GAS–LIQUID CHROMATOGRAPHIC STUDIES OF ELECTRON DONOR–ACCEPTOR SYSTEMS

III. THE INTERACTIONS OF AROMATIC DONORS WITH 1,3,5-TRINITROBENZENE

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1,3,5-Trinitrobenzene (TNB) has been used extensively as the electron acceptor molecule in studies of charge-transfer (CT) interactions, as have most of the nitro-substituted benzenes, and there are numerous quantitative determinations of its complexing power with aromatic hydrocarbons and their substituted derivatives (see *e.g.* ref. 1). TNB has also been used as an electron acceptor stationary phase in gas–liquid chromatography (GLC) by BROWN[2] in his investigations of the electron donor–acceptor properties of organic molecules. However, no specific retention data were published in this work. Polynitro-aromatic compounds may also be used as stationary phases in column chromatography as evidenced by the work of AYRES AND MANN[3] with tetranitrobenzylpolystyrene. These workers observed a linear correlation between complex formation on linear tetranitrobenzylpolystyrene and chromatographic behaviour on tetranitrobenzylpolystyrene resin using aromatic electron donors.

The purpose of this study was to investigate the properties of TNB as a stationary phase in the light of our previous work[4]. We have measured retention volumes for series of electron donors eluted from TNB at 130° and have thus obtained activity coefficients at infinite dilution, γ, for the donors in these solutions. The solutes were also chromatographed from silicone oil (SO) at the same temperature to evaluate relative retentions, R (see Table II). The results of this chromatographic study are compared with association constants for CT complex formation measured spectroscopically in solution. In some cases the donor–TNB systems studied by the GLC method have not been studied spectroscopically and, where available, comparisons have been drawn with CT complexes of these donors with acceptors of similar size to TNB, *e.g.* picric acid.

EXPERIMENTAL

The chromatograph and the preparation of the columns have been described previously[4]. The columns were constructed from 4 mm I.D. glass tubing and were

either 0.75 or 2.0 m in length (TNB) or 1.0 or 2.0 m in length (SO). The stationary phase was deposited onto the silazane treated celite support by dissolving a weighed amount of TNB in dichloromethane, adding this solution to the celite and then allowing the solvent to evaporate.

Measurements were made relative to a reference standard and for this 1,2,3,5-tetramethylbenzene was found to be suitable and was frequently chromatographed. Some loss (~ 10 %) of stationary phase was noted at the temperature of operation, this being allowed for by measurement relative to the reference.

Materials

1,3,5-Trinitrobenzene. This was obtained commercially and recrystallized twice from aqueous ethanol, m.p. 122°.

Silicone oil. May and Baker's "Embaphase" product was used without further treatment.

Solutes. These were purified as in the previous work or were pure commercial samples.

RESULTS

Spectroscopic values of the association constants for CT complexes with TNB of the donors used in this study are shown in Table I. (K^C denotes that the donor

TABLE I

SPECTROSCOPIC ASSOCIATION CONSTANTS FOR TNB COMPLEXES

Donor	K^C ($l \cdot mole^{-1}$)	KX	T(°C)	*Ref.*
Carbon tetrachloride solvent				
Naphthalene	4.0	41.5	20	5
1,2,3,5-Tetramethylbenzene	2.35	24.4	20	5
Styrene	1.7	18	20	5
m-Xylene	0.87	9	20	5
N,N-Dimethylaniline	3.4	35.4	19–20	6
Diphenyl	1.0	10.4	25	7
Chloroform solvent				
Mesitylene		2.67	25	8
Naphthalene		17.0	25	8
Aniline		5.1	25	8
N,N-Dimethylaniline	1.3	16.3	20	6
		9.4	25	8
		22.9	25	9
o-Toluidine		5.8	25	8
m-Toluidine		6.5	25	8
p-Toluidine		7.5	25	8
Cyclohexane solvent				
Aniline	3.0	28.1	20	6
N-Methylaniline	7.7	72.0	20	6
N-Ethylaniline	8.4	78.5	19.8	6
N-*n*-Propylaniline	7.3	68.3	18.5	6
N,N-Dimethylaniline	9.6	89.8	20	6
N,N-Diethylaniline	6.5	60.8	20	6
N,N-Di-*n*-propylaniline	6.5	60.8	20	6

concentration is expressed in molarity and K^X that the donor concentration is in mole fraction units.) Although various solvents have been used there are sufficient data in a common solvent for some comparative observations to be made, but not enough pertaining to structurally similar compounds to demonstrate a linear relationship between $1/\gamma$ or R and K^X.

In Table II specific retention volumes at 130° on TNB, V_{gI}, and on SO, V_{gII}, are shown, together with their ratio $R(= V_{gI}/V_{gII})$ and values of γ for those compounds for which vapour pressures are available.

