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IDENTIFICATION OF 1,3,5-TRIAMINO-2,4,6-TRINITROBENZENE IMPURITIES BY TWO-DIMENSIONAL THIN-LAYER CHROMATOGRAPHY

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SUMMARY

A two-dimensional thin-layer chromatographic method capable of identifying twelve impurities of 1,3,5-triamino-2,4,6-trinitrobenzene is described. The method is applied to the analysis of toluene and acetone extracts of various 1,3,5-triamino-2,4,6-trinitrobenzene samples. The identified impurities include 1,3,5-trichloro-2,4,6- trinitrobenzene, 1,3-dinitro-2,4,5,6-tetrachlorobenzene, 1,3-dinitro-2,4,6-trichlorobenzene and their partially aminated products. In addition, trace amounts of several unknown compounds were detected. From the identified products, it is possible to explain the small amount of chlorine (0.5%) that is commonly found in 1,3,5-triamino-2,4,6-trinitrobenzene samples.

INTRODUCTION

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) is an explosive that possesses excellent thermal stability and sensitivity characteristics. These properties make TATB an attractive candidate for special applications. However, the properties of any explosive are dependent on the purity of the material. A recent pilot-plant study on the synthesis of TATB[1] prompted us to develop a convenient method for identifying the impurities associated with the product.

KAPLAN *et al.*[2] used column chromatography and solvent extraction to isolate the by-products of TATB. By chemical and spectrophotometric methods, they identified the major impurities as being ammonium chloride, 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) and the partially aminated products of TCTNB. In a complex mixture of this type, thin-layer chromatography (TLC) is a more effective method of separating and identifying closely related compounds than column or paper chromatography. Gas chromatography was ruled out because some of the TATB impurities melt with decomposition at elevated temperatures. In this paper, we describe a two-dimensional TLC method for identifying twelve impurities found in TATB and the application of the method to the analysis of toluene and acetone extracts of various TATB samples.

REAGENTS AND EQUIPMENT

The applicator, chromatojar, Silica Gel G and glass plates (200 × 200 mm) were purchased from Brinkmann Instruments, Inc.

Zinc metal dust, AR grade, was obtained from Mallinckrodt Chemical Works.

All solvents were reagent grade and were used as received. Light petroleum ether with a boiling range of 30–60° was purchased from Merck & Co., Inc.

The spray reagent consisted of 0.25% *p*-diethylaminobenzaldehyde (*p*-DEAB) and 0.25 N HCl in absolute ethanol.

A MISCO lambda pipette or a capillary melting-point tube was used as the sample applicator.

A fluorescent light source was used to view the chromatogram.

All the compounds used in this investigation were obtained from residues extracted from crude TATB samples, purified by TLC. The identity of each purified fraction was established by melting-point determinations, elemental analyses, infrared and mass spectrometry, and, in several instances, microhydrogenation.

EXPERIMENTAL

Preparation of thin layers

A slurry consisting of 30 g of Silica Gel G and 1 g of zinc dust in 65 ml of distilled water was prepared and coated on five glass plates by pulling the applicator across the plates at a constant speed with a Bodine speed reducer motor. After being exposed to the atmosphere for 15 min, the Silica Gel G–Zn plates were activated at 110° for 2 h before use.

R_G measurement

The migration rate (R_G value) of each compound relative to that of TCTNB (reference compound) was measured on an activated Silica Gel G–Zn plate using approximately thirty solvent systems. The *p*-DEAB–HCl reagent was sprayed on the chromatogram to locate the compounds. At best, a one-dimensional TLC system would separate about ten of the twelve components included in this study. Consequently, a two-dimensional plot of the R_G values was made. 1,2-Dichloroethane (solvent I) and a 1:9 acetone–light petroleum mixture (solvent II) were found to separate completely all twelve components. A plot of the R_G values as determined in solvents I and II is shown in Fig. 1.

Procedure

An aliquot containing 100–200 µg of impurities is pipetted to a point approximately 1 in. from the lower right-hand corner of an activated Silica Gel G–Zn plate. The diameter of the spot is kept at or below 0.5 in. The plate is chromatographed in 200 ml of solvent I for 1 h, exposed to the atmosphere for 10 min to evaporate the solvent, and re-chromatographed at 90° to the direction of flow of solvent I in an equal volume of solvent II for an additional 1 h.

