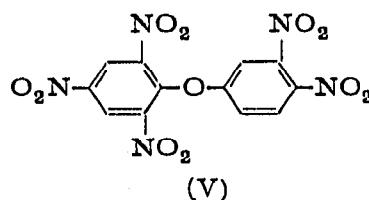
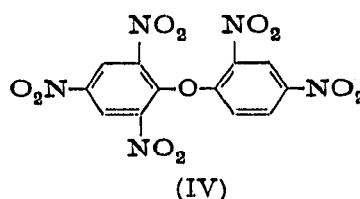
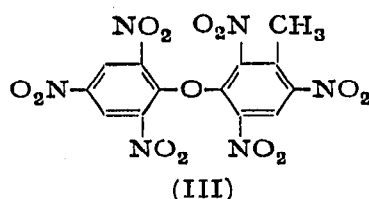
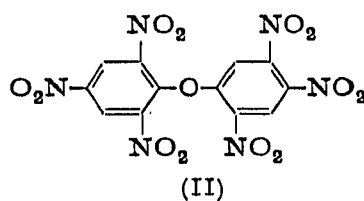
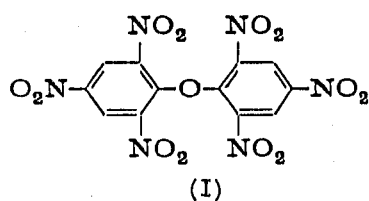


THE THIN-LAYER CHROMATOGRAPHY OF 2,4-DINITROPHENYL ETHERS OF SOME HYDROXY COMPOUNDS

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INTRODUCTION

Polynitrophenyl ethers are intermediates in the synthesis of explosives, *e.g.* 2,4,6,2',4',6'-hexanitrodiphenyl ether (I), 2,4,6,3',4',6'-hexanitrodiphenyl ether (II)^{1,2}, 2,4,6,2',4',6'-hexanitro-3'-methyldiphenyl ether (III)³, 2,4,6,2',4'-pentanitrodiphenyl ether (IV)^{4,5}, 2,4,6,3',4'-pentanitrodiphenyl ether (V)¹.



Polynitrodiphenyl ethers containing one to three nitro groups per molecule but \leq two nitro groups per benzene nucleus, such as *o*-nitrodiphenyl ether, 2,4-dinitrodiphenyl ether, 2,2'-dinitrodiphenyl ether, 2,4,2'-trinitrodiphenyl ether or their mixtures containing less than an average of 2.5 nitro groups per molecule, are employed as plasticizers in ammonium nitrate-based solid rocket propellants^{6,7}. Such nonionic surfactants when added to the molten mix of ammonium nitrate and thermoplastic cellulose ester reduce the consistency of the molten mix at the extrusion pressure needed to form a propellant grain⁸. These rocket propellants contain 60–82 % of the plasticizer, which contributes towards their high burning rates (> 0.16 in./sec at

1000 lb./sq. in. chamber pressure), low pressure exponents (<0.65), and high dimensional stability over a wide temperature range.

Thus for the synthesis of explosives in good yields and for the analysis of solid rocket propellants a rapid characterization of these compounds becomes essential.

Though the investigation of polyphenyl ethers by thin-layer chromatography (TLC) employing a multiple development technique has been reported by NEALEY⁹, and of phenol ethers from some essential oils by STAHL¹⁰ and KLOUWEN AND HEIDE¹¹, no appreciable work has been done on the TLC of polynitrodiphenyl ethers. This may be partly due to the lipophilic character of such compounds.

In the present work 2,4-dinitrophenyl ethers of some aromatic hydroxy compounds were studied by TLC employing different adsorbents. In particular reversed phase TLC, utilising cellulose-CaSO₄ plates impregnated with 5 % sesame oil and 10 % olive oil, gave excellent separations. It was possible to separate distinctly and characterize up to 2 γ of each compound.

