IDENTIFICATION OF ETHYL CENTRALITE–NITROGEN TETROXIDE REACTION PRODUCTS*

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INTRODUCTION

In the course of an investigation to evaluate the effective capacity of various stabilizers to react with nitrogen tetroxide[1], it was found that very few qualitative methods were available to identify the reaction products. The ethyl centralite–nitrogen tetroxide (EC–N_2O_4) reaction was of particular interest to us, since ethyl centralite (EC) is one of the more commonly used stabilizers in nitrocellulose formulations.

SHROEDER *et al.* describe a column chromatographic method of separating and estimating the EC derivatives in smokeless powder[2]; however, this technique was found to be inadequate for our purpose. Other quantitative methods devised for the determination of a specific EC derivative were inapplicable for identification work.

This article presents a two-dimensional thin-layer chromatographic method for the separation and identification of twenty-five ethyl centralite nitration products. The method is applied to the analysis of the EC–N_2O_4 reaction products.

REAGENTS AND EQUIPMENT

Applicator, chromatojar, silica gel G, and glass plates (200 × 200 mm), purchased from Brinkman Instruments, Inc.

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

Reagent grade solvents. Petroleum ether from Merck & Co., Inc., with boiling range from 30–60°.

Spray reagents. 0.003 % dichlorofluorescein in ethanol; 0.25 % *p*-diethylaminobenzaldehyde (*p*-DEAB) and 0.2 N HCl in absolute ethanol.

An Agla micrometer syringe or capillary melting point tube used as a sample applicator.

Kensco short wavelength ultraviolet light source.

EXPERIMENTAL

Preparation of thin layer

Modification of STAHL's technique for thin layer preparation was necessary in order to incorporate the zinc dust into the silica gel G, a procedure described in an earlier

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publication[3]. A slurry mixture was prepared by adding 30 g of silica gel G and 1 g of zinc dust to 65 ml of rapidly stirred water. Coating was accomplished by pulling the applicator with a Bodine speed reductor motor at a constant speed over five glass plates. The silica gel G–Zn plates were activated at 120° overnight before use.

R_G measurement

With twenty-five authentic samples on hand, the migration rate of each compound with respect to ethyl centralite (reference compound) was measured in ten different solvents. From cross-plots of the R_G values, 1,2-dichloroethane (solvent I) and ethyl acetate–petroleum ether (25:75) (solvent II) were found to be the most efficient solvent pair. Fig. 1 represents a two-dimensional plot of the R_G values as measured in solvents I and II. Only 4-nitrophenol was found to tail on migration.
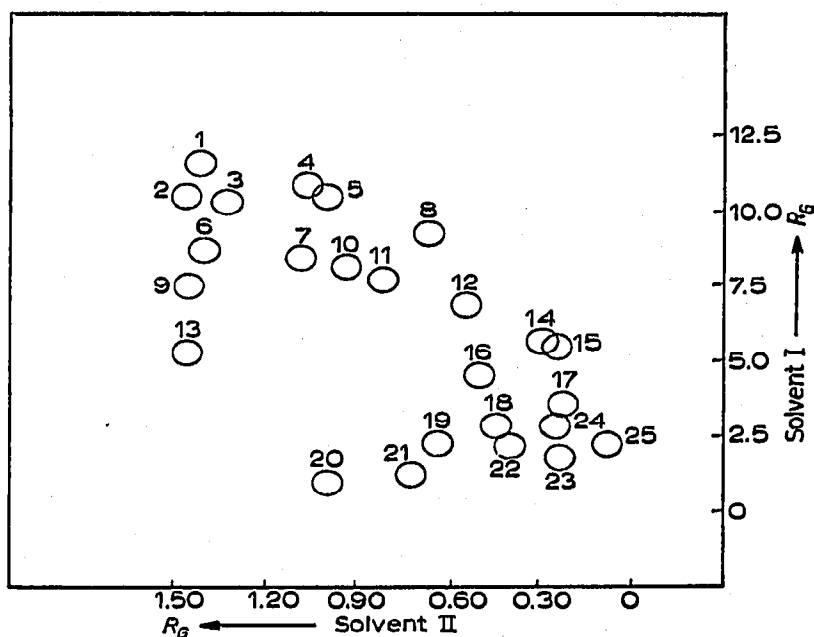

Fig. 1. R_G measurements of nitro ethyl centralites and related compounds. (1) nitrobenzene; (2) 2-nitroEA; (3) 2,4,6-trinitroEA; (4) N,2,4,6-tetranitroEA; (5) 1,3-dinitrobenzene; (6) 1,3,5-trinitrobenzene; (7) N-nitroso-4-nitroEA; (8) 2,4-dinitroEA; (9) N-nitrosoEA; (10) 2-nitroaniline; (11) 4-nitroEA; (12) N-nitroso-2-nitroEA; (13) EA; (14) 4-nitroaniline; (15) 2,4-dinitroaniline; (16) 2,2',4,4'-tetranitroEC; (17) 2,4,4'-trinitroEC; (18) 2,4'-dinitroEC; (19) 4-nitroEC; (20) EC; (21) 2-nitroEC; (22) 2,2'-dinitroEC; (23) 4-nitrophenol; (24) 4,4'-dinitroEC; (25) 2,4-dinitroEC.