The separated products are located by spraying the plate uniformly with the spray reagent. The plate is heated with a hair dryer, particularly in the TCTNB region, to intensify the colored spots. The chromatogram is viewed over a fluorescent

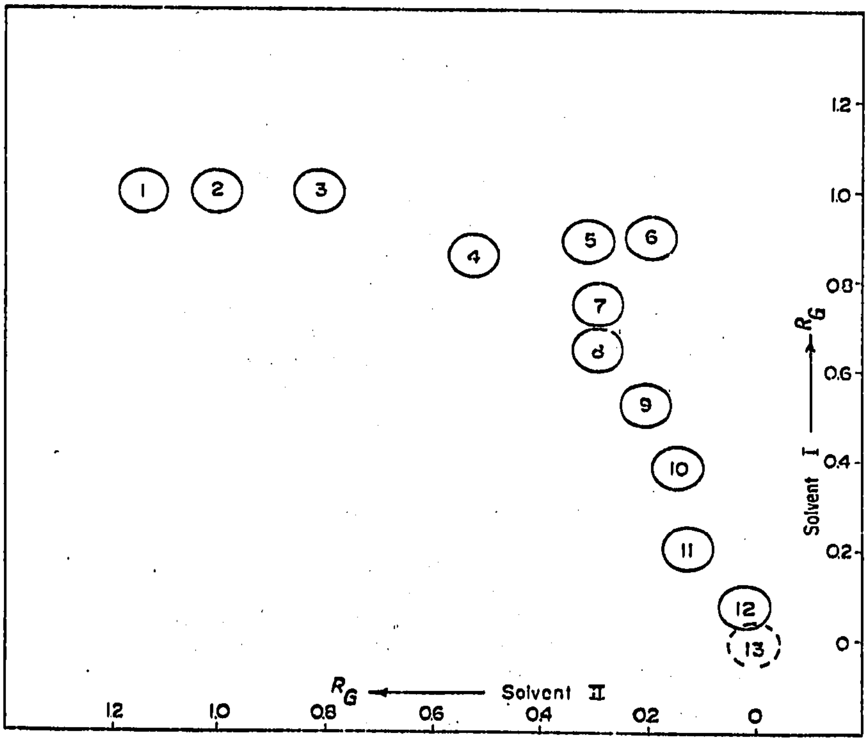

Fig. 1. Two-dimensional plot of R_G measurements of TATB impurities. Compounds: 1 = 1,3-dinitro-2,4,5,6-tetrachlorobenzene; 2 = 1,3,5-trichloro-2,4,6-trinitrobenzene (reference compound); 3 = 1,3-dinitro-2,4,6-trichlorobenzene; 4 = 2,6-dinitro-3,4,5-trichloroaniline; 5 = 2,4-dinitro-3,5,6-trichloroaniline; 6 = 3,5-dinitro-2,4,6-trichloroaniline; 7 = 3,5-dichloro-2,4,6-trinitroaniline; 8 = 1,3-diamino-5,6-dichloro-2,4-dinitrobenzene; 9 = 1-chloro-3,5-diamino-2,4,6-trinitrobenzene; 10 = 1-chloro-3,5-diamino-2,6-dinitrobenzene; 11 = 1-chloro-3,5-dinitro-2,4,6-triaminobenzene; 12 = 1,3-dinitro-2,4,6-triaminobenzene; 13 = point of sample application.

light source, and a tracing of the chromatogram is made. This tracing is then compared with a chromatogram obtained from a synthetic mixture to identify the products.

RESULTS AND DISCUSSION

Fig. 1 indicates that all twelve components are completely separated. To substantiate these results, a synthetic mixture of all the components was chromatographed; a tracing of the developed chromatogram is shown in Fig. 2. The similarity of Figs. 1 and 2 is remarkable, and for identification work the TLC method is more than adequate.

Residues obtained from toluene extracts of pilot-plant TATB samples were analyzed by this procedure. The identified products are listed in Table I in approximate order of decreasing concentration as estimated from the size and intensity of the spots.

The complexity of the extracts is evident. 1,3-Dinitro-2,4,5,6-tetrachlorobenzene (DNtetraCB), 1,3-dinitro-2,4,6-trichlorobenzene (DNTCB) and 3,5-dinitro-2,4,6-trichloroaniline (DNTCA) are the major components. With the exception of the unknown compounds located above the 2,6-dinitro-3,4,5-trichloroaniline, the

