

CHARGE-TRANSFER COMPLEXES OF 2,4,6-TRINITROTOLUENE AND *m*-DINITROBENZENE WITH SOME AMINES

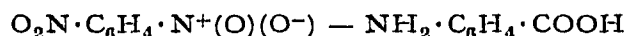
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(Received November 1st, 1966)

The field of charge-transfer complexes has been investigated recently by several chromatographic techniques. Unsaturated lipids have been resolved on columns of silica gel impregnated with silver nitrate¹. Gas chromatography with stationary phases containing silver nitrate has been widely applied in the separation of olefins and other unsaturated compounds²⁻⁶. Benzene and some alkylbenzenes have been separated by GC on E-301 containing 2,4-dinitro-chlorobenzene⁷. In addition, the study of the complexes between olefins and 1,3,5-trinitrobenzene by GC is also reported⁸. Unsaturated fatty acid methyl esters and triglycerides have been resolved as their silver ion π -complexes by reversed phase paper partition chromatography⁹. Thin-layer chromatography has been employed in the investigations of the complexes of silver with terpenes¹⁰⁻¹³, glycerides¹⁴ and allylic-propenylic isomers¹⁵. The separation of the π -complexes of *m*-dinitrobenzene; 2,4-dinitrotoluene; 2,4,6-trinitrotoluene; 2,4,6-trinitroanisole and tetryl with some hydrocarbons on TLC has been carried out¹⁶.

Aromatic amines, being π -donors, form complexes with hybrid structures involving a dative and no bond¹⁷. The formation of charge-transfer complexes by nitro compounds with aromatic donors is attributed to the polarization of the nitro group. On the basis of the study of the complexes of *o*-, *m*-, *p*-aminobenzoic acids and their sodium salts with *m*-dinitrobenzene (*m*-DNB) it has been proposed that only one nitro group participates in the formation of a 1:1 complex¹⁸.



The very weak physical bonding between amines and nitro aromatic compounds is readily ruptured by solvents, adsorption forces, temperature, etc. Probably in view of these difficulties it has not been possible to study such complexes by TLC in the past.

The present paper describes a study of the π -complexes of a number of aromatic amines with 2,4,6-trinitrotoluene (*s*-TNT) and *m*-dinitrobenzene (*m*-DNB) employing a thin-layer chromatographic procedure. It has been possible to clearly resolve the charge transfer complexes formed from 1-2 μg of the individual amines.

EXPERIMENTAL

The different solvents employed were dried and freshly distilled. Kodak photographic plates (22 × 22 cm) were used as supports and the ascending irrigation

technique adopted for resolution of the compounds. The distances travelled by solvent fronts in the cases of *s*-TNT and *m*-DNB complexes were 18.5 and 17.0 cm, respectively. The temperature of irrigation was $18 \pm 1^\circ$. The highly colored complexes could be easily located.

Adsorbents

- (1) Kieselgel G (E. Merck).
- (2) Cellulose powder, ashless (Whatman, 100 mesh, B.S.S.) containing 1% calcium sulphate.
- (3) Cellulose acetate (acetyl content 28.6%, 100 mesh, B.S.S.) containing 1% calcium sulphate.
- (4) Kieselguhr G (E. Merck).

Compounds

The complexes were prepared by taking one mole each of *s*-TNT or *m*-DNB and amine in a suitable solvent (10 mole), warming the mixture till the solution was clear and allowing it to cool in a refrigerator. The complexes were further crystallized from the same solvent till there was no rise in melting point. For *s*-TNT complexes ethanol was used and for *m*-DNB complexes benzene.

Preparation, spotting and irrigation of plates

The plates were coated by taking a freshly prepared slurry of the adsorbent in an appropriate solvent, pouring it on the plates and tilting them from side to side. The plates were left overnight at room temperature and activated at 110° for one hour (except cellulose acetate plates, which were activated at 60° in a vacuum oven for 3 h). These were impregnated with *s*-TNT/*m*-DNB by irrigating with a 3% solution of these compounds in acetone. The amounts of the adsorbents, solvents etc., are given in Table I.