EXPERIMENTAL

The solvents employed were dried and distilled; Kodak photographic glass plates (22 × 22 cm) and an ascending irrigation system were employed, the temperature of irrigation being $32^{\circ} \pm 1^{\circ}$. The distance travelled by the solvent front in each case was 20 cm. The compounds were detected under an ultra-violet "Chromatolite" lamp emitting short wave (2537 Å) radiation.

Adsorbents

1. Silica gel G (200 mesh, B.S.S.).
2. Neutral alumina (M. Woelm, 200 mesh, B.S.S.) containing 20 % calcium sulphate.
3. Acidic alumina (M. Woelm, 200 mesh, B.S.S.) containing 20 % calcium sulphate.
4. Basic alumina (M. Woelm, 200 mesh, B.S.S.) containing 20 % calcium sulphate.
5. Cellulose powder, ashless (Whatman, 100 mesh, B.S.S.) containing 1 % calcium sulphate.

Compounds

The 2,4-dinitrophenyl ethers were prepared according to the method of BOST AND NICHOLSEN¹² by refluxing the clear ethanolic solution of the hydroxy compound (1 mole) with 2,4-dinitrochlorobenzene (1 mole, except in the case of catechol where 2 moles were used) and sodium hydroxide (1.5 moles) for 2 h. The contents were poured into an excess of ice water and the resultant crystalline mass repeatedly crystallised from ethyl alcohol. The 2,4-dinitrophenyl ethers of the following compounds were prepared:

Phenol (m.p. $76-77^{\circ}$ *, 69° ¹², 70° ^{13,14}); *o*-chlorophenol (m.p. 99° *, 99° ¹²); *o*-nitrophenol (m.p. 118° *, 142° ¹², 119° ¹⁵); *m*-nitrophenol (m.p. $134-135^{\circ}$ *, 138° ¹², 136° ¹⁶); *p*-nitrophenol (m.p. 120° *, 120° ¹²); *o*-cresol (m.p. 90° *, 90° ¹²); *m*-cresol

* Melting points observed by authors.

TABLE I

Sample No.	Coating	Wt. of adsorbent (g)	Solvent	Activation temperature (°C) and time (h)	Average coating adsorbent (mg/cm ²)
1	Silica gel G	30	Chloroform-methanol (2:1), 100 c.c.	110, 0.5	3.62
2	Silica gel G buffered with 0.5 N oxalic acid	30	0.5 N oxalic acid (20 c.c.) and methanol (80 c.c.)	110, 0.5	3.70
3	Silica gel G buffered with 0.5 N Na ₂ CO ₃	30	0.5 N sodium carbonate (20 c.c.) and methanol (80 c.c.)	110, 0.5	3.68
4	Alumina (neutral)-CaSO ₄	30	Water 70 c.c.	160, 0.5	9.2
5	Alumina (acidic)-CaSO ₄	30	Water 70 c.c.	160, 0.5	9.2
6	Alumina (basic)-CaSO ₄	30	Water 70 c.c.	160, 0.5	9.2
7	Cellulose-CaSO ₄	25.25	Water 100 c.c.	110, 1.0	6.8

