

CHARGE-TRANSFER COMPLEXES OF HIGH EXPLOSIVES LIKE 2,4,6-TRINITROCHLOROBENZENE (PICRYL CHLORIDE) AND 1,3,5-TRINITROBENZENE (*s*-TNB) WITH SOME AMINES

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INTRODUCTION

Charge-transfer complexes are increasingly becoming important tools for the separation and identification of a variety of organic compounds. This has been efficiently achieved through suitable chromatographic techniques. During the separation of saturated and unsaturated aliphatic compounds by gas chromatography it was observed that the presence of isolated double bonds increases the intermolecular forces of interaction with electron acceptor stationary phases as compared with saturated compounds¹. Closely related disubstituted phenylacetic acids like 3-methoxy-4-hydroxy- and 4-methoxy-3-hydroxy derivatives, were separated by impregnating Gas-Chrom P with neopentyl succinate². During the study of the substituted aniline-2,4,7-trinitrofluorenone systems it was noted that charge-transfer does play a significant role in gas-liquid chromatography³. The complexes of picric acid with polynuclear aromatic compounds have been separated by thin-layer chromatography⁴.

High explosives like 2,4,6-trinitrotoluene (*s*-TNT), *m*-dinitrobenzene (*m*-DNB), 2,4,6-trinitrophenyl-*N*-methyl-nitramine (tetryl) and 2,4-dinitrochlorobenzene (DNCB) form charge-transfer complexes with amines. This is due to the polarization of their nitro groups. Such π -complexes have recently been investigated by employing thin-layer chromatographic techniques^{5,6}. The charge-transfer complexes constitute an important medium for the rapid identification of micro amounts of high explosives.

In the present paper the study of the charge-transfer complexes of two explosives, *viz.* 2,4,6-trinitrochlorobenzene (picryl chloride or PC) and 1,3,5-trinitrobenzene (*s*-TNB) with aromatic amines is reported. By employing a thin-layer chromatographic technique it has been possible to clearly characterize the π -complexes formed from 2-3 μ g of the individual amine. In addition by utilizing a suitable aromatic amine for impregnation of the plate in order to convert the explosives into their π -complexes, it was possible to separate six explosives, *viz.* *s*-TNT, *s*-TNB, PC, *m*-DNB, DNCB and tetryl from their mixture. The procedure is useful in ordnance stores where explosives in various mixtures have to be tested.

EXPERIMENTAL

All solvents used were dried and freshly distilled. Kodak photographic glass plates (22 × 22 cm) were employed as supports for thin layers of various adsorbents

and irrigation was performed with an ascending system for separation of the π -complexes. The temperature of irrigation was $21 \pm 1^\circ$. Since the complexes were highly colored they could be easily located.

Adsorbents

1. Kieselgel G (E. Merck).
2. Kieselguhr G (E. Merck).
3. Cellulose acetate (acetyl content 38.6 %, 100 mesh, B.S.S.) containing 1 % CaSO_4 .
4. Cellulose benzoate (benzoyl content 42.6 %, 100 mesh, B.S.S.) containing 1 % CaSO_4 .
5. Cellulose powder ashless (Whatman, 100 mesh, B.S.S.) containing 1 % CaSO_4 .

Preparation, spotting of complexes and irrigation of plates

The plates were prepared by pouring on them a homogenous slurry of the adsorbent in a suitable solvent and tilting the plates from side to side. This procedure gave uniform coatings of the adsorbents. The plates were dried at room temperature for 18 h and subsequently activated at 110° for 1 h (cellulose acetate and benzoate plates were activated at 80° for 2 h in a vacuum oven). The activated plates were coated with picryl chloride/s-TNB by irrigating their 3 % solutions in acetone. For the resolution of the explosive mixture, the plates were impregnated with a 3 % solution of an amine (in the present case α -naphthylamine). The quantities of different adsorbents, solvents, and average coatings are recorded in Table I.

