CONTINUOUS TNT PROCESS STUDIES

III. THIN-LAYER CHROMATOGRAPHIC ANALYSIS OF OXIDATION PRODUCTS FROM NITRATION

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SUMMARY

Thin-layer chromatographic separations are shown of all major oxidation products from various steps of the continuous TNT nitration process and of nitration compounds resulting from impurities in the toluene used for nitration. This technique has been used to correlate the formation of the various oxidation products with plant operating conditions and thereby exercise control on the nitration process to minimize oxidation.

INTRODUCTION

Two earlier papers in this series dealt with the thin-layer (TLC)[1] and gas chromatographic (GC)[2] analysis of samples from the continuous TNT process. The first paper describes the nitration system but was devoted principally to the purification process. The second paper describes a method for determining the amount of the various nitrotoluenes in the organic phase with the aid of response factors and normalization techniques. This third paper deals only with the TLC investigations of oxidation products in nitration.

Although several analytical techniques have been reported for quantitative analysis of TNT, only a few have been concerned with oxidation products, since the majority of the products are present in minor quantities. GEHRING[3] used NMR to analyze the red oil exudate which appears on the surface of crude TNT after it has stood for several days. This material represents a highly concentrated source of impurities. GEHRING ascribes the color of this exudate to the red 2,4-dinitrobenzoic acid (2,4-DNBA). Other compounds detected by NMR were 2,4,6-trinitrobenzoic acid (TNBA), 2,4,6-trinitrobenzaldehyde (TNBAl), 3,4-dinitrobenzoic acid (3,4-DNBA), *m*-dinitrobenzene (DNB), and α-nitrato-2,4,6-trinitrotoluene (α-nitrato-TNT).

YASUDA[4] reports a TLC separation where oxidation products such as trinitrobenzene (TNB) and α-nitrato-TNT were observed in TNT. Several other papers report results from an intensive investigation of oxidation products resulting from the nitration of several aromatic compounds as analyzed by TLC methods (op. cit. ref. 1).

In the first paper by the authors[1], some oxidation products inherent to the

continuous TNT process were reported; however, at that time several compounds were noted which had not been identified. The present paper represents a compilation of oxidation products found in the continuous TNT nitration process. Observation of these compounds with the sensitive spray reagent ethylenediamine (EDA) does not require prior impurity enhancement techniques necessary by other methods.

Samples from mono- through tri-nitration stages have been analyzed by TLC and the results correlated with nitrating conditions, thus permitting control of the process to minimize the formation of oxidation products.

EXPERIMENTAL

Apparatus

Silica gel with starch binder (MN-Kiesel Gel S/UV-254) was purchased from Brinkmann Instruments Inc.; applicator and glass plates (200 × 200 mm) were purchased from Kensington Scientific Co.; a 50-μl syringe was used to deliver samples into the support.

Reagent

Isomers of mono-, di-, and tri-nitrotoluene were obtained as described in a previous publication[2]. The TNB, 4,6-dinitro-o-cresol (4,6-DNOC), 3,4-DNBA, and 2,4-DNBA were purchased from Eastman Organic Chemicals, Rochester, N.Y. The TNBA and picric acid were purchased from J. T. Baker Chemicals, Philipsburg, N.J. The DNB was purchased from Aldridge Chemical Company, Milwaukee, Wisc., and TNBAl from K&K Laboratories Inc., Plainsview, N.Y. The 2,4,6-trinitroethylbenzene (TNEB)[5] and 2,4,6-trinitro-m-xylene (TNX)[6] were prepared according to URBANSKI. The 2,4,6-trinitrobenzyl alcohol (TNBOH)[7] was prepared through hydrolysis of the 2,4,6-trinitrobenzyl bromide (TNBB)[8]. The α-nitrato-TNT was prepared by reaction of the TNBB with silver nitrate[9]. The white compound (2,2'-dicarboxy-3,3',5,5'-tetranitroazoxybenzene) was obtained from the Radford continuous TNT process and purified by ether recrystallization. The monocarboxy white compound (MCTNAB) was obtained by aqueous reflux of white compound[10]. The 2,6-dinitro-p-cresol (2,6-DNPC) was obtained by nitration of p-cresol with dilute nitric acid. The 3-hydroxy-4,6-dinitrobenzoic acid was obtained by $KMnO_4$ oxidation of 2,4,5-TNT.

Preparation of thin-layer plates

Thirty grams of support were added to 75 ml of warm water and the temperature raised to near boiling with vigorous agitation to assure mixing of the starch binder. A 500-μm gate was used to control plate thickness and plates were activated at 100° for 2 h and then stored in a desiccator over indicating silica gel.