TABLE II

Sample No.	2,4-Dinitrophenyl ethers of the following compounds	Silica gel G			Buffered silica gel G (0.5 N oxalic acid)			Buffered silica gel G (0.5 N sodium carbonate)		
		Benzene	Toluene	Benzene-ethanol (10:1)	Benzene	Toluene	Benzene-ethanol (10:1)	Benzene	Toluene	Benzene-ethanol (10:1)
1	Phenol	0.8	0.53	0.91	0.67	0.45	0.92	0.66	0.57	0.36
2	<i>o</i> -Chlorophenol	0.77	0.55	0.83	0.61	0.42	0.96	0.73	0.55	0.35
3	<i>o</i> -Nitrophenol	0.33	0.14	0.52	0.15	0.12	0.61	0.30	0.12	0.19
4	<i>m</i> -Nitrophenol	0.41	0.20	0.51	0.23	0.16	0.64	0.42	0.22	0.22
5	<i>p</i> -Nitrophenol	0.42	0.18	0.50	0.23	0.16	0.61	0.40	0.23	0.23
6	<i>o</i> -Cresol	0.73	0.56	0.71	0.50	0.39	0.71	0.68	0.55	0.40
7	<i>m</i> -Cresol	0.72	0.53	0.72	0.47	0.41	0.69	0.66	0.52	0.40
8	<i>p</i> -Cresol	0.74	0.54	0.70	0.42	0.46	0.68	0.63 [†]	0.51	0.39
9	Catechol	0.27	0.11	0.47	0.09	0.08	0.55	0.25	0.11	0.21
10	Resorcinol	0.35	0.17	0.51	0.12	0.12	0.58	0.28	0.11	0.22
11	α -Naphthol	0.76	0.59	0.76	0.44	0.53	0.72	0.68	0.56	0.23
12	β -Naphthol	0.78	0.58	0.75	0.48	0.54	0.76	0.70	0.53	0.44
13	Thymol	0.90	0.72	0.87	0.59	0.64	0.80	0.78	0.66	0.61
14	Trinitrothymol	0.49	0.32	0.52	0.25	0.25	0.61	0.43	0.28	0.23
15	<i>p</i> -Bromophenol	0.87	0.62	0.84	0.51	0.53	0.77	0.75	0.61	0.56
16	<i>l</i> -Menthol	0.48	0.34	0.56	0.26	0.23	0.68	0.47	0.32	0.29

(m.p. 74^{°*}, 74^{°12}); *p*-cresol (m.p. 93.5^{°*}, 93.5^{°12}, 93^{°14}); catechol (m.p. 131–132^{°*}); resorcinol (m.p. 192^{°*}, 194^{°12}, 184^{°17}); α -naphthol (m.p. 128^{°*}, 128^{°12}); β -naphthol (m.p. 95^{°*}, 95^{°12,18}); thymol (m.p. 67^{°*}, 67^{°12}); trinitrothymol (m.p. 85^{°*}); *p*-bromophenol (m.p. 141^{°*}, 141^{°12}); *l*-menthol (m.p. 79–80^{°*}).

Preparation of thin-layer plates, application of the compounds and irrigation of the plates

The plates were prepared by pouring a freshly prepared slurry of the adsorbent in a suitable solvent on to the glass plates and tilting the plates from side to side so that they were uniformly coated. The plates were left at room temperature overnight and activated at an appropriate temperature before use. The quantities of the adsorbents, solvent and temperature of activation etc. are given in Table I.

For reversed phase TLC, the cellulose plates were impregnated with 10% olive oil and 5% sesame oil by slowly irrigating (ascending) the plates with solutions of the respective oils in petrol ether (40–60[°]).

Acetone solutions of the individual polynitrodiphenyl ethers (10 μ l containing 2 γ) were spotted with a standard micro capillary on the plates. The plates were irrigated with different solvent systems. The solvent systems along with the R_F values of compounds are given in Table II.

* Melting points observed by authors.

