

Studies with 2,4-dinitrophenyl derivatives of some amines by thin-layer chromatography

Nitrodiphenylamines and related compounds are employed as oxidation inhibitors in double base propellants used in rocket motors, take-off throttles, gas generators etc. These amines when incorporated into a propellant improve its specific impulse, burning characteristics and enable it to stick to the rocket tube¹⁻³. For example the stabilizing effect of some of the additives in double base propellants has been found to be of the order: 2-nitrodiphenylamine > N-nitrosodiphenylamine > centralite > nitroguanidine > 2,4-dinitrodiphenylamine > diphenylamine⁴. 2,4-Dinitrodiphenylamine is used as surface-active agent (up to 0.2 % by weight of the salts) in explosive compositions consisting of sodium chloride, ammonium nitrate and either nitroglycerine or a mixture of nitroglycerine and nitroglycol⁵.

HANSSON AND ALM⁶ have reported the separation of some diphenylamine derivatives on thin layers of silicic acid. YASUDA⁷ has identified, by two-dimensional thin-layer chromatography employing silica gel G, the products from diphenylamine in PBX-9404, a plastic-bonded explosive, as well as those prepared by treatment of diphenylamine and 2-nitrodiphenylamine with N₂O₄.

In view of the great utility of dinitrophenyl derivatives of amines, the data on their micro-separation will be useful for the identification of these compounds. The present paper describes a procedure for the characterization of 2,4-dinitrophenyl derivatives of amines up to a concentration of 1.5 μ g employing a thin-layer chromatographic technique.

Experimental

The solvents employed were freshly dried and distilled. Ilford photographic glass plates 24 × 24 cm were used as thin-layer supports, the distance travelled by solvent being 21 cm. The plates were irrigated at 21 ± 2°. The highly coloured compounds could easily be seen.

Adsorbents

- (1) Silica gel G (E. Merck)
- (2) Neutral alumina (M. Woelm, 200 mesh, B.S.S.) with 20 % CaSO₄ (200 mesh)
- (3) Basic alumina (M. Woelm, 200 mesh, B.S.S.) with 20 % CaSO₄ (200 mesh)
- (4) Acidic alumina (M. Woelm, 200 mesh, B.S.S.) with 20 % CaSO₄ (200 mesh)
- (5) Kieselgel G (E. Merck)

Compounds

The 2,4-dinitrophenyl derivatives of amines were prepared by taking an amine (1 mole), 2,4-dinitrochlorobenzene (1.1 mole), sodium carbonate (5 moles) and ethyl alcohol (30 moles) in a round bottomed flask and refluxing the mixture for 2 h. The contents were poured over crushed ice, the resultant crystalline precipitate filtered on a sintered funnel and repeatedly washed with dilute hydrochloric acid till free from amine; washing is then completed with water. The compounds were repeatedly crystallized from ethyl alcohol and their melting points, together with those in the literature, are given below:

2,4-Dinitrodiphenylamine, m.p. 159° (156°⁸, 160°⁹); 2,4-dinitro-2'-methyl-di-

phenylamine, m.p. 128° (120°⁸); 2,4-dinitro-3'-methyl-diphenylamine, m.p. 164° (160°⁸); 2,4-dinitro-4'-methyl-diphenylamine, m.p. 136° (136°⁸); 2,4-dinitrophenyl-piperidine, m.p. 91° (93°⁸, 93°⁹); 2,4-dinitro-3'-chloro-diphenylamine, m.p. 184° (184°⁸); 2,4-dinitro-4'-chloro-diphenylamine, m.p. 166° (167°⁸, 165°¹⁰); 2,4-dinitro-2'-methoxy-diphenylamine, m.p. 164° (151°⁸, 164°¹¹); 2,4-dinitro-4'-methoxy-diphenylamine, m.p. 140° (141°⁸); 2,4-dinitrophenyl- α -naphthylamine, m.p. 188° (190°⁸, 197°⁹); 2,4-dinitrophenyl- β -naphthylamine, m.p. 172° (179°⁸, 174°⁹).

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

An homogenous slurry of the adsorbent in a suitable solvent was poured on the glass plates, which were tilted from side to side in order to give a uniform coating.