TABLE I

DETAILS OF THIN-LAYER COATINGS OF VARIOUS ADSORBENTS

No.	Coating	Wt. of the adsorbent (g)	Solvent	Average coating of adsorbent (mg/cm ²)
1	Kieselgel G	26	Chloroform (50 cc) -methanol (20 cc)	8.2
2	Cellulose-CaSO ₄	26.25	Water (90 cc)	7.1
3	Cellulose acetate-CaSO ₄	26.25	Water (90 cc)	7.3
4	Kieselguhr G	32	Ethanol (65 cc)	6.8

Ethanol solutions of different amines (10 μ l) containing 1-2 μ g were spotted with a standard microcapillary on the plates. This resulted in deep-colored spots of the complexes. Spots of crystalline complexes as well as those formed in solution were also placed adjacent to the above spots. The plates were left in a desiccator for one hour, after which they were irrigated with different solvent systems. Table II gives the melting points of the complexes, solvent systems, and R_F values.

TABLE II

 R_F VALUES OF VARIOUS CHARGE-TRANSFER COMPLEXES

S. No.	Complexes of <i>s</i> -TNT/ <i>m</i> -DNB with the following amines	<i>s</i> -TNT complexes		Adsorbents: Kieselgel G impregnated with 3% <i>s</i> -TNT			
		<i>M. p.</i> observed	<i>M. p.</i> reported	Solvents:	Toluene- ethylene dichloride* (95:5)	Toluene- monochloro- benzene* (3:2)	Ben- zophen- one (1:1)
1	N-Methylaniline	—	—		0.82	0.67	0.61
2	N,N-Dimethylaniline	45-46	—		0.86	0.76	0.90
3	Aniline	84-85	83-84 ¹⁰		0.57	0.50	0.31
4	α -Naphthylamine	144	141.5 ¹⁰		0.63	0.52	0.20
5	β -Naphthylamine	144	113.5 ¹⁰		0.58	0.42	0.21
6	<i>o</i> -Anisidine	82	—		0.54	0.43	0.34
7	<i>p</i> -Anisidine	50-51	—		0.32	0.22	0.14
8	<i>m</i> -Chloroaniline	71-72	—		0.68	0.61	0.58
9	<i>p</i> -Chloroaniline	59	—		0.60	0.51	0.44
10	Diphenylamine	34-35	31 ¹⁰		0.88	0.78	0.91
11	<i>o</i> -Toluidine	61-62	53-55 ¹⁰		0.61	0.56	0.49
12	<i>m</i> -Toluidine	67-68	62-63 ¹⁰		0.55	0.45	0.41
13	<i>p</i> -Toluidine	70-71	63-64 ²⁰		0.49	0.41	0.35
14	<i>m</i> -Phenylenediamine	78-79	—		0.09	0.05	0.00