Sampling and sample preparation

A 2-ml sample of the organic phase from a nitration vessel was pipetted into 5 ml of water in a preweighed 25-ml volumetric flask, thus quenching the nitration and oxidation reactions. The flask was then diluted to volume with acetone and the solution analyzed immediately.

Separation procedure

Due to the wide range of nitration and oxidation products encountered in the continuous process, no single solvent system was found which could separate all components. Two solvent systems were generally employed, *viz.* (1) a non-polar 50:45:5 benzene–cyclohexane–ethyl acetate mixture (solvent system No. 1), and (2) a more polar system, 50:30:20 benzene–ethyl ether–ethanol (solvent system No. 2). Since samples taken from various stages of nitration contained small amounts of entrained acid, several drops of ammonium hydroxide were added to the eluting solvent to curtail tailing. Care must be taken not to use excess ammonium hydroxide; too much can change the order of elution. A $25 \mu l$ aliquot was placed about 1 in. from the bottom of the plate and developed in a chromatographic tank containing the desired solvent mixture. After development, the plate was allowed to dry for visualization with UV light and subsequent spraying with EDA.

RESULTS AND DISCUSSION

A non-polar separation with solvent system No. 1 is shown in Fig. 1. This system gives a good separation of the mono-, di-, and trinitrotoluenes from the various nitration vessels. These samples often contain two compounds with R_F values slightly greater than that of 2,4,6-TNT, and one with an R_F value lower than that of 2,4,5-TNT. They were previously reported as unknowns[1], and have subsequently
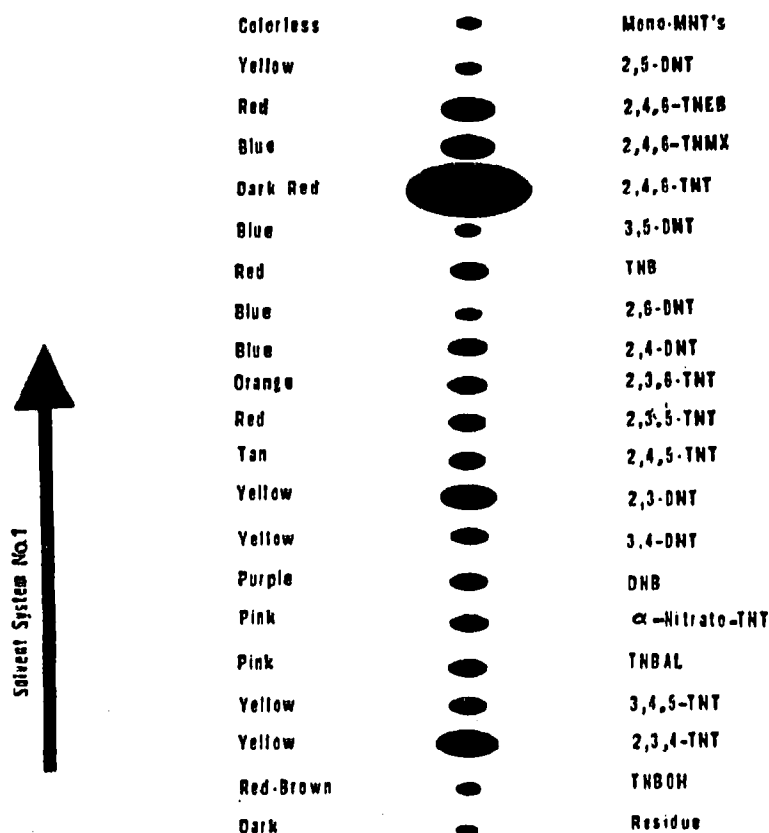

Fig. 1. TLC separation of crude TNT using solvent system No. 1. Color produced with ethylene-diamine spray reagent. Support: starch-bound silica gel.

been identified as TNEB, TNX, and DNB. These compounds result from the nitration of ethylbenzene, xylene, and benzene present as impurities in toluene.

Several of the compounds resulting from the oxidation of the methyl group of TNT are also separated with this solvent system, *viz.* TNBOH, TNBA1, and α-nitrato-TNT. The α-nitrato-TNT undoubtedly results from nitration of the TNBOH. The TNBA1 and α-nitrato-TNT produce distinguishable colors with the EDA spray reagent as indicated in Fig. 1. The latter also gives a characteristic blue reaction product with diphenylamine–sulfuric acid reagent, indicative of a nitrate ester. Also shown in this separation is TNB, which is found in all nitration vessels, and results from the decarboxylation of TNBA.