TABLE I

DETAILS OF DIFFERENT ADSORBENTS, SOLVENTS AND AVERAGE THIN-LAYER COATINGS

Serial Coating No.		Weight of the adsorbent (g)	Solvent	Average coating of adsorbent (mg/cm^2)
1	Kieselgel-G	32	Chloroform (60 c.c.) + methanol (40 c.c.)	8.4
2	Kieselguhr G	32	Methanol (95 c.c.)	7.2
3	Cellulose benzoate- CaSO_4	26	Water (35 c.c.) + ethanol (30 c.c.)	8.2
4	Cellulose acetate- CaSO_4	26	Water (35 c.c.) + ethanol (30 c.c.)	8.1
5	Cellulose- CaSO_4	28	Water (90 c.c.)	7.6

The picryl chloride/s-TNB-amine complexes were directly prepared on the chromatoplates, which had been treated with the explosives, by spotting ethanolic solutions of individual amines ($10 \mu\text{l}$ containing $2-3 \mu\text{g}$). This produced deep colored spots of the π -complexes. The plates were left in the chromatography jar in solvent vapours for half an hour and subsequently irrigated.

Similarly an α -naphthylamine treated plate was spotted with $2-3 \mu\text{g}$ of each of the different explosives along with their mixture. The plates were irrigated in a similar fashion. Table II shows the R_F values of various π -complexes along with their colors.

TABLE IIA
R_F VALUES AND COLORS OF THE π -COMPLEXES WITH PICRYL CHLORIDE
 Adsorbent: Kieselgel G impregnated with 3% picryl chloride.

Serial No.	Complexes of picryl chloride with the following amines	Color	<i>R_F</i> values			
			Toluene-ethylene dichloride (9:1)	Monochloro-benzene-ethyl acetate (95:5)	Monochloro-benzene-ethyl chloride (9:1)	Xylene-ethylene dichloride (4:1)
1	N-Methylaniline	brick red	0.42	0.54	0.43	0.41
2	N,N-Dimethylaniline	light brick red	0.62	0.65	0.54	0.52
3	N,N-Diethylaniline	deep yellow	0.74	0.71	0.68	0.59
4	Aniline	orange	0.66	0.66	0.53	0.56
5	α -Naphthylamine	upper spot orange lower spot pink	0.71 0.23	0.77 0.43	0.61 0.27	0.61 0.26
6	β -Naphthylamine	orange	0.68	0.75	0.57	0.58
7	<i>o</i> -Anisidine	pink	0.63	0.70	0.52	0.54
8	<i>p</i> -Anisidine	pink	0.50	0.62	0.40	0.43
9	<i>m</i> -Chloroaniline	upper spot deep yellow lower spot orange	0.69 0.39	0.77 0.50	0.58 0.37	0.64 0.42
10	<i>p</i> -Chloroaniline	deep yellow	0.65	0.74	0.55	0.62
11	Diphenylamine	grey	0.84	0.88	0.79	0.83
12	<i>o</i> -Toluidine	upper spot deep yellow lower spot pink	0.74 0.24	0.82 0.38	0.64 0.25	0.66 0.27
13	<i>m</i> -Toluidine	orange	0.70	0.78	0.62	0.63
14	<i>p</i> -Toluidine	orange	0.68	0.76	0.60	0.60
15	Benzidine	pink	0.25	0.53	0.14	0.18

TABLE IIB

 R_F VALUES AND COLORS OF THE π -COMPLEXES WITH *s*-TNBAdsorbent: Kieselgel G impregnated with 3% *s*-TNB.