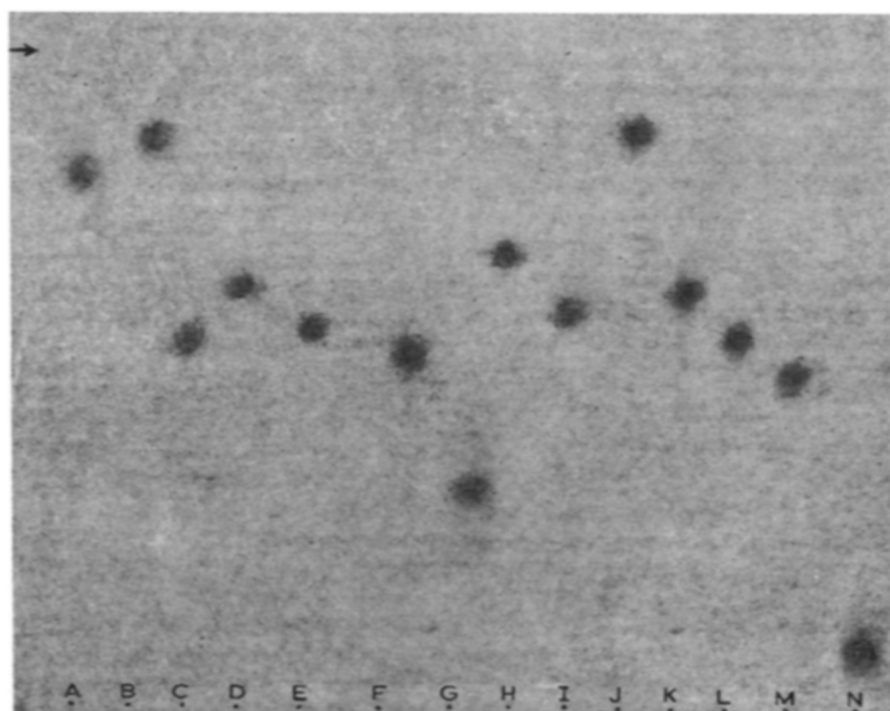
* Solvent contained 3% *s*-TNT/*m*-DNB.** Solvent saturated with *m*-DNB.

Fig. 1. Chromatoplate showing the separation of charge-transfer complexes of 2,4,6-trinitrotoluene with the following amines: A = N-Methylaniline; B = N,N-dimethylaniline; C = aniline; D = α -naphthylamine; E = β -naphthylamine; F = *o*-anisidine; G = *p*-anisidine; H = *m*-chloroaniline; I = *p*-chloroaniline; J = diphenylamine; K = *o*-toluidine; L = *m*-toluidine; M = *p*-toluidine; N = *m*-phenylenediamine. Adsorbent: Kieselgel G impregnated with 3% *s*-TNT; solvent: toluene-ethylene dichloride (95:5) containing 3% *s*-TNT; system: ascending.

<i>m</i> -DNB complexes		Adsorbents: Kieselgel G impregnated with 3% <i>m</i> -DNB					
ne- ne wide*	<i>M.p.</i> observed	<i>M.p.</i> reported	Solvents:	Toluenc- monochloro- benzene* (3:2)	Petroleum ether- ethyl acetate** (9:1)	Petroleum ether- ethylene dichloride* (1:1)	Petroleum ether- ethyl acetate** (95:5)
	—	—	—	—	0.72	0.90	0.83
—	—	—	—	0.82	1.00	0.91	0.97
40-41	41.5 ²¹ , 44.2 ²²	—	—	0.48	0.80	0.59	0.27
67	—	—	—	0.50	0.73	0.64	0.21
58	63.8 ²¹	—	—	0.43	0.62	0.57	0.17
—	—	—	—	0.40	0.82	0.59	0.30
—	—	—	—	0.22	0.43	0.31	0.08
—	—	—	—	0.61	0.87	0.70	0.38
—	—	—	—	0.46	0.72	0.62	0.23
—	—	—	—	0.84	1.00	0.93	0.83
—	—	—	—	0.47	0.87	0.65	0.41
—	—	—	—	0.40	0.81	0.61	0.33
—	—	—	—	0.37	0.75	0.55	0.28
—	—	—	—	0.07	0.07	0.06	0.00