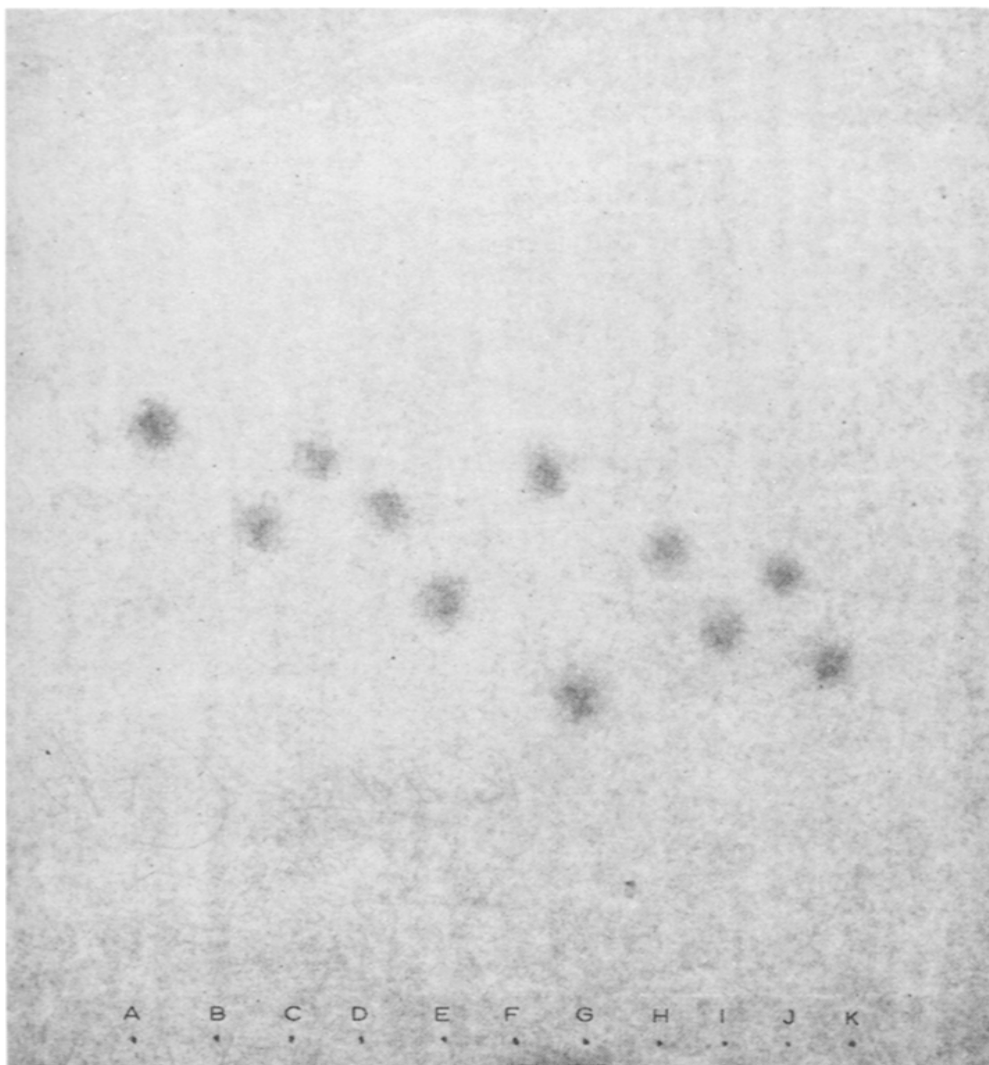


Fig. 1. Thin-layer chromatogram showing the separation of the following compounds: A = 2,4-dinitrodiphenylamine; B = 2,4-dinitro-4'-methyl-diphenylamine; C = 2,4-dinitro-2'-methyl-diphenylamine; D = 2,4-dinitro-3'-methyl-diphenylamine; E = 2,4-dinitrophenylpiperidine; F = 2,4-dinitro-3'-chloro-diphenylamine; G = 2,4-dinitro-4'-methoxy-diphenylamine; H = 2,4-dinitrophenyl- β -naphthylamine; I = 2,4-dinitrophenyl- α -naphthylamine; J = 2,4-dinitro-4'-chloro-diphenylamine; K = 2,4-dinitro-2'-methoxy-diphenylamine. Adsorbent: basic alumina (Woelm); solvent: xylene; technique: ascending.

TABLE I

| Coating | Wt. of adsorbent for four plates | Solvent | Average coating (mg/sq. cm) |
|---|--|---|-----------------------------|
| Silica gel G | 25 g | Water, 50 c.c. | 6.3 |
| Buffered Silica gel G | 25 g | 0.1 M acetic acid, 25 c.c. + 0.1 M sodium acetate, 25 c.c. | 6.8 |
| Buffered Silica gel G | 25 g | 0.05 M borax, 50 c.c. | 6.5 |
| Alumina, neutral-basic-acidic-CaSO ₄ | Alumina, 20 g + CaSO ₄ , 5 g | Water, 50 c.c. | 8.2 |
| Kieselgel G | 25 g | Water, 50 c.c. | 5.4 |
| Kieselgel G, acidic | 25 g | 6 N HCl, 50 c.c. | 5.7 |

The plates were dried overnight at room temperature, activated at 110° for half an hour, and weighed before spotting. The various details of the adsorbents, average coatings etc., are given in Table I.