TABLE I

ANALYSIS OF RESIDUES FROM TOLUENE EXTRACTS OF VARIOUS TATB SAMPLES

Sample	*Identified products*
Extract residue from typical TATB prepared from crude TCTNB	1,3-Dinitro-2,4,5,6-tetrachlorobenzene = 1,3-dinitro-2,4,6-trichlorobenzene = 3,5-dinitro-2,4,6-trichloroaniline >; 2,6-dinitro-3,4,5-trichloroaniline = 2,4-dinitro-3,5,6-trichloroaniline = 1,3-diamino-5,6-dichloro-2,4-dinitrobenzene = 1-chloro-3,5-diamino-2,6-dinitrobenzene = 1-chloro-3,5-dinitro-2,4,6-triaminobenzene >; 1,3,5-trichloro-2,4,6-trinitrobenzene = unknown x_1 > unknown x_2
Extract residue from TATB prepared from purified TCTNB	3,5-Dinitro-2,4,6-trichloroaniline >; 1,3-dinitro-2,4,5,6-tetrachlorobenzene = 1,3,5-trichloro-2,4,6-trinitrobenzene >; 1,3-dinitro-2,4,6-trichlorobenzene >; 2,6-dinitro-3,4,5-trichloroaniline = 2,4-dinitro-3,5,6-trichloroaniline = 1,3-diamino-5,6-dichloro-2,4-dinitrobenzene >; 1-chloro-3,5-dinitro-2,4,6-triaminobenzene = unknown x_1 = unknown x_2
Extract residue from TATB–incomplete amination	1,3-Dinitro-2,4,5,6-tetrachlorobenzene = 1,3-dinitro-2,4,6-trichlorobenzene >; 1,3,5-trichloro-2,4,6-trinitrobenzene = 3,5-dinitro-2,4,6-trichloroaniline >; 2,6-dinitro-3,4,5-trichloroaniline = 1,3-diamino-5,6-dichloro-2,4-dinitrobenzene = 1-chloro-3,5-diamino-2,6-dinitrobenzene >; 1-chloro-3,5-dinitro-2,4,6-triaminobenzene = 2,4-dinitro-3,5,6-trichloroaniline >; 3,5-dichloro-2,4,6-trichloroaniline >; unknown x_1 = unknown x_2
Crude TCTNB	1,3,5-Trichloro-2,4,6-trinitrobenzene ≫ 1,3-dinitro-2,4,5,6-tetrachlorobenzene >; 1,3-dinitro-2,4,6-trichlorobenzene

origin of the partially aminated products can be explained on the basis of DNtetraCB, DNTCB and TCTNB. The unknown compounds are not present in sufficient amounts for their chemical analyses to be carried out.

In analyzing the crude TCTNB, appreciable amounts of DNtetraCB and DNTCB were found in the sample. The partial nitration of 1,3,5-trichlorobenzene (TCB), used as a starting material in the TATB process, produces DNTCB. However, the presence of DNtetraCB is disconcerting. Two possible routes can lead to DNtetraCB: either 1,2,3,5-tetrachlorobenzene may be present as an impurity in TCB, or DNtetraCB may be produced during the nitration of TCB by "transchlorination". It is of interest to determine the origin of the DNtetraCB, as half of the impurities listed in Table I are derived directly from it.

It is noteworthy that the partially aminated products of TCTNB are missing from Table I. This is in contrast with the results of KAPLAN *et al.*[2]. In addition, they did not mention the amino derivatives of DNtetraCB and DNTCB. Differences in the

TABLE II

ANALYSIS OF CONCENTRATE FROM SOXHLET EXTRACTION (ACETONE) OF TATB SAMPLES

Sample	*Identified products*
Extract from pilot-plant crude TATB	1-Chloro-3,5-dinitro-2,4,6-triaminobenzene > 1-chloro-3,5-diamino-2,6-dinitrobenzene > 1,3-diamino-5,6-dichloro-2,4-dinitrobenzene > 1,3-dinitro-2,4,6-triaminobenzene > 3,5-dinitro-2,4,6-trichloroaniline = 1-chloro-3,5-diamino-2,4,6-trinitrobenzene > unknown x_4 > 1,3-dinitro-2,4,5,6-tetrachlorobenzene = 1,3,5-trichloro-2,4,6-trinitrobenzene = 1,3-dinitro-2,4,6-trichlorobenzene > 2,6-dinitro-3,4,5-trichloroaniline = 2,4-dinitro-3,5,6-trichloroaniline = 3,5-dichloro-2,4,6-trinitroaniline = unknown x_1 = unknown x_3 > unknown x_2
Extract from pilot-plant crude TATB—steamed for 3 h	1-Chloro-3,5-dinitro-2,4,6-triaminobenzene ≫ 3,5-dichloro-2,4,6-trinitroaniline = 1-chloro-3,5-diamino-2,6-dinitrobenzene > 1-chloro-3,5-diamino-2,4,6-trinitrobenzene = 1,3-dinitro-2,4,6-triaminobenzene > 3,5-dinitro-2,4,6-trichloroaniline > unknown x_3
Extract from TATB—steamed for 3 h oven-dried at 100° for 16 h and at 150° for 24 h	1-Chloro-3,5-dinitro-2,4,6-triaminobenzene ≫ 1-chloro-3,5-diamino-2,4,6-trinitrobenzene = 3,5-dichloro-2,4,6-trinitroaniline > 1,3-diamino-5,6-dichloro-2,4-dinitrobenzene > 3,5-dinitro-2,4,6-trichloroaniline = unknown x_3 = 1,3-dinitro-2,4,6-triaminobenzene > 2,4-dinitro-3,5,6-trichloroaniline
Extract from TATB prepared from purified TCTNB	1-Chloro-3,5-diamino-2,6-dinitrobenzene > 3,5-dinitro-2,4,6-trichloroaniline = 3,5-dichloro-2,4,6-trinitroaniline = 1,3-dinitro-2,4,6-triaminobenzene