Serial No.	Complexes of <i>s</i> -TNB with the following amines	Color	R_F value				
			Petrol ether-ethyl acetate (9:1)*	Xylene-ethyl acetate (4:1)	Benzene-xylene (1:1)	Toluene	Toluene-mono-chlorobenzene (3:2)
1	N-Methylaniline	brown	0.65	0.55	0.45	0.46	0.31
2	N,N-Dimethylaniline	violet	0.86	0.81	0.53	0.57	0.42
3	N,N-Diethylaniline	deep violet	0.93	0.88	0.62	0.63	0.53
4	Aniline	deep yellow	0.37	0.42	0.22	0.26	0.16
5	α -Naphthylamine	brick red	0.35	0.49	0.25	0.32	0.21
6	β -Naphthylamine	brown	0.23	0.44	0.23	0.28	0.17
7	<i>o</i> -Anisidine	chocolate	0.46	0.50	0.19	0.25	0.16
8	<i>p</i> -Anisidine	brownish grey	0.16	0.24	0.06	0.09	0.03
9	<i>m</i> -Chloroaniline	yellow	0.41	0.52	0.38	0.42	0.32
10	<i>p</i> -Chloroaniline	deep yellow	0.29	0.40	0.29	0.35	0.22
11	Diphenylamine	brick red	0.74	0.84	0.81	0.84	0.74
12	<i>o</i> -Toluidine	orange	0.43	0.47	0.24	0.29	0.17
13	<i>m</i> -Toluidine	orange	0.38	0.43	0.21	0.24	0.14
14	<i>p</i> -Toluidine	orange	0.33	0.38	0.18	0.21	0.12
15	Benzidine	dirty brown	0.05	0.19	0.05	0.26	0.00

* Saturated with *s*-TNB.

The resolutions of complexes of picryl chloride and *s*-TNB with amines are given in Fig. 1 and Fig. 2, respectively, whereas the separations of tetryl, *s*-trinitrobenzene, picryl chloride, *m*-dinitrobenzene, *s*-trinitrotoluene, 2,4-dinitrochlorobenzene as α -naphthylamine π -complexes are shown in Fig. 3. Their respective R_f values were 0.45, 0.53, 0.57, 0.59, 0.63 and 0.67.

DISCUSSION AND RESULTS

In order to get the best resolutions of the π -complexes it was essential to pre-saturate the plates for about half an hour with the vapours of the irrigating solvent system. All the complexes were highly labile and broke down into the respective explosive and amine when run on plates untreated with the explosive. In addition it was also necessary to have 2-3 % explosive compound in the irrigating solvent. Similarly, when the plates were treated with a 3 % solution of α -naphthylamine, the same amine was also dissolved in the irrigating solvent. Both adsorption and solvent forces were found to play a dominant role in the process. Cellulose powder impregnated