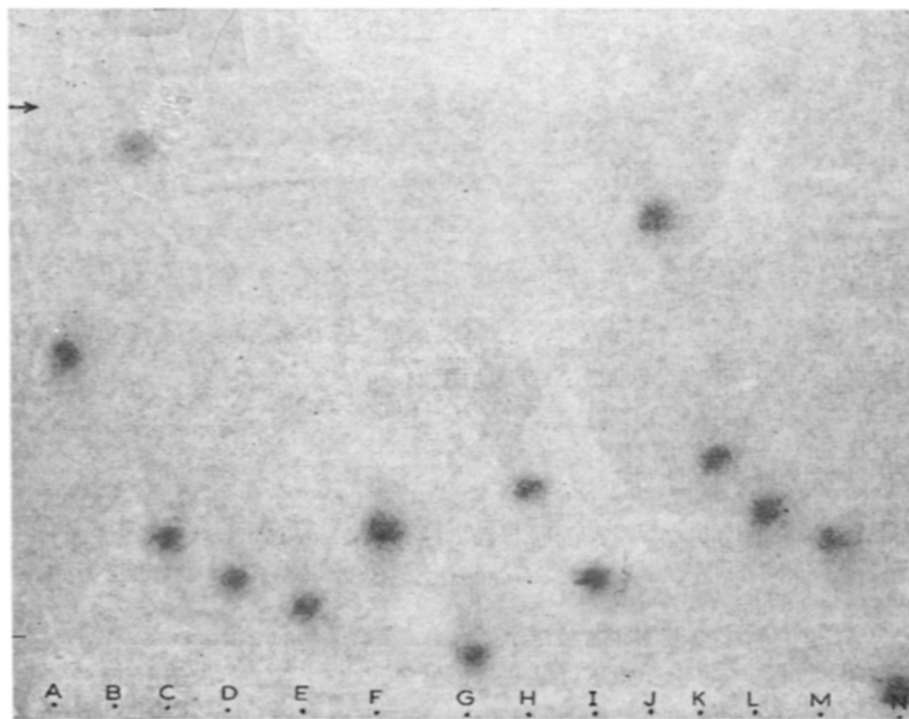


Fig. 2. Chromatoplate depicting the resolution of charge-transfer complexes of *m*-dinitrobenzene with amines (A—N). Adsorbent: Kieselgel G with 3% *m*-DNB; solvent: petroleum ether-ethyl acetate (95:5) saturated with *m*-DNB; system: ascending.

Specimen chromatoplates depicting the resolutions of charge-transfer complexes of 2,4,6-trinitrotoluene and *m*-dinitrobenzene with amines are represented in Figs. 1 and 2, respectively.

DISCUSSION AND RESULTS

The crystalline complexes of *s*-TNT and *m*-DNB with amines when run on Kieselgel G, cellulose-CaSO₄, and cellulose acetate-CaSO₄ plates (untreated with *s*-TNT/*m*-DNB) broke down completely into nitroaromatic compounds and amines in all possible polar and non-polar solvents tried. The adsorption forces proved to be so strong that irrigation even at -10° was a failure. Only in the case of Kieselguhr G did the complexes not break and travel up to the solvent front when irrigated with solvents like dioxan, benzene, toluene, xylene, chloroform-xylene (80:20).

Kieselgel G impregnated with 3 % *s*-TNT or *m*-DNB proved to be the best adsorbent for the sharp separation of the complexes. In order to further check the breakdown of the complexes a 3 % addition of *s*-TNT/*m*-DNB to the irrigating solvent was found necessary. It was observed that the general patterns of migrations of both *s*-TNT and *m*-DNB complexes were the same. The mobilities of the complexes were almost in the order of the basicities of their amines. Aniline being a stronger base compared to *N*-methylaniline and *N,N*-dimethylaniline, its complexes were strongly adsorbed on the plates resulting in lower *R_F* values. The complexes of *p*-anisidine migrate less than those of *p*-chloroaniline. *p*-Toluidine being more basic than aniline, its complexes have lower *R_F* values than that of the latter. The low *R_F* values of *m*-phenylenediamine complexes are due to the strong basicity of the π -donor. Further, the *R_F* values of the complexes of *p*-substituted amines were lower than those of *meta* and *ortho* substituted amines, e.g. *p*-anisidine complex < *o*-anisidine complex; *p*-toluidine complex < *m*-toluidine complex < *o*-toluidine complex; *p*-chloroaniline complex < *m*-chloroaniline complex.