A considerable number of oxidation products remain at or near the origin when the plate is developed with solvent system No. 1. A more polar solvent system gives the separation shown in Fig. 2. Less polar compounds travel with the solvent front and a good separation is obtained for the more polar oxidation products. Not all compounds shown in the separation appear in any one sample.
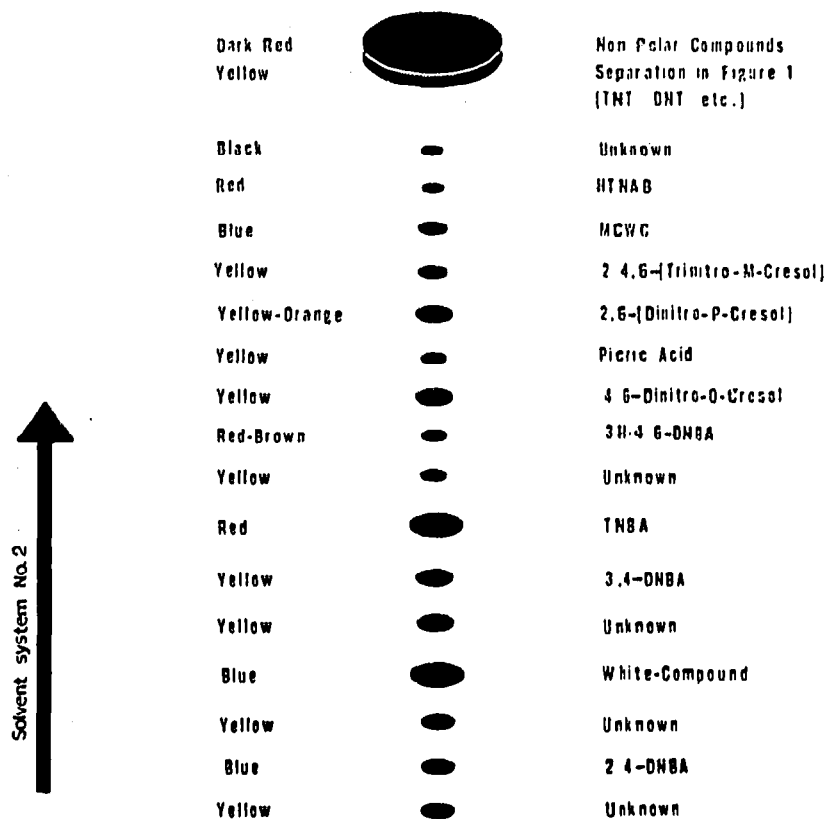

Fig. 2. TLC separation of crude TNT using solvent system No. 2. Color produced with ethylenediamine spray reagent. Support: starch-bound silica gel.

The TLC separations described above have been used as a diagnostic tool to relate nitrating conditions with operating difficulties and/or product quality problems. The results of these studies are described below.

The major oxidation products in samples from the first stage of nitration are 2,6-DNPC and 4,6-DNOC. Quantitative analysis for these cresols was made following TLC separation with excision of the bands, and subsequent colorimetric development

with EDA, a method similar to that of GLOVER AND KAYSER[11]. Estimates of the concentration of these cresols can also be made from the size of their TLC spots relative to standards. The concentration of cresols found in the early stages of nitration is generally between 0.2 and 0.5 %. The amount of these cresols formed during nitration was found to be inversely related to the strength of the acid in the first two nitration vessels, *i.e.*, the higher the total acidity, the lower the concentration of nitrocresols.

The nitrocresols are not found in nitrators above nitrator 2 as they are destructively oxidized in the higher acid strengths present in the latter stages of nitration.

Three oxidation products are generally present which are quite useful from a diagnostic standpoint. These are α-nitrato-TNT, TNBAl, and TNBOH. Under good operating conditions these compounds will be seen in small quantities in nitrators 1 through 3 with the highest concentration being found in nitrator 2. They are not present in the higher nitrators under proper nitrating conditions. An increase in the concentration of these products is indicative of an oxidizing condition generally caused by a high nitronium ion concentration as a result of high oleum and/or nitric acid concentrations in nitrators 3 through 6. An excellent correlation between oxidation products and nitric acid concentration can be seen by comparing Figs. 3 and 4, where the samples analyzed were taken when the nitric acid concentration in all nitrators was normal and high, respectively.

White compound and TNBA are two other oxidation products which can serve as a measure of the reactions occurring in nitration. These two compounds are present in most nitrating vessels but are found in highest concentrations in nitrators 2 and 3. Again the amount of these two products formed is a function of total acidity in the nitrators and the ratio of sulfuric acid to nitric acid.