Procedure

An acetone solution containing 0.5–1 mg of the EC–N$_2$O$_4$ reaction products is transferred to a point approximately 1.5 in. from the lower right-hand corner of an activated silica gel G/Zn plate. The sample is chromatographed in 250 ml of solvent I for an hour. After exposure of the plate to the atmosphere for 10 min, the sample is rechromatographed at 90° to the direction of flow of solvent I in an equal volume of solvent II for an additional hour. The separated products are located by spraying the plate with dichlorofluorescein and viewing the chromatoplate under a short wavelength ultraviolet light source. The location of EC is marked, and the plate is resprayed with p-DEAB. All the nitroso, nitro, and partially substituted amino compounds develop immediately.

RESULTS AND DISCUSSION

Fig. 1 indicates that twenty-four compounds can be separated and identified. The combined properties of both solvents tend to separate the nitro-derivatives of ethylaniline (EA) and EC into two groups; the upper-half of the chromatogram contains the nitroEA compounds, and the lower-half contains the nitroEC compounds. In the case of the nitroEC derivatives, solvent I separates these compounds according to the degree of nitration. This fact, coupled with chemical tests, was extremely useful in identifying the dinitroEC isomers that could not be prepared in sufficient quantities for elemental analyses.

A twenty-five component mixture was chromatographed by the described procedure. Fig. 2 is a tracing of the developed chromatogram. The components are found in the locations predicted from Fig. 1, but are somewhat closer together. This is attributed to the influence of each compound on the migration rate of the others. The
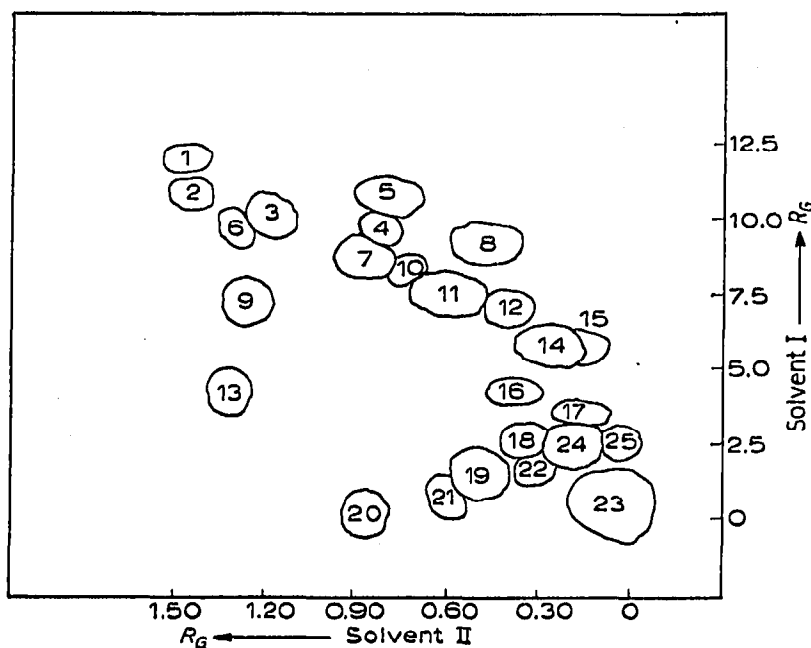

Fig. 2. Two-dimensional thin-layer chromatography of synthetic mixture. Compounds as identified in Fig. 1 caption.

4-nitro- and 2,4-dinitroanilines overlap; however, the p-DEAB reagent develops the spots red and brown, respectively, to make identification possible. Therefore, from the location and the color of the developed spots, all the compounds included in this work can be identified.

Samples of $EC-N_2O_4$ reaction products aged for different lengths of time were analyzed. The results are listed in Table I in the approximate order of decreasing concentration.

The complexity of the reaction products is evident. The dinitroEC derivatives are the major products. The presence of aniline, benzene, and phenolic compounds is an indication that degradation of EC and/or its nitro derivatives has occurred. This behavior of EC is in contrast to the diphenylamine (DPA) stabilizer; the DPA molecule remains intact during the nitrosation and/or nitration process. As one would expect,

TABLE I

IDENTIFICATION OF EC–N$_2$O$_4$ REACTION PRODUCTS

Sample	Identified products

(A) EC–N$_2$O$_4$ reaction products (aged 1 day)	4,4'-dinitroEC =
	 2,4'-dinitroEC >
	 2,2'-dinitroEC >
	 N-nitroso-4-nitroEA >
	 2,4-dinitroEC >
	 unknown >
	 4-nitrophenol >
	 traces of
	     N-nitroso-2-nitroEA
	     2,2',4,4'-tetranitroEC
	     2,4-dinitroEA
	     4-nitroaniline
	     2,4,4'-trinitroEC
	     nitrobenzene