Attempts to prepare and run the complexes of 2,4-dinitrodiphenylamine with *s*-TNT and *m*-DNB failed. This could be due to the presence of electron attracting groups in the donor molecule, which renders the charge-transfer linkage highly unstable.

It was noted that the colors of *s*-TNT and *m*-DNB complexes with *N*-methyl- and *N,N*-dimethylaniline disappeared within half an hour on drying the plates after irrigation. This shows that their complexes are weaker by comparison with aniline which could be due to partial neutralization of the basic charge on the amino group by methyl groups.

ACKNOWLEDGEMENTS

Thanks are due to Dr. H. K. ACHARYA, Assistant Director (Chemistry) and Dr. KARTAR SINGH, Director, Defence Science Laboratory, Delhi, for encouragement.

SUMMARY

Charge-transfer complexes of 2,4,6-trinitrotoluene and *m*-dinitrobenzene with aromatic amines have been studied by employing a thin-layer chromatographic

technique. Excellent resolution of the complexes was achieved on Kieselgel G plates impregnated with the acceptor molecule and employing nonpolar solvents. It was possible to characterize distinctly the complexes formed from 1-2 μg of individual amines.

REFERENCES

- 1 B. DE VRIES, *Chem. Ind. (London)*, (1962) 1049.
- 2 J. SHABTAI, *J. Chromatog.*, 18 (1965) 302.
- 3 J. SHABTAI, *Israel J. Chem.*, 1 (1963) 300.
- 4 J. SHABTAI, J. HERLING AND E. GIL-AV, *J. Chromatog.*, 11 (1963) 32.
- 5 R. J. CVETANOVIC, F. J. DUNCAN AND W. E. FALCONER, *Can. J. Chem.*, 41 (1963) 2095.
- 6 E. K. C. LEE AND F. S. ROWLAND, *Anal. Chem.*, 36 (1964) 2181.
- 7 K. MALINOWSKA, *Chem. Anal. (Warsaw)*, 9 (1964) 353.
- 8 R. J. CVETANOVIC, F. J. DUNCAN AND W. E. FALCONER, *Can. J. Chem.*, 42 (1964) 2410.
- 9 A. G. VERESHCHAGIN, *J. Chromatog.*, 17 (1965) 382.
- 10 R. IKAN, *J. Chromatog.*, 17 (1965) 591.
- 11 M. V. SCHANTZ, S. JUVONEN AND R. HEMMING, *J. Chromatog.*, 20 (1965) 618.
- 12 V. A. PASESHNICHENKO AND A. R. GUSEVA, *Prikl. Biokhim. Mikrobiol.*, 1 (1965) 559.
- 13 E. STAHL AND H. VOLLMANN, *Talanta*, 12 (1965) 525.
- 14 C. B. BARRETT, M. S. J. DALLAS AND F. B. PADLEY, *Chem. Ind. (London)*, (1962) 1050.
- 15 G. M. NANO AND A. MARTELLI, *J. Chromatog.*, 21 (1966) 349.
- 16 M. FRANCK-NEUMANN AND P. JÖSSANG, *J. Chromatog.*, 14 (1964) 280.
- 17 R. E. MILLER AND W. F. K. WYNNE-JONES, *J. Chem. Soc.*, (1959) 2375.
- 18 B. V. TRONOV AND N. V. SYRNEVA, *Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Technol.*, 3 No. 4 (1960) 752.
- 19 T. URBANSKI, *Chem. Technol. Explosives, (Warszawa)*, 1 (1964) 311.
- 20 I. ISENBERG AND S. L. BAIRD, *J. Am. Chem. Soc.*, 84 (1962) 3803.
- 21 T. URBANSKI, *Chem. Technol. Explosives (Warszawa)*, 1 (1964) 239.
- 22 P. V. ROMBURGH, *Chem. Zentr.*, II (1911) 444.

J. Chromatog., 29 (1967) 120-125