

CHROM. 4207

Estimation of compounds formed during the production of 2-nitrodiphenylamine

2-Nitrodiphenylamine is known as the best oxidation inhibitor and is currently employed in double base rocket propellants¹. This stabilizer is produced by a continuous process starting from chlorobenzene. The later compound on nitration with boron trifluoride-dinitrotetroxide ($\text{BF}_3\text{-N}_2\text{O}_4$) complex² gives a mixture of 2-nitrochlorobenzene, 4-nitrochlorobenzene and 2,4-dinitrochlorobenzene. The crude mixture is reacted³ with aniline in the presence of alkali carbonates resulting in 2-nitrodiphenylamine as the major product along with 4-nitrodiphenylamine, 2,4-dinitrodiphenylamine and some unreacted nitro compounds. In order to check the course of reaction and to obtain an optimum yield of the stabilizer, it becomes essential to estimate various products rapidly.

BEREI AND VASÁROS⁴ have reported the separation of *o*-, *m*- and *p*-chloronitrobenzene by thin-layer chromatography (TLC) on silica gel plates. OBRUBA AND NAVRATIL⁵ have described a procedure for the separation and determination of chlorobenzene nitration products based on TLC and polarography. FISHBEIN⁶ has studied the separation of isomeric halonitrobenzenes employing TLC on Silica Gel DF-5. Diphenylamine and its derivatives have been resolved on thin-layer plates^{7,8}. In addition, *o*-, *m*- and *p*-nitrochlorobenzenes have been studied by gas chromatography⁹ using a pyrex glass column packed with 4% QF-I (trifluoropropyl methyl silicone fluid) on acid-washed DMCS-pretreated Chromosorb G.

The present paper describes the separation of 2-nitrodiphenylamine, 4-nitrodiphenylamine, 2,4-dinitrodiphenylamine, 2-nitrochlorobenzene, 4-nitrochlorobenzene and 2,4-dinitrochlorobenzene from the reaction mixture by TLC; and also the quantitative estimation of these compounds using UV spectroscopy. It was possible to estimate 2–3 μg of each compound in the mixture. The procedure is useful in studying the course of the reaction during the production of 2-nitrodiphenylamine.

Experimental

The authentic compounds were crystallized twice from ethanol and had sharp melting points. All the irrigating solvents were freshly dried and distilled. Ilford photographic glass plates 24 \times 24 cm were used for TLC. The distance travelled by the solvents in each case was 20 cm. The plates were irrigated at $18 \pm 2^\circ$ and the spots marked under short wave (2537 Å) UV light (Chromatolite lamp).

Chlorobenzene on nitration with boron trifluoride-dinitrotetroxide complex gave the mixture M_1 , containing 2-nitrochlorobenzene, 4-nitrochlorobenzene and 2,4-dinitrochlorobenzene. M_1 , on condensation with aniline in the presence of alkali carbonate for 9 h, and after working up the reaction mass, gave the product M_2 which was found to be a mixture of six compounds *viz.*, 2-nitrodiphenylamine, 4-nitrodiphenylamine, 2,4-dinitrodiphenylamine, 2-nitrochlorobenzene, 4-nitrochlorobenzene and 2,4-dinitrochlorobenzene.

Sorbents. (i) Silica Gel G (E. Merck); (ii) Silica Gel G (E. Merck) + magnesium silicate (3:1); (iii) basic alumina (M. Woelm, 200 mesh with 30% CaSO_4).

Preparation of the thin-layer plates, application of spots and irrigation of plates.

A good slurry of the adsorbant in a suitable solvent was prepared and poured on the glass plates. These were tilted from side to side in order to give a uniform coating. The plates were left for 18 h at room temperature, activated at 120° for 15 min and weighed. The specifications concerning the sorbents, average coating thickness etc., are shown in Table I.