If TNT is taken from the acid washer prior to purification in the continuous process and allowed to stand at a slightly elevated temperature, a red oil exudate will form, as was observed for crude TNT from the batch process. This exudate is a concentrated sample of oxidation products including tetranitromethane and is quite sensitive to mechanical stimuli. The red oil also contains 2,4- and 3,4-DNBA,

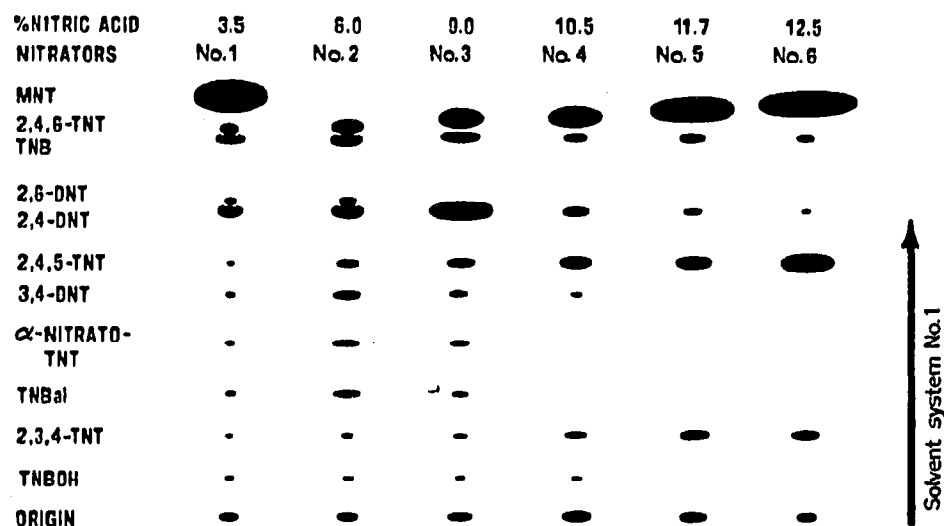| %NITRIC ACID	3.5	6.0	9.0	10.5	11.7	12.5	
NITRATORS	No.1	No.2	No.3	No.4	No.5	No.6	
MNT							
2,4,6-TNT							
TNB							
2,6-DNT							
2,4-DNT							
2,4,5-TNT							
3,4-DNT							
α-NITRATO-TNT							
TNBal							
2,3,4-TNT							
TNBOH							
ORIGIN							Solvent system No.1

Fig. 3. TLC separation of the continuous nitration of toluene, normal nitric acid values using solvent system No. 1.

picric acid, and 3-hydroxy-4,6-dinitrobenzoic acid. The latter results from oxidation of the 2,4,5-TNT.
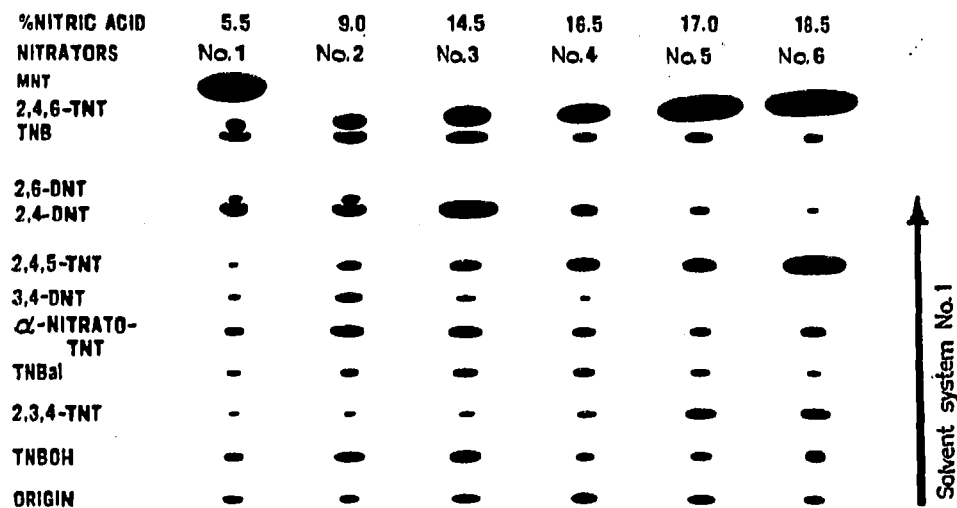

Fig. 4. TLC separation of the continuous nitration of toluene, high nitric acid values using solvent system No. 1.

Another compound detected in the red oil exudate was 2 or 2'-hydroxy-3,3',5,5'-tetranitroazoxybenzene (HTNAB), resulting from the oxidation of MCTNAB[10]. A similar oxidation of white compound produces severe degradation and one compound, indicated as an unknown above the HTNAB in Fig. 2, matches in color and R_F value with a fraction in the red oil exudate. This suggests that some oxidative degradation of white compound does occur in the continuous process.

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