The compounds were dissolved in ethanol and 2 μ l of each solution containing

TABLE II

R_F VALUES OF 2,4-DINITROPHENYL DERIVATIVES OF SOME AMINES ON VARIOUS ADSORBENTS AND IN VARIOUS SOLVENTS

| Names of the compounds | Silica gel G | | | Silica gel G buffered with 0.1 M acetic acid + 0.1 M sodium acetate | | | Silica gel G buffered with 0.05 M borax | | |
|--|---------------------------------|------------------------|------------------------------------|---|------------------------|------------------------------------|---|------------------------|------------------------------------|
| | Toluene-monochlorobenzene (1:1) | Toluene-acetone (99:1) | Toluene-ethylene dichloride (95:5) | Toluene-monochlorobenzene (1:1) | Toluene-acetone (99:1) | Toluene-ethylene dichloride (99:5) | Toluene-monochlorobenzene (1:1) | Toluene-acetone (99:1) | Toluene-ethylene dichloride (95:5) |
| 2,4-Dinitrophenylpiperidine | 0.23 | 0.76 | 0.58 | 0.34 | 0.40 | 0.38 | 0.27 | 0.52 | 0.25 |
| 2,4-Dinitrodiphenylamine | 0.30 | 0.86 | 0.55 | 0.34 | 0.50 | 0.44 | 0.28 | 0.69 | 0.32 |
| 2,4-Dinitro-2'-methyl-diphenylamine | 0.36 | 0.80 | 0.63 | 0.44 | 0.55 | 0.55 | 0.38 | 0.70 | 0.41 |
| 2,4-Dinitro-3'-methyl-diphenylamine | 0.47 | 0.64 | 0.76 | 0.43 | 0.56 | 0.54 | 0.40 | 0.67 | 0.39 |
| 2,4-Dinitro-4'-methyl-diphenylamine | 0.20 | 0.83 | 0.63 | 0.43 | 0.57 | 0.52 | 0.33 | 0.72 | 0.38 |
| 2,4-Dinitro-3'-chloro-diphenylamine | 0.48 | 0.73 | 0.79 | 0.47 | 0.60 | 0.57 | 0.39 | 0.69 | 0.41 |
| 2,4-Dinitro-4'-chloro-diphenylamine | 0.42 | 0.57 | 0.78 | 0.30 | 0.64 | 0.51 | 0.40 | 0.46 | 0.45 |
| 2,4-Dinitro-2'-methoxy-diphenylamine | 0.45 | 0.68 | 0.58 | 0.17 | 0.48 | 0.32 | 0.24 | 0.32 | 0.27 |
| 2,4-Dinitro-4'-methoxy-diphenylamine | 0.18 | 0.46 | 0.42 | 0.24 | 0.30 | 0.28 | 0.17 | 0.48 | 0.17 |
| 2,4-Dinitrophenyl- α -naphthylamine | 0.28 | 0.66 | 0.76 | 0.41 | 0.60 | 0.63 | 0.37 | 0.53 | 0.42 |
| 2,4-Dinitrophenyl- β -naphthylamine | 0.54 | 0.70 | 0.75 | 0.48 | 0.57 | 0.59 | 0.38 | 0.50 | 0.38 |

1.5 μg of the compound were spotted with a standard microcapillary. The plates were irrigated by ascending technique. Fig. 1 shows the resolutions of these compounds on a thin-layer chromatoplate. The R_F values are given in Table II.

Discussion and results

It has been observed that 2,4-dinitrophenyl derivatives of amines when run on cellulose-CaSO₄ plates produced profuse tailing, and it was thought that this might be due to the strong adsorption effects of the DNP-radicals. Tailing of these compounds still resulted even in reversed phase systems using cellulose-CaSO₄ plates impregnated with 1-5% castor oil, olive oil, sesame oil or silicone grease and employing solvent systems containing various proportions of alcohols like ethanol, *n*-propanol and *n*-butanol with water.

In general silica gel G buffered with 0.05 *M* borax produced lower R_F values when compared with silica gel G buffered with 0.1 *M* acetic acid and 0.1 *M* sodium acetate when toluene-monochlorobenzene and toluene-ethylene dichloride were employed as solvents. Only 2,4-dinitro-4'-chloro-diphenylamine and 2,4-dinitro-2'-methoxy-diphenylamine were exceptions for the first solvent system.