TABLE I

| Coating | Wt. of the adsorbent for four plates | Solvent | Average coating (mg/cm ²) |
|---------------------------------|--------------------------------------|----------------|---------------------------------------|
| Silica Gel G | 20 g | Water, 45 c.c. | 5.9 |
| Silica Gel G-magnesium silicate | 20 g | Water, 50 c.c. | 6.2 |
| Basic alumina-CaSO ₄ | 20 g | Water, 45 c.c. | 5.8 |

The reaction products along with the standard compounds were dissolved in acetone-ethanol (3:1). 5 μ l of each solution were spotted with a micropipette; the standard spots contained 2-3 μ g of the compound. Ascending development was employed for irrigating the plates. A typical thin-layer chromatogram is shown in Fig. 1 and the R_F values are recorded in Table II.

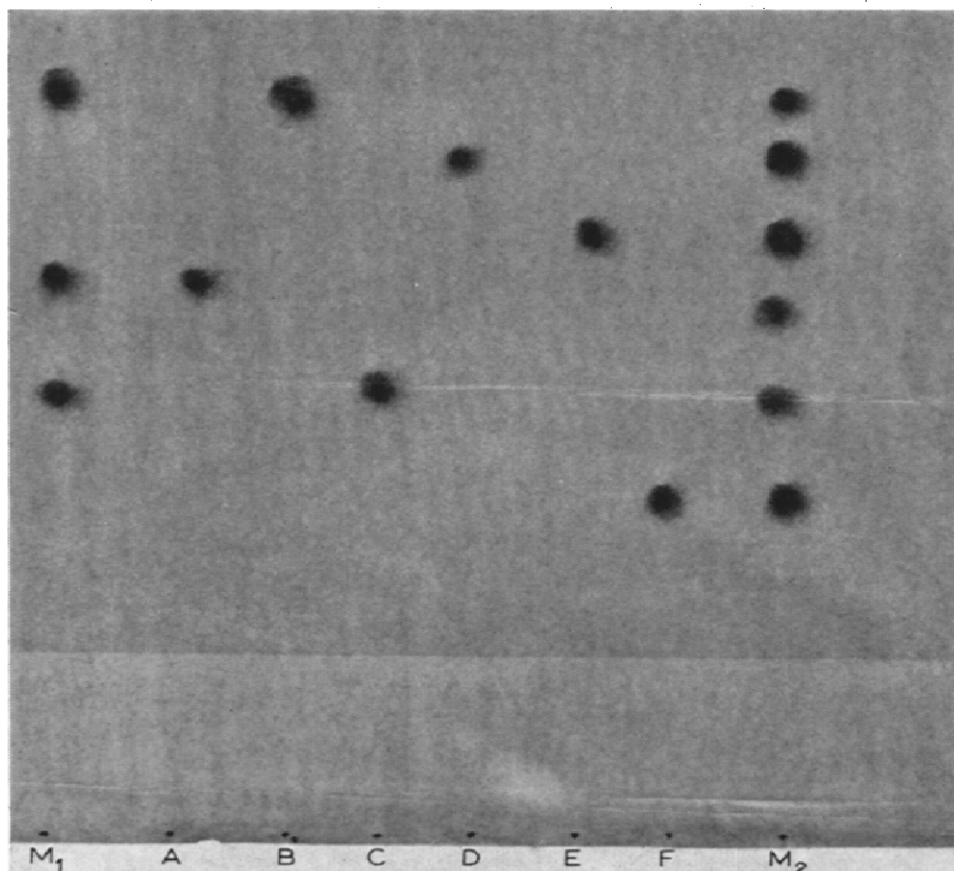


Fig. 1. Separation of 2-nitrodiphenylamine and related compounds on a thin-layer chromatogram. M_1 = nitration product of chlorobenzene; A = 2-nitrochlorobenzene; B = 4-nitrochlorobenzene; C = 2,4-dinitrochlorobenzene; D = 2-nitrodiphenylamine; E = 4-nitrodiphenylamine; F = 2,4-dinitrodiphenylamine; M_2 = condensation product of M_1 with aniline. Sorbent: Silica Gel G (E. Merck); Solvent: petr. ether-ethyl acetate (9:1); technique, ascending.

