JOURNAL OF CHROMATOGRAPHY

CHROM. 4800

SEPARATION AND IDENTIFICATION OF TETRYL AND RELATED COMPOUNDS BY TWO-DIMENSIONAL THIN-LAYER CHROMATOGRAPHY

STANLEY K. YASUDA

University of California, Los Alamos Scientific Laboratory, Los Alamos, N.M. 87544 (U.S.A.)

(Received April 29th, 1970)

SUMMARY

A two-dimensional TLC method for the separation and identification of tetryl and related compounds is described. Production-grade tetryl contains N-methyl-N,2,4-trinitroaniline, picryl chloride, picric acid, picramide or N,2,4,6-tetranitroaniline, and N-methyl-2,4,6-trinitroaniline. Samples heated at 120° for 48 h contain picric acid and 2,4,6-trinitroanisole as the major decomposition products, with decreasing amounts of picramide and/or N,2,4,6-tetranitroaniline, N-methyl-2,4,6-trinitroaniline, 1,3,5-trinitrobenzene, and N-methyl-N,2,4-trinitroaniline.

INTRODUCTION

Thin-layer chromatography (TLC), as a method of separating organic compounds, enables the analyst to perform qualitative and quantitative analyses on substances present in minute quantities. With proper selection of substrate and solvent, separations of simple and complex mixtures, not possible by conventional techniques, can be achieved by TLC. A requirement to identify the impurities associated with N-methyl-N,2,4,6-tetranitroaniline (tetryl) prompted us to investigate the applicability of the technique to this problem.

Several studies on the thermal decomposition of tetryl have been reported in the literature, but only DUBOVITSKII *et al.*[1] attempted to identify the degradation products, using column chromatography and UV absorption for this purpose. The two-dimensional TLC method described below provides a convenient and simple method of separating and identifying the components of such mixtures.

REAGENTS AND EQUIPMENT

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

All solvents were reagent grade. Petroleum ether with a boiling range of 30 to 60° was used.

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

The spray reagent consisted of 0.25 g of *p*-diethylaminobenzaldehyde (*p*-DEAB) and 2.1 ml of concentrated HCl made up to 100 ml with absolute ethanol.

Sample aliquots were delivered with an Agla micrometer syringe.

Several of the compounds included in this study were not available commercially. The N-methyl-2,4-dinitroaniline and N-methyl-2,6-dinitroaniline were prepared by condensing methylamine with the corresponding chlorodinitrobenzene. The procedure of GLAZER *et al.* was used for the preparation of N-methyl-N,2,4-trinitroaniline[2]. The purity of these samples was established by TLC, chemical tests, melting point, and elemental analyses.

EXPERIMENTAL

Preparation of thin layer

A slurry consisting of 30 g of Silica Gel G and 0.5 g of zinc dust in 65 ml of distilled water was prepared and coated on five glass plates by pulling the applicator across them at a constant speed with a Bodine speed-reducer motor. The coated plates were air-dried for 15 min and activated at 110° for 2 h before use.

R_G measurement

Twenty-three compounds related to tetryl were assembled, and the R_G value for each was measured relative to 1,3-dinitrobenzene on an activated Silica Gel G–zinc plate using a variety of solvents. To locate the spots, *p*-DEAB–HCl was