Alumina (acidic) + CaSO ₄			Alumina (basic) + CaSO ₄			Alumina (neutral) + CaSO ₄			Cellulose + 1% CaSO ₄					
									10% Olive oil			5% Sesame oil		
Benzene	Toluene	Hexane-ethyl acetate (17:3)	Benzene	Toluene	Hexane-ethyl acetate (17:3)	Benzene	Toluene	Hexane-ethyl acetate (17:3)	90% ethyl alcohol	90% isopropyl alcohol	95% isopropyl alcohol	90% ethyl alcohol	90% isopropyl alcohol	95% isopropyl alcohol
0.84	0.78	0.90	0.48	0.47	0.52	0.51	0.58	0.31	0.87	0.50	0.81	0.71	0.60	0.57
0.48	0.45	0.91	0.96	0.81	0.90	0.81	0.80	0.80	0.61	0.60	0.84	0.46	0.78	0.70
0.71	0.42	0.29	0.55	0.42	0.28	0.58	0.45	0.80	0.84	0.86	0.84	0.80	0.91	0.85
0.73	0.48	0.50	0.56	0.44	0.56	0.58	0.49	0.17	0.78	0.63	0.75	0.60	0.74	0.73
0.66	0.34	0.48	0.61	0.56	0.45	0.67	0.54	0.14	0.78	0.77	0.76	0.60	0.76	0.66
0.93	0.70	0.96	0.81	0.90	0.92	0.93	0.90	0.77	0.69	0.65	0.76	0.53	0.65	0.72
0.93	0.67	0.92	0.84	0.81	0.91	0.91	0.82	0.90	0.67	0.67	0.84	0.42	0.71	0.64
0.92	0.66	0.89	0.86	0.81	0.94	0.94	0.82	0.89	0.68	0.80	0.80	0.40	0.57	0.60
0.61	0.28	0.50	0.47	0.30	0.30	0.39	0.20	0.09	0.70	0.67	0.60	0.23	0.33	0.50
0.22	0.28	0.52	0.42	0.20	0.26	0.44	0.27	0.60	0.56	0.56	0.54	0.36	0.62	0.63
0.79	0.71	0.33	0.84	0.35	0.47	0.91	0.80	0.66	0.54	0.60	0.71	0.40	0.47	0.53
0.17	0.65	0.69	0.84	0.66	0.83	0.91	0.93	0.86	0.52	0.52	0.64	0.60	0.59	0.56
0.93	0.77	0.94	0.93	0.73	0.86	0.94	0.46	0.87	0.54	0.58	0.76	0.81	0.90	0.62
0.85	0.58	0.93	0.73	0.61	0.64	0.76	0.78	0.22	0.81	0.91	0.98	0.51	0.65	0.78
0.93	0.70	0.71	0.87	0.70	0.85	0.89	0.63	0.62	0.63	0.62	0.74	0.90	0.80	0.58
0.89	0.55	0.71	0.79	0.59	0.68	0.50	0.63	0.25	0.90	0.80	0.88	0.88	0.86	0.90

A typical chromatogram showing the separation of these compounds on silica gel G buffered with 0.5 *N* sodium carbonate is given in Fig. 1.

DISCUSSION

Owing to their lipophilic character the polynitrodiphenyl ethers could not be resolved as distinct spots on cellulose-CaSO₄ plates impregnated with 5-10% dimethyl formamide in acetone, when solvents like ethanol-water, cyclohexane or *n*-octane were used for irrigation. Profuse tailing resulted when compounds on cellulose-CaSO₄ plates, which had been impregnated with a 1% solution of silicone high vacuum grease (Edwards') in benzene, were subsequently irrigated with ethanol-water. Even cellulose acetate-CaSO₄ coated plates failed to resolve them with various combinations of solvents for hydroxy compounds.

Silica gel G plates buffered with 0.5 *N* oxalic acid produced lower *R_F* values compared with unbuffered silica gel G when the same irrigating solvents, benzene or toluene, were used. This is contrary to expectation, since a NO₂ group imparts an acidic character to the molecule and lower pH should help in its mobility. However, benzene-ethanol (10:1) gave higher *R_F* values on the acidic silica gel G than on an unbuffered adsorbent. The *R_F* values on 0.5 *N* sodium carbonate buffered silica gel G with solvent systems benzene or toluene were almost the same as those on the un-