For those complexes studied in carbon tetrachloride solution a general trend between $1/\gamma$ or R and K^X is observed. The spectroscopic values were obtained by

TABLE II

VALUES OF THE SPECIFIC RETENTION VOLUMES ON TNB AND SO

R and γ measured at 130° for aromatic electron donors.

Donor	V_{gI}	V_{gII}	R	γ
Aniline	991.5	84.1	11.8	0.54
o-Toluidine	1671.5	142.2	11.8	0.53
m-Toluidine	1962.2	145.7	13.5	0.51
p-Toluidine	1726.9	139.9	12.34	0.53
p-Ethylaniline	2138.7	239.4	8.93	0.41
N-Methylaniline	1153.5	136.3	8.46	0.69
N,N-Dimethylaniline	991.5	159.9	6.2	0.69
N,N-Diethylaniline	775.4	328.9	2.36	1.92
N,N-Dimethyl-*o*-toluidine	154.7	147.0	1.05	3.43
N,N-Dimethyl-*p*-toluidine	1464.4	261.8	5.59	0.79
N,N-Dimethyl-2,4-xylidine	227.5	238.1	0.95	
N,N-Dimethyl-2,6-xylidine	129.8	200.3	0.65	
N,N-Dimethylbenzylamine	117.4	125.6	0.93	
N-Ethyl-N-methylaniline	805.6	261.8	3.08	
N,N-Dimethyl-*m*-toluidine	1608.7	271.0	5.93	
N,N-Dimethyl-*p*-ethylaniline	1779.9	434.7	4.09	
N,N-Dimethyl-*p*-isopropylaniline	1461.9	584.9	2.50	
N,N-Diethyl-*p*-toluidine	1131.7	515.2	2.20	
N-Ethylaniline	1266.2	193.1	6.56	
o-Ethylaniline	1809.3	219.1	8.26	
N,*n*-Propylaniline	1680.4	320.2	5.25	
N,N-Di-*n*-propylaniline	1111.3	781.4	1.42	
Tetralin	374.0	246.5	1.52	
Indane	180.3	125.6	1.44	
Indene	416.3	130.3	3.19	
1,2,3,4-Tetramethylbenzene	543.4	233.3	2.33	1.75
1,2,4,5-Tetramethylbenzene	357.6	191.9	1.86	2.22
1,2,3,5-Tetramethylbenzene	374.0	194.2	1.93	1.98
Diphenyl	2803.2	716.0	3.92	1.66
Thionaphthene	1809.3	283.9	6.37	
1,3,5-Trimethylbenzene	110.8	85.3	1.30	2.50
1,2,4-Trimethylbenzene	149.7	99.5	1.50	2.12
o-Xylene	82.4	55.6	1.48	1.89
m-Xylene	60.9	48.5	1.26	2.22
p-Xylene	61.4	48.5	1.27	2.15
Ethylbenzene	41.8	46.2	0.90	2.97
Styrene	104.5	54.6	1.91	1.69
Isopropylbenzene	42.1	66.3	0.63	4.63
Naphthalene	1619.3	261.9	6.18	0.75
n-Butylbenzene	81.7	138.1	0.59	5.95

various workers and in view of the possible errors involved in their measurement, the lack of an exact correlation is not too surprising. A comparison of the K^X values determined in chloroform with $1/\gamma$ and R show the same trend as that exhibited by the elution of amines from trinitrofluorenone[4], the primary amines having much higher $1/\gamma$ values due to some additional interaction (hydrogen-bonding or strong dipole–dipole).

DISCUSSION

Aromatic amines

The spectroscopic study in cyclohexane of substituted aniline–TNB complexes suggests for the secondary amine series an order of complexing ability of N-ethyl > N-methyl > N-*n*-propylaniline[6]. For the tertiary amines, the spectroscopic results suggest that the complexing power remains constant with increasing alkyl chain length after the N,N-diethyl compound, and that these higher N,N-dialkyl substituted anilines form weaker complexes than N,N-dimethylaniline[6]. This interpretation is supported by the $1/\gamma$ and R values (Table II), but these values suggest a further considerable decrease in complexing power, in going from N,N-diethyl to N,N-di-*n*-propylaniline. Unlike the behaviour with trinitrofluorenone *para* substitution in the anilines decreases R in this solvent. If any non-CT complexing association mechanism is assumed to be constant for the toluidines, then the $1/\gamma$ and R values would suggest *m*-toluidine as the strongest electron donor of the three (*cf.* Table II). In the tertiary amine series R for N,N-dimethyl-*p*-toluidine is less than that for the *meta*-isomer and both of these are less than R for N,N-dimethylaniline itself, implying that they form weaker complexes than N,N-dimethylaniline in spite of the additional electron-releasing methyl group. Alternatively this decrease in R reflects the increased length and spatial requirements of the donor and thus any increased steric hindrance to the solution of aliphatic groups in an aromatic solvent. Increasing the chain length of the *para* substituent in the N,N-dimethylaniline series decreases R in the order *p*-H > *p*-Me > *p*-Et > *p*-iso-Pr, and in the *para*-substituted N,N-diethylanilines *p*-H > *p*-CH_3.