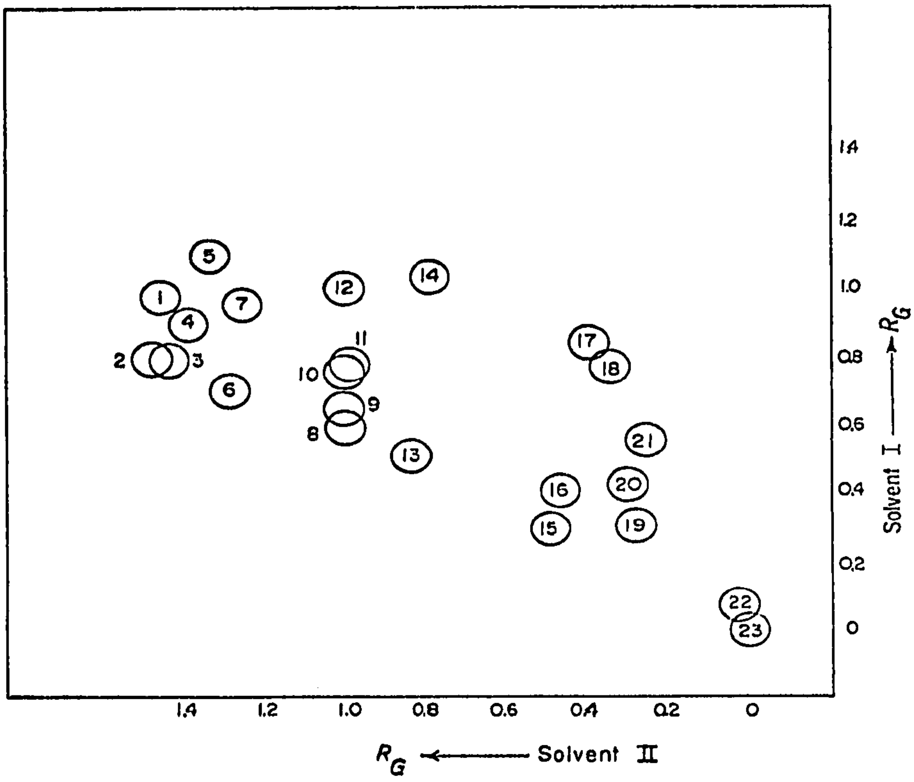

Fig. 1. R_G measurements of tetryl and related compounds. For identification of compounds, see Table I.

TABLE I

IDENTIFICATION OF THE SPOTS IN FIGS. 1 AND 2 OF TETRYL AND RELATED COMPOUNDS
Abbreviations of colors: y = yellow, b = brown, o = orange, r = red and g = gray.

No.	*Compound*	*Self-indicator*	*Color with p-DEAB*
1	1-Chloro-2,4,6-trinitrobenzene (picryl chloride)	—	y-b
2	N,N-Dimethylaniline	—	y to g
3	1,3,5-Trinitrobenzene (TNB)	—	o
4	2,4,6-Trinitroanisole	+	y
5	1-Chloro-2,4-dinitrobenzene	—	y
6	N-Methylaniline	—	y
7	N-Methyl-2,6-dinitroaniline	+	y
8	2,4,6-Trinitroaniline (picramide)	+	o
9	N,2,4,6-Tetranitroaniline	—	b
10	N-Methyl-2,4,6-trinitroaniline	+	y-b
11	*o*-Nitroaniline	+	y
12	1,3-Dinitrobenzene (reference compound)	—	o
13	N-Methyl-N,2,4,6-tetranitroaniline (tetryl)	—	y-b
14	1-Chloro-2,6-dinitrobenzene	—	o
15	3,5-Dinitroaniline	+	y
16	*m*-Nitroaniline	—	y
17	2,4-Dinitroanisole	—	o
18	N-Methyl-2,4-dinitroaniline	+	y
19	2,4-Dinitroaniline	+	o
20	*p*-Nitroaniline	—	r
21	N-Methyl-N,2,4-trinitroaniline	—	y
22	2,4-Dinitrophenol	+	o
23	2,4,6-Trinitrophenol (picric acid)	—	b

used as the spray reagent. By cross-plotting the R_G values, chloroform (solvent I) and a 1 : 3 ethyl acetate–petroleum ether mixture (solvent II) were found to be the most effective solvent pair. Fig. 1 shows a plot of the data obtained with solvents I and II. The colors developed with the *p*-DEAB reagent and the selfindicating compounds are listed in Table I.

Procedure

A benzene solution containing 0.3–0.5 mg of sample is applied about 1 in. from the lower right-hand corner of an activated Silica Gel G–zinc plate. The sample is chromatographed in 200 ml of solvent I for 55 min and then exposed to the atmosphere for 10 min. In an equal volume of solvent II, the sample is rechromatographed at 90° to the direction of flow of solvent I for an additional 55 min. The visible spots are located, and the chromatogram is sprayed with *p*-DEAB–HCl reagent. With the exception of N,N-dimethylaniline, which requires 1 h for color development, the components react immediately to form brown, yellow, and red spots on the chromatogram.

RESULTS AND DISCUSSION

Fig. 1 indicates that 23 compounds can be partially or completely resolved for identification purposes. To verify this, a synthetic mixture consisting of all the