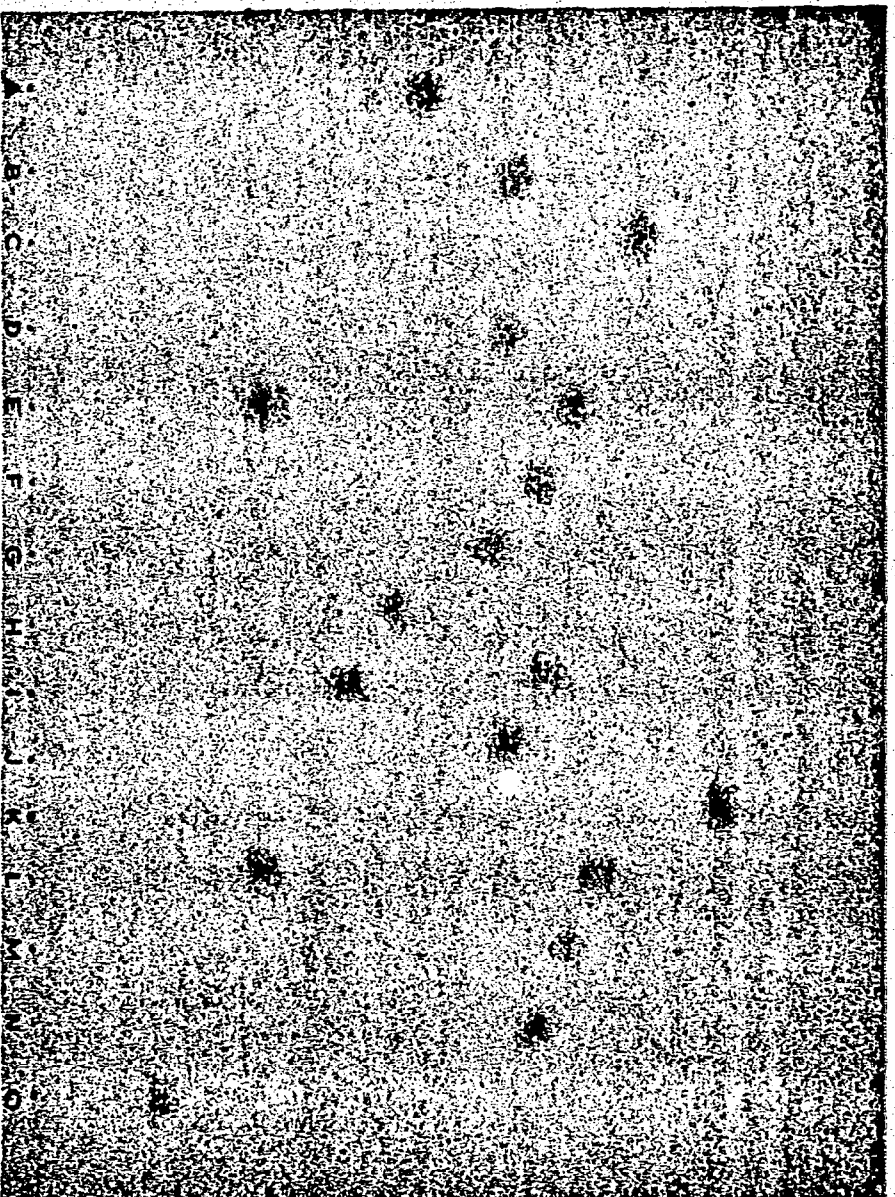


Fig. 1. Thin-layer chromatogram showing the separations of charge-transfer complexes of 2,4,6-trinitrochlorobenzene (picryl chloride) with amines. A = *N*-Methylaniline; B = *N,N*-dimethylaniline; C = *N,N*-diethylaniline; D = aniline; E = α -naphthylamine; F = β -naphthylamine; G = *o*-anisidine; H = *p*-anisidine; I = *m*-chloroaniline; J = *p*-chloroaniline; K = diphenylamine; L = *o*-toluidine; M = *m*-toluidine; N = *p*-toluidine; O = benzidine. Adsorbent: Kieselgel G (E. Merck) impregnated with 3 % PC; solvent system: monochlorobenzene-ethylene dichloride (9:1) containing 3 % PC; system: ascending.