SOLVENT SYSTEMS

| | Neutral alumina | | Basic alumina | | | Acidic alumina | | | Kieselgel G | | Kieselgel G + 6 N HCl | | | |
|---|-------------------------------|-------------------------------|---------------|-------------------------------|-------------------------------|----------------|------------------------------|-------------------------------|-------------------------------|--------|--------------------------|---------|--------|---------|
| | Xylene-petrol ether (95:5) | Benzene-petrol ether (1:1) | Xylene | Xylene-petrol ether (95:5) | Benzene-petrol ether (1:1) | Xylene | Xylene-petrol ether (1:5) | Benzene-petrol ether (1:1) | Benzene-petrol ether (4:1) | Xylene | Toluene | Benzene | Xylene | Toluene |
| 9 | 0.43 | 0.69 | 0.37 | 0.36 | 0.57 | 0.38 | 0.37 | 0.49 | 0.51 | 0.41 | 0.44 | 0.54 | 0.27 | 0.36 |
| 1 | 0.50 | 0.73 | 0.50 | 0.46 | 0.65 | 0.62 | 0.58 | 0.53 | 0.70 | 0.53 | 0.58 | 0.65 | 0.35 | 0.47 |
| 5 | 0.53 | 0.82 | 0.45 | 0.49 | 0.67 | 0.48 | 0.52 | 0.61 | 0.68 | 0.56 | 0.64 | 0.70 | 0.40 | 0.43 |
| 5 | 0.49 | 0.80 | 0.44 | 0.45 | 0.63 | 0.43 | 0.50 | 0.59 | 0.65 | 0.58 | 0.62 | 0.71 | 0.42 | 0.51 |
| 7 | 0.54 | 0.74 | 0.42 | 0.44 | 0.60 | 0.52 | 0.49 | 0.57 | 0.67 | 0.52 | 0.61 | 0.68 | 0.39 | 0.45 |
| 8 | 0.47 | 0.71 | 0.46 | 0.47 | 0.62 | 0.46 | 0.43 | 0.63 | 0.72 | 0.57 | 0.65 | 0.74 | 0.44 | 0.52 |
| 3 | 0.45 | 0.74 | 0.38 | 0.38 | 0.73 | 0.42 | 0.44 | 0.45 | 0.75 | 0.49 | 0.59 | 0.80 | 0.45 | 0.56 |
| 8 | 0.48 | 0.80 | 0.32 | 0.40 | 0.78 | 0.35 | 0.39 | 0.41 | 0.53 | 0.36 | 0.42 | 0.59 | 0.30 | 0.35 |
| 0 | 0.27 | 0.37 | 0.29 | 0.22 | 0.33 | 0.33 | 0.25 | 0.26 | 0.32 | 0.27 | 0.30 | 0.30 | 0.18 | 0.25 |
| 1 | 0.48 | 0.79 | 0.35 | 0.45 | 0.70 | 0.51 | 0.40 | 0.55 | 0.73 | 0.50 | 0.56 | 0.79 | 0.43 | 0.54 |
| 0 | 0.44 | 0.61 | 0.40 | 0.37 | 0.55 | 0.49 | 0.38 | 0.48 | 0.66 | 0.52 | 0.57 | 0.72 | 0.41 | 0.50 |

Kieselgel G treated with 6 N HCl produced lower migrations of the compounds compared to Kieselgel G when xylene and toluene were employed as solvents.

All the three types of alumina proved to be excellent adsorbents for 2,4-dinitrophenyl derivatives. In general the mobilities of these compounds on basic alumina were lower than on neutral alumina.

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The detection and identification of antioxidants containing nitrogen in synthetic aviation lubricants after separation by thin layer chromatography

A paper chromatographic method for the detection and identification of nitrogen-containing antioxidants has been reported previously¹. Subsequently, it was found that a disadvantage of this method was that Aroclor 1254, which is sometimes present in synthetic aviation lubricants as an extreme pressure (E.P.) agent, interferes with the detection of some of the antioxidants. Other additives and complex organic molecules which are present, e.g. polyalkylene oxides, esters derived from mono- and dibasic acids, triaryl phosphates and silicone anti-foaming agents do not interfere. To overcome the difficulty of detecting antioxidants in the presence of Aroclor 1254, a thin-layer chromatographic method has been developed.

Experimental and results

Preliminary experiments using neutral and basic layers of silica gel showed that better separations, and increased R_F values, could be obtained on basic layers. The antioxidants studied and the R_F values obtained using two solvent systems are given in Table I.

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