TABLE II

| Sample No. | Name of compound | Silica Gel G | | | Silica Gel G-magnesium silicate | | | Basic alumina-calcium sulphate | | | | | |
|------------|--------------------------|----------------------------------|----------------------------------|---------------------------|---------------------------------|-----------------------------------|----------------------------------|--------------------------------|-----------------------------------|----------------------------------|---------------------------|---------------------------------|------|
| | | Petrol-ether-cyclohexanone (9:5) | Petrol-ether-ethyl acetate (9:1) | Toluene-dichloride (95:5) | Cyclohexane-ethyl acetate (9:1) | Petrol-ether-cyclohexanone (95:5) | Petrol-ether-ethyl acetate (9:1) | Toluene-dichloride (95:5) | Petrol-ether-cyclohexanone (95:5) | Petrol-ether-ethyl acetate (9:1) | Toluene-dichloride (95:5) | Cyclohexane-ethyl acetate (9:1) | |
| 1 | 2-Nitrochlorobenzene | 0.78 | 0.68 | 0.80 | 0.64 | 0.69 | 0.60 | 0.78 | 0.71 | 0.66 | 0.87 | 0.87 | 0.81 |
| 2 | 4-Nitrochlorobenzene | 0.68 | 0.91 | 0.93 | 0.86 | 0.62 | 0.82 | 0.83 | 0.86 | 0.61 | 0.93 | 0.91 | 0.89 |
| 3 | 2,4-Dinitrochlorobenzene | 0.57 | 0.54 | 0.70 | 0.52 | 0.51 | 0.39 | 0.70 | 0.48 | 0.50 | 0.72 | 0.81 | 0.52 |
| 4 | 2-Nitrodiphenylamine | 0.69 | 0.83 | 0.65 | 0.83 | 0.60 | 0.71 | 0.74 | 0.82 | 0.58 | 0.92 | 0.83 | 0.87 |
| 5 | 4-Nitrodiphenylamine | 0.80 | 0.73 | 0.77 | 0.65 | 0.87 | 0.59 | 0.61 | 0.69 | 0.65 | 0.81 | 0.71 | 0.76 |
| 6 | 2,4-Dinitrodiphenylamine | 0.47 | 0.41 | 0.48 | 0.50 | 0.41 | 0.28 | 0.46 | 0.42 | 0.43 | 0.55 | 0.65 | 0.47 |

Quantitative analysis. The resolved spots from the reaction mixtures as well as the standards were carefully scraped off on to a micro-sintered funnel, extracted with absolute ethanol and the extract made up to a known volume. The absorption spectra were recorded with an UV Beckmann DK 2A Spectrophotometer. The percentage transmission for the different compounds was measured at their characteristic maxima: 2,4-dinitrodiphenylamine, 350.5 m μ ; 2-nitrodiphenylamine, 282 m μ ; 4-nitrodiphenylamine, 258 m μ ; 2,4-dinitrochlorobenzene, 242 m μ ; 2-nitrochlorobenzene, 252 m μ ; and 4-nitrochlorobenzene, 270.5 m μ . The amounts of the compounds formed were calculated from standard curves.

Results and discussion

Silica Gel G and basic alumina were excellent adsorbents for the resolution of the above mentioned compounds. However, Silica Gel G-magnesium silicate plates produced tailing. The solvent system played an important role. Petroleum ether-ethyl acetate (9:1) and cyclohexane-ethyl acetate (9:1) moved 2-nitrodiphenylamine to a higher R_F value than 4-nitrodiphenylamine when compared with other systems.

The compounds could be perfectly separated from the reaction mass on thin-layer plates and after elution estimated spectroscopically from the intensities of their sharp maxima.

The procedure is quite rapid and could be conveniently used for following the course of a reaction during the production of 2-nitrodiphenylamine.

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