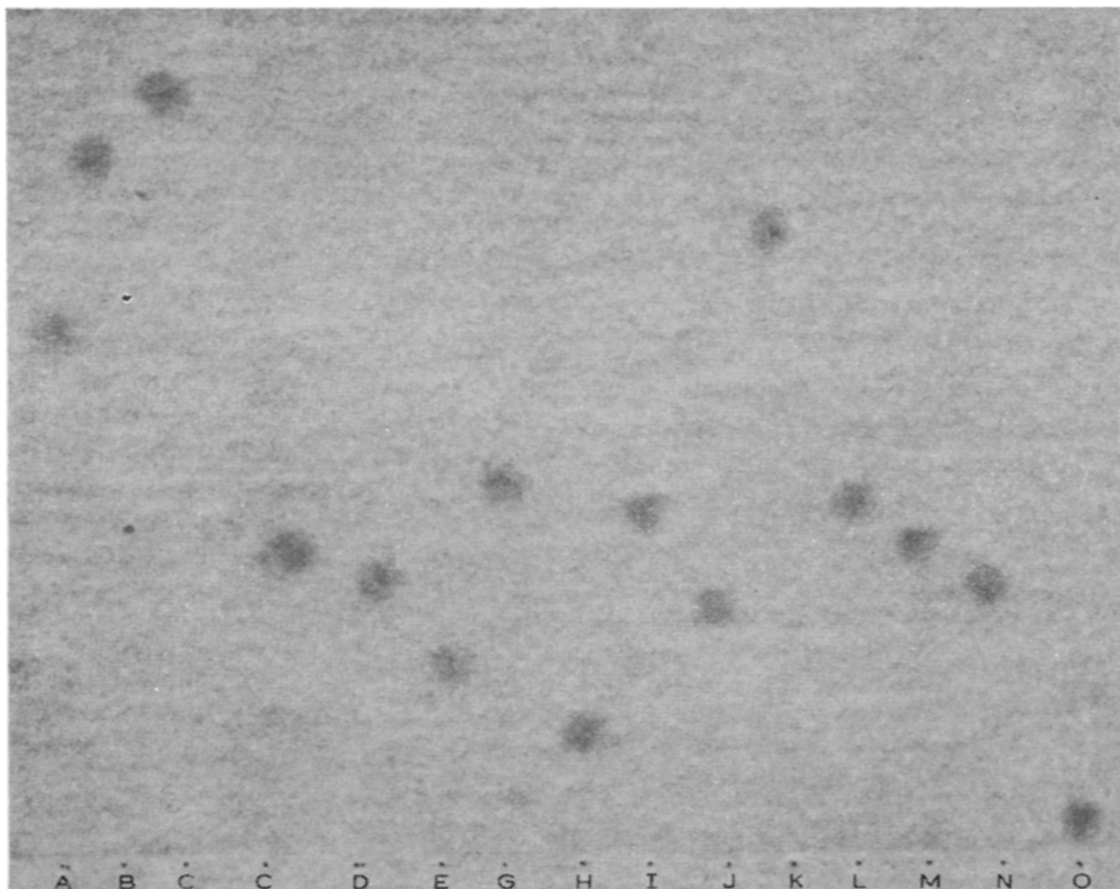


Fig. 2. Thin-layer chromatogram showing the charge-transfer complexes of 2,4,6-trinitrobenzene (*s*-TNB) with amines (A-O). Adsorbent: Kieselgel G (E. Merck) impregnated with 3% *s*-TNB; solvent system: petrol ether-ethyl acetate (9:1) saturated with *s*-TNB; system: ascending.

ed with 5-10% olive oil, cellulose benzoate, and cellulose acetate were not found to be useful adsorbents. Since the adsorption capacity of Kieselguhr G is minimum the complexes migrated up to the solvent front.

Kieselgel G containing 3% PC/*s*-TNB-amine proved to be the best medium for the study of the π -complexes. For irrigation of plates non-polar solvents are to be preferred over polar ones, which have a drastic rupturing effect on the complexes.

As in the cases of π -complexes of other explosives with amines already reported^{5,6}, the movements of PC/*s*-TNB-amine complexes were observed to be in relation to the basicities of the amines. Complexes with less basic amines had higher mobilities than the more basic ones *e.g.* N,N-diethylaniline > N,N-dimethylaniline > N-methylaniline > aniline. Like other nitroaromatic explosives, the complexes of *para*-substituted anilines with PC/*s*-TNB had lower migrations than with *ortho*- or *meta*-substituted amines. Picryl chloride with α -naphthylamine, *m*-chloroaniline and *p*-toluidine after irrigation gave two spots in each case. The spots with higher R_F values had lighter colors compared to those with lower R_F . This interesting phenomenon of the formation of two spots was not observed with other explosives. This is probably due to the formation of π -complexes of varying molecular proportions or to intermolecular hydrogen bondings.

