product had an uncorrected melting point of 185–186°.

Procedure

For the quantitative determination of HNBB and MPDM in TNT, 1–1.5 g of sample were accurately weighed into a 25-ml volumetric flask and diluted to volume with dichloromethane. 4 μl of the sample solution were injected into the liquid chromatograph which operated with reagent grade dichloromethane at a flow rate of 1 ml/min and a pressure of 600 p.s.i. Quantitative data were obtained by comparison of peak heights to those of external standards of the pure materials.

RESULTS AND DISCUSSION

NMR spectroscopy was used to identify the reaction product between 2,4,6-TNT and 2,4,5-TNT as MPDM. The structure of this compound is shown in Fig. 1.

In the NMR spectrum, three types of aromatic hydrogen are observed. $H_{3'}$ and $H_{5'}$ are equivalent and occur as a singlet at 9.20 p.p.m. (60MHz) relative to tetramethylsilane. Shifts at 8.88 p.p.m. and 7.13 p.p.m. are assigned to protons H_5 and H_2,

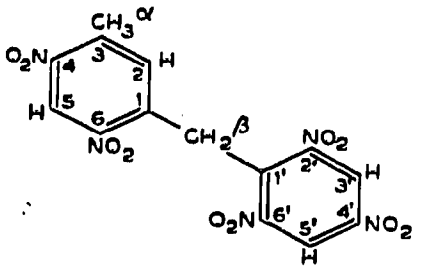

Fig. 1.

respectively. The methyl proton, H_α, occurs as a singlet at 2.50 p.p.m. and the intensity indicates that only one methyl group is present. The methylene H_β attached to the two deactivated aromatic rings occurs as a singlet at 4.77 p.p.m.

The formation of MPDM undoubtedly results from the nucleophilic attack of the 2,4,6-trinitrobenzyl ion (TNT, $pK = 14.45$)[5] in the *meta* position of 2,4,5-TNT analogous to the sellite reaction. The nucleophilic substitution of the 2,4,6-trinitrobenzyl anion on 2,3,4-TNT also occurs to yield 3-methyl-2,2',4',6,6'-pentanitrodiphenylmethane. The NMR spectrum for this compound was consistent with the proposed structure. This compound was never detected in TNT taken either from the continuous or batch processes. The reason for its absence is most probably due to steric hindrance to substitution in the *meta* position of 2,3,4-TNT.

In the liquid chromatographic determination of HNBB and MPDM separation of the two compounds from each other and from TNT is very good, as shown in Fig. 2. All isomers of dinitrotoluene (DNT) and TNT have the same elution time and are included in the peak labeled "TNT". None of the compounds normally found in the final product interfere with the determination of HNBB and MPDM. However, 2,4,6-trinitrobenzaldehyde, which is sometimes present in a concentrated sample of impurities, appears as a shoulder on the leading edge of the MPDM peak.

The precision of the method was established from replicate determinations of samples containing varying amounts of the two purification byproducts. The coefficient of variation was found to be 1.0% for MPDM and 1.5% for HNBB. The sen-

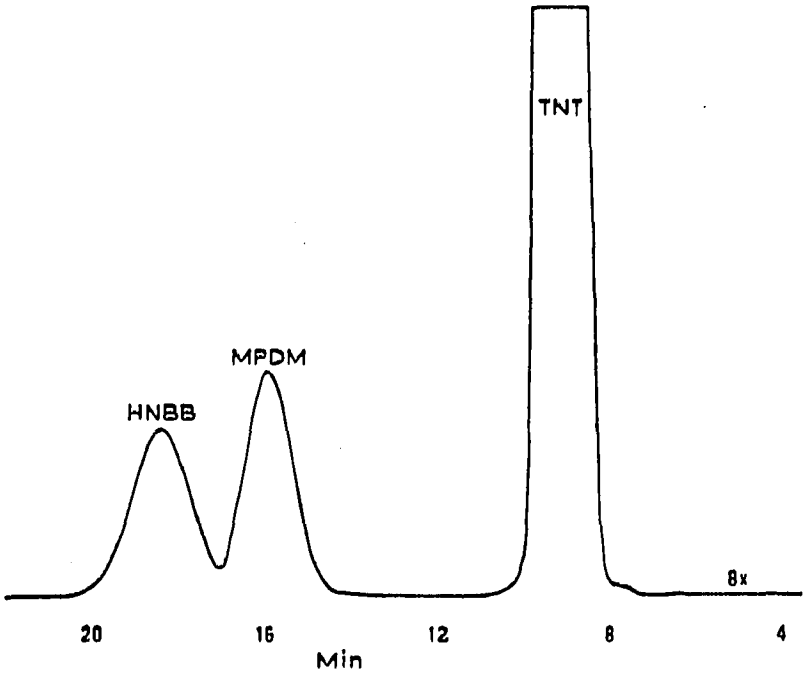

Fig. 2. Liquid chromatographic separation of TNT purification byproducts, Column: Porasil A 2 m × 2 mm; solvent: dichloromethane; flow rate: 1 ml/min.

sitivity of the method can be varied with the sample size taken for analysis; however, the limit of detection for either MPDM or HNBB with the instrumentation used is in the nanogram range.

The liquid chromatographic method has been used for the analysis of TNT samples from both the continuous and batch processes. In samples from the continuous process, the concentration of HNBB usually varies between 0.1 and 0.5% and the MPDM from 0.1 to 0.3%. The primary reason for variations in concentrations of these two compounds is the pH at which purification is conducted[1]. Other factors, such as ratio of TNT to aqueous phase, recycle flows, etc., can also affect the amount of these byproducts made. The effect of pH on byproduct formation for a given set of operating conditions is shown in Table I.

Very little of either of the byproducts is made in the batch process. Although only a limited number of batch process TNT samples have been analyzed, the maximum concentration found was 0.06% MPDM and 0.01% HNBB. The concentration

TABLE I

THE EFFECT OF pH ON BYPRODUCT FORMATION

pH	*HNBB (%)*	*MPDM (%)*
9.0	0.35	0.28
8.7	0.29	0.25
8.5	0.21	0.18
8.2	0.06	0.08
8.0	0.02	0.06
7.5	<0.01	0.03
7.0	<0.01	<0.01

of MPDM is always higher than the HNBB in samples from the batch process while the reverse is true for TNT from the continuous process. The primary reason for difference in the concentrations of the byproducts produced in the two processes is the temperature at which purification takes place. In the continuous process, liquid TNT at about 80° is contacted with the aqueous sodium sulfite solution to effect removal of the β and γ isomers. In the batch process, the TNT is crystallized and the particles contacted with sodium sulfite solution at a temperature of about 55°.

The liquid chromatographic method for the analysis of HNBB and MPDM has proved quite valuable in the control of the continuous process. The results have been used to calculate the amount of freezing point lowering which can be expected from these two byproducts, thus allowing operating personnel to determine whether the production of low quality TNT, as measured by freezing point, is the result of problems in purification or in nitration.

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