starting materials and reaction conditions used by the two laboratories account for these differences.

Acetone extracts of various TATB samples were also analyzed. 3 g samples were extracted for 30–40 h, the extracts were concentrated to 3 ml and aliquots were analyzed by TLC. Table II summarizes the impurities identified in the extracts. In view of these findings, it is not surprising that TATB samples submitted for element analyses are commonly found to contain about 0.5% Cl.

A peculiar behavior of the 1-chloro-3,5-dinitro-2,4,6-triaminobenzene spot was observed with the acetone-extracted samples. The major component appeared as an elongated spot with a "ghosting" effect adjacent to it. It was also displaced from the position predicted in Fig. 1. The compound was isolated from the thin layer, and its infrared spectrum was found to be identical with that of 1-chloro-3,5-dinitro-2,4,6-triaminobenzene. It has been established that the low solubility of this material in solvents I and II and the high concentration of sample applied on the thin layer produced the observed results.

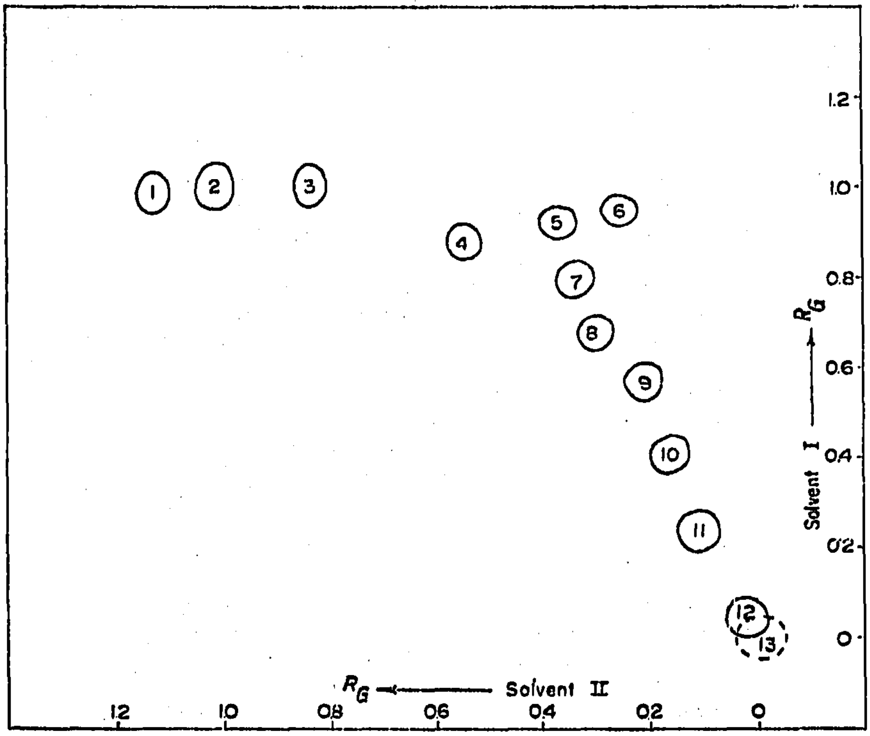

Fig. 2. Two-dimensional separation of synthetic mixture of TATB impurities. Compounds as in Fig. 1.

The detection limit of the spray reagent was briefly investigated. With the exception of DNtetraCB, 0.5 μg of each compound can be chromatographed and detected; DNtetraCB requires about 0.8 μg.

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