From Fig. 3 it can be seen that any nitroaromatic explosive can be quickly detected when present in admixture with other explosives. Tetryl was very strongly bound compared to other explosives. *s*-Trinitrotoluene had higher mobility than *s*-TNB, due to a decrease in electron affinity as a result of the introduction of a methyl group in the ring.

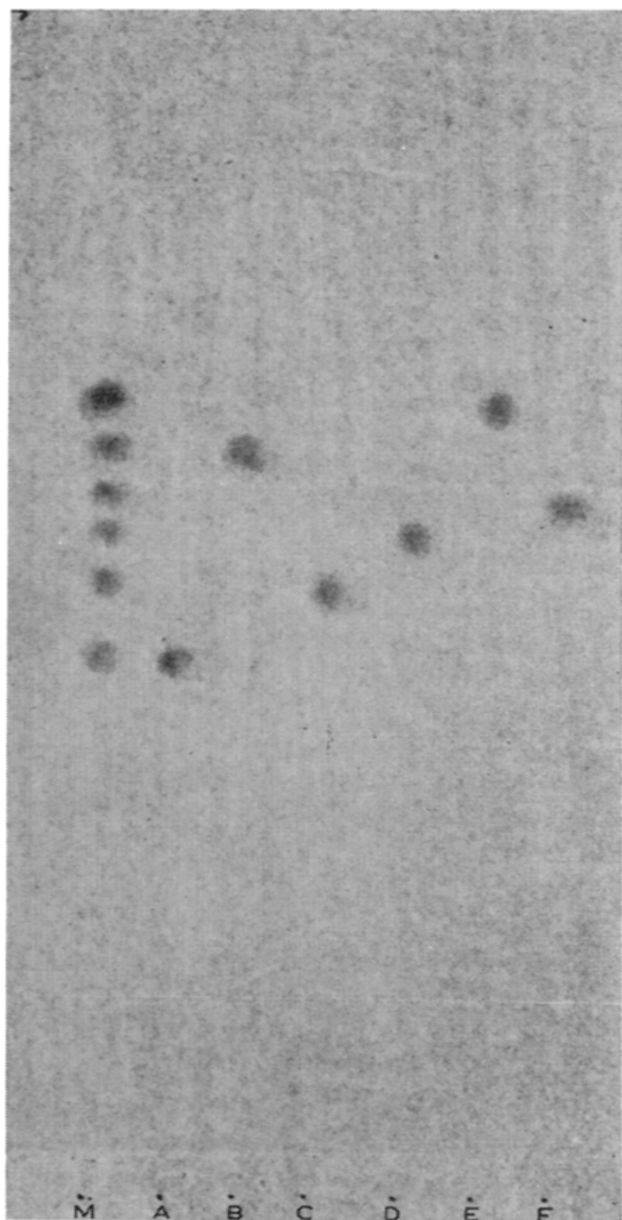


Fig. 3. Thin-layer chromatogram showing the resolution of six explosives from a mixture as charge-transfer complexes with α -naphthylamine. M = Mixture of explosives A-F; A = tetryl; B = *s*-TNT; C = *s*-TNB; D = picryl chloride; E = DNCE; F = *m*-DNE. Adsorbent: Kieselgel G (E. Merck) containing 3% α -naphthylamine; solvent system: toluene-ethylene dichloride (9:1) with 3% α -naphthylamine; system: ascending.

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SUMMARY

The study of the charge-transfer complexes of high explosives *viz.* 2,4,6-trinitrochlorobenzene (picryl chloride) and 1,3,5-trinitrobenzene (s-TNB) with aromatic amines is described. The complexes could be directly prepared on thin layer plates and quickly resolved up to 2-3 μg . The explosives could be easily identified in their mixtures by running their π -complexes. The procedure is of great importance for the rapid detection of explosives in ordnance stores.

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