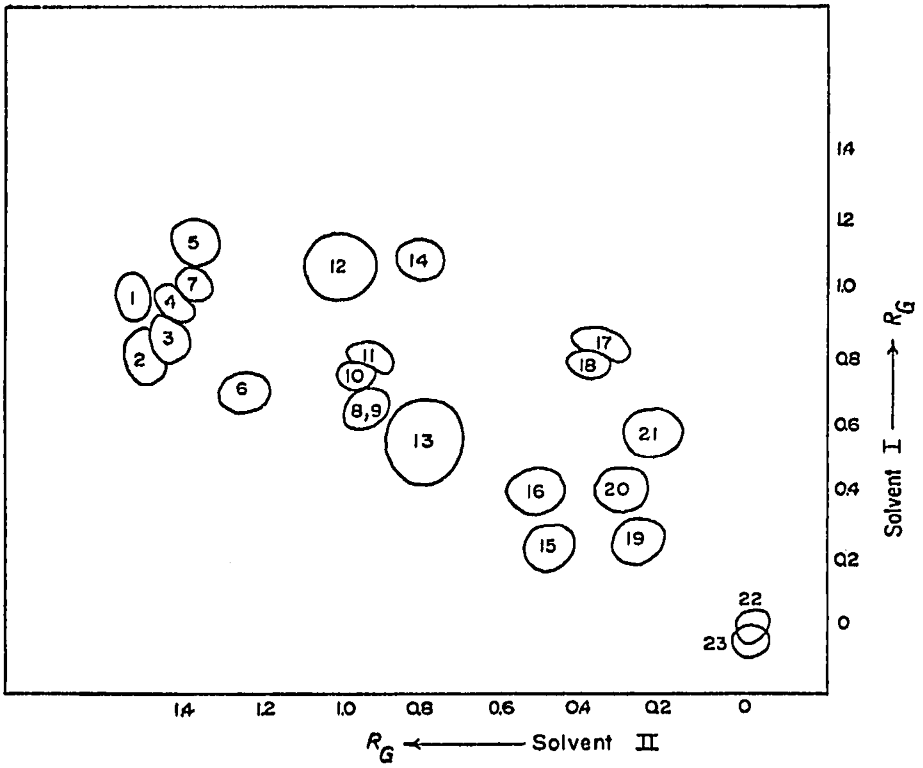

Fig. 2. Two-dimensional thin-layer chromatography of a synthetic mixture. For identification of compounds, see Table I.

TABLE II

IMPURITIES IN TWO TYPICAL LOTS OF PRODUCTION-GRADE BEFORE AND AFTER HEATING

Sample	*Impurities*
Tetryl A	N-Methyl-N,2,4-trinitroaniline > picric acid > picramide or N,2,4,6-tetranitroaniline = picryl chloride
Tetryl B	N-Methyl-N,2,4-trinitroaniline > picryl chloride > picric acid > N-methyl-2,4,6-trinitroaniline (trace)
Tetryl A (heated at 120°, 48 h)	Picric acid ≥ 2,4,6-trinitroanisole > N-methyl-2,4,6-trinitroaniline > picramide or N,2,4,6-tetranitroaniline > TNB (trace) N-methyl-N,2,4-trinitroaniline (trace)
Tetryl B (heated at 120°, 48 h)	Picric acid > 2,4,6-trinitroanisole > picramide or N,2,4,6-tetranitroaniline > TNB (trace) N-methyl-N,2,4-trinitroaniline (trace)

components was prepared and chromatographed. Fig. 2 is a tracing of the developed chromatogram.

In general, the relative position of each compound is similar to that shown in Fig. 1. N-Methyl-2,6-dinitroaniline is displaced further than predicted, while picramide and N,2,4,6-tetranitroaniline overlap completely, making identification impossible. Slight displacement of a compound is expected in a complex mixture of this sort, as the migration rate of each component is affected by the migration of other components in the sample.

The detection limit of each compound was determined after chromatographing the sample. With the exception of N-methylaniline and N,N-dimethylaniline, 0.5 to 1 μg of each compound can be readily detected with the *p*-DEAB reagent. N-Methylaniline and N,N-dimethylaniline require 4 and 8–10 μg, respectively.

Production-grade and heated tetryl samples were analyzed by this methcd. The impurities found are listed in Table II in the approximate order of decreasing concentration.

An unexpected impurity, N-methyl-N,2,4-trinitroaniline, was found in production-grade tetryl. Its identity was established by comparing the melting point and R_G value with those of an authentic sample.

With the heated tetryl samples, the 2,4,6-trinitroanisole, picric acid, and N-methyl-2,4,6-trinitroaniline listed in Table I were also reported by DUBOVITSKII, *et al.*; however, the picramide or N,2,4,6-tetranitroaniline, and the traces of TNB and N-methyl-N,2,4-trinitroaniline, were not reported by these authors.

ACKNOWLEDGEMENTS

The author thanks P. N. NEUMAN for the preparation of certain nitroaromatic compounds. This work was done under the auspices of the U. S. Atomic Energy Commission.

REFERENCES

1 F. I. DUBOVITSKII, G. B. MANELIS AND L. P. SMIRNOV, *Russ. J. Phys. Chem. (Engl. Transl.)*, 35 (1961) 255.

2 J. GLAZER, E. D. HUGHES, C. K. INGOLD, A. T. JAMES, G. T. JONES AND E. ROBERTS, *J. Chem. Soc.*, (1950) 2675.