(B) EC–N$_2$O$_4$ reaction products (aged 1 month)	4,4'-dinitroEC =
	 2,4'-dinitroEC >
	 2,2'-dinitroEC >
	 N-nitroso-4-nitroEA =
	 4-nitrophenol >
	 2,4-dinitroEC >
	 unknown >
	 2,2',4,4'-tetranitroEC >
	 4-nitroaniline =
	 2,4-dinitroEA >
	 traces of
	     N-nitroso-2-nitroEA
	     nitrobenzene
	     2,4,4'-trinitroEC

(C) EC–N$_2$O$_4$ reaction products (aged 6 months)	4,4'-dinitroEC =
	 2,4'-dinitroEC >
	 2,2'-dinitroEC >
	 N-nitroso-4-nitroEA >
	 4-nitrophenol >
	 2,4-dinitroEC >
	 2,2',4,4'-tetranitroEC >
	 2-nitroEA ≫
	 4-nitroEA =
	 2,4-dinitroEA >
	 N-nitroso-2-nitroEA >
	 N-2,4,6-tetranitroEA >
	 N-nitrosoEA =
	 4-nitroaniline >
	 traces of
	     nitrobenzene,
	     2,4,4'-trinitroEC,
	     and 4 unknowns

the degradation of EC–N$_2$O$_4$ reaction products increases with age, as shown in the 6 months-old sample.

It is disconcerting to find unidentified compounds in the reaction products. For example, the unknown located below the N-nitroso-4-nitroEA spot (see Fig. 1) in samples A and B could not be readily isolated to determine its identity; however, from the location of the spot, it is thought to be one of the isomers of dinitroaniline.

The degree of completion of the EC–N_2O_4 reaction was also determined. It was found that 99 % of the EC reacted with N_2O_4 under the conditions used to study stabilizer capacity toward N_2O_4. A similar result was found for the DPA–N_2O_4 reaction, as reported in an earlier publication[1].

By comparing the major reaction products of EC and DPA, it is possible to explain why DPA is a more efficient scavenger of N_2O_4 than EC. The predominant products of the EC–N_2O_4 reaction are the dinitroEC compounds, whereas the DPA–N_2O_4 reaction yields mainly the N-nitroso-dinitro-, dinitro-, and trinitroDPA derivatives. Therefore, the higher nitrosated and nitrated DPA derivatives account for DPA having a higher capacity toward N_2O_4 than EC.

The need for two spray reagents is obvious. Ethyl centralite cannot be detected with p-DEAB because it has no nitro group. On the other hand, dichlorofluorescein will detect in the neighborhood of 5 μg of EC, but will not distinguish overlapping spots such as the 4-nitro- and 2,4-dinitroanilines. With the p-DEAB reagent, all the nitroso, nitro, and partially substituted amino compounds can be detected in amounts of 1–4 μg.

Approximately 70 % of the authentic samples were not available commercially; therefore, they were prepared or isolated from the nitration products of EC. The 2-nitro-N-ethylaniline (2-nitroEA) was prepared by condensing 1-chloro-2-nitrobenzene with ethylamine. The 4-nitroEA was obtained through the hydrolysis of N-ethyl-4-nitroacetanilide with KOH. By using standard nitrosation procedures, the corresponding nitroso-nitro compounds were synthesized. The remaining nitroEA derivatives were isolated from the nitration products of EC via thin layer chromatography.

The nitroEC derivatives were the most difficult samples to obtain. The 2-nitroEC and 4-nitroEC required the preparation of nitrocarbanilyl chloride intermediates which were then condensed with EA to obtain the desired compounds[4]. The 4,4'-dinitro-, trinitro-, and tetranitroEC derivatives were isolated from the nitration products of EC. The 2,2'-dinitro-, 2,4'-dinitro-, and 2,4-dinitroEC derivatives were separated from the EC–N_2O_4 reaction products only in minute quantities. With the exception of these three dinitroEC isomers, all samples were purified by thin-layer chromatography and characterized by m.p. and elemental analysis.

The identity of the three dinitroEC compounds was established through chemical and chromatographic methods. Under suitable conditions, acid hydrolysis of these compounds should yield the EA derivatives. Accordingly, a known sample (2,4,4'-trinitroEC) was hydrolyzed in concentrated sulfuric acid at 80° for 10 min. After the solution was neutralized, and the hydrolyzed products extracted with methylene chloride, thin-layer chromatography revealed 4-nitroEA, 2,4-dinitroEA and a small amount of unhydrolyzed trinitroEC in the extract. Under similar conditions of acid hydrolysis, followed by thin-layer chromatographic analysis, 2,2'-dinitro-, 2,4'-dinitro- and 2,4-dinitroEC showed the expected EA derivatives, proving conclusively the identity of the parent compounds.

SUMMARY

A two-dimensional thin-layer chromatographic method for the separation and identification of the numerous products produced in the nitration of ethyl centralite is described. The method is applied to the analysis of ethyl centralite–nitrogen tetroxide reaction products. Two spray reagents used in conjunction with the silica gel G/Zn plate offer a sensitive detection method for each of the compounds.

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