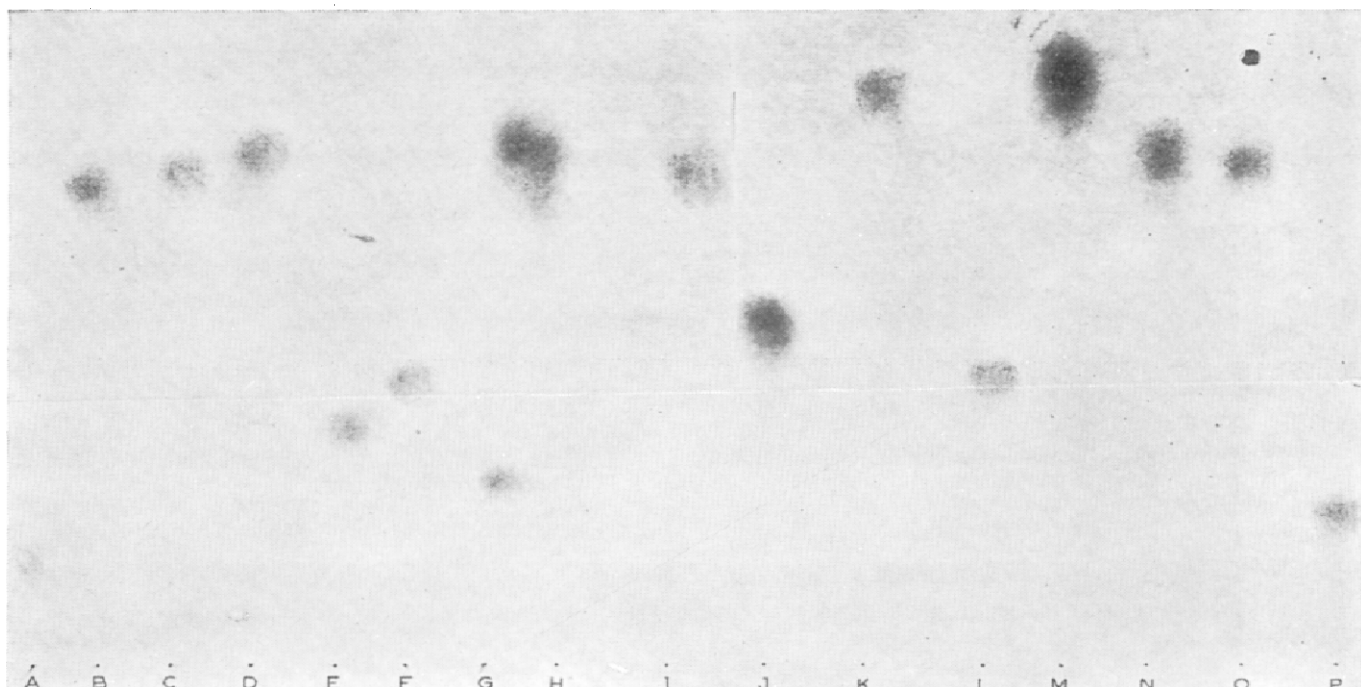


Fig. 1. Thin-layer chromatogram showing the separation of 2,4-dinitrophenyl ethers of the following phenols: A = catechol; B = *p*-cresol; C = *m*-cresol; D = *o*-cresol; E = *p*-nitrophenol; F = *m*-nitrophenol; G = *o*-nitrophenol; H = *o*-chlorophenol; I = phenol; J = *l*-menthol; K = *p*-bromophenol; L = trinitrothymol; M = thymol; N = β -naphthol; O = α -naphthol; P = resorcinol. Adsorbent: silica gel G buffered with 0.5 *N* sodium carbonate. System: benzene (ascending). Photograph taken under ultra-violet light.

buffered adsorbent, while benzene-ethanol (10:1) gave lower R_F values on the basic adsorbent.

All the three types of alumina, *i.e.* acidic, basic or neutral, were found to be excellent adsorbents for the resolution of ethers.

Cellulose-CaSO₄ plates containing 5% sesame oil or 10% olive oil gave very good separations with aqueous mixtures of various alcohols. Loading the plates with 20% of any of these oils had a profuse tailing effect on the compounds. The effect of different glycerides on the mobility of polynitrodiphenyl ethers on reversed phase TLC will, however, be a subject of a separate communication.

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SUMMARY

Polynitrodiphenyl ethers are employed as plasticizers in solid rocket propellants and also form important intermediates in the synthesis of high explosives. The thin-layer chromatography of the 2,4-dinitrodiphenyl ethers of some hydroxy aromatic compounds has been studied. Excellent resolution of the compounds was obtained with alumina-calcium sulphate as an adsorbent, and also on reversed phase systems employing cellulose-calcium sulphate plates impregnated with 5-10% vegetable oils.

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