If the nitrogen atom of the amino group is attracted to an unsubstituted position (2,4 or 6) of the TNB molecule as in the case with the indole and skatole complexes of TNB in the solid state[10], then *meta* substitution in the aniline molecule should be favourable to CT complexing on steric grounds: *i.e.* if the component molecules are directly superimposed with the rings parallel for maximum overlap, then the *meta* substituent in the aniline molecule is situated over an unsubstituted position of the TNB molecule. Accordingly the *meta*-substituted anilines of Table II have larger R values than their *ortho* or *para* isomers. The R values for *ortho*-substituted aniline and N,N-dimethylaniline are the lowest of their respective groups due to their "shielding" effect on the nitrogen atom and in N,N-dimethyl-*o*-toluidine to twisting of the dimethylamino group.

Values of the apparent activity coefficients γ are, where calculable, less than one in this system with the exceptions of N,N-diethylaniline and N,N-dimethyl-*o*-toluidine. $\gamma < 1$ corresponds to strong complex formation, *i.e.* a "decreased escaping tendency" of the solute. For these two compounds there are steric factors ("shielding") reducing the effective donor strength and thus $\gamma > 1$. In Fig. 1 the variation of R with

the number of carbon atoms of the nitrogen atom substituent of the aniline is shown for the compounds studied, from which it can be seen that there is an almost linear relationship for the secondary amines. The tertiary amines show a similar relationship to that between log K^C and n as obtained by FOSTER AND HAMMICK[6] and may also tend towards a minimum value.

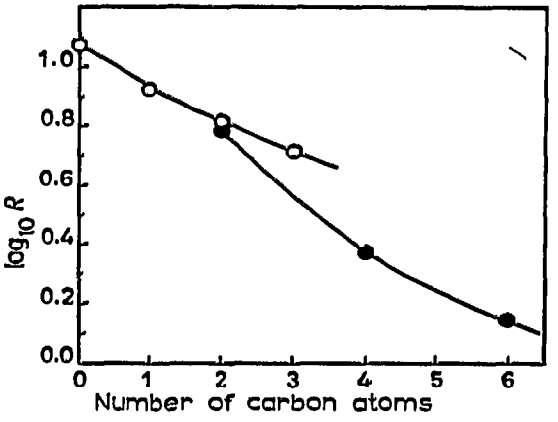

Fig. 1. Number of carbon atoms in the N-alkyl group *vs.* $\log_{10} R$. (○) Secondary amines; (●) tertiary amines.

Aromatic hydrocarbons

The successive methylation of benzene increases the donor strength of the molecule and the R values obtained for the series dimethyl through tetramethyl benzenes increase in that order, showing that CT interaction predominates over any solute–solvent repulsion arising from the increase in the number of non-aromatic carbon atoms. There is one exception, 1,3,5-trimethylbenzene, which has a smaller R value than *o*-xylene. The complexing order of methyl-substituted benzenes suggested by the R values is

1,2,3,4- > 1,2,3,5- > 1,2,4,5- > 1,2,4- > 1,2- > 1,3,5- > 1,3- > 1,4-

On the basis of the inductive effects of the methyl groups (assuming that *para* interactions are stronger than *ortho* interactions) one might expect a complexing order of:

1,2,4,5- > 1,2,3,4- > 1,2,3,5- > 1,2,4- > 1,4- > 1,2- > 1,3,5- > 1,3-

and for the tetra-substituted compounds this is the observed spectroscopic order of association constants for their chloranil complexes[11]. The order of complexing suggested by the R values for the xylenes (*o*- > *p*- ≈ *m*-) may be loosely compared with the K^C-values obtained for the picric acid complexes with these donors[12], these being not inconsistent with the R values although there is hardly any significant difference between the three of them.

In contrast to the donors containing nitrogen, no strong steric effects appear to be present in these complexes. If one assumes that the components have their rings superimposed and parallel, then one would expect the 1,2,3,5-, 1,3,5- and 1,3-substituted compounds to form the strongest complexes of their respective isomer groups. The only pattern that emerges is that the R value falls as the number of adjacent methyl groups decreases, although it would seem that the smaller steric interference of

the 1,2,3,5-isomer is more important than the greater inductive release of the 1,2,4,5-isomer. Increasing the length of the chain in an alkyl-substituted benzene decreases R' as is seen in the series: ethylbenzene > isopropylbenzene > *n*-butylbenzene, the K^C values for their picric acid complexes being respectively 0.74, 0.59 and 0.57 $l \cdot mole^{-1}$ relative to the *p*-xylene complex (= 1 $l \cdot mole^{-1}$)[12].

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SUMMARY

1,3,5-Trinitrobenzene has been used as a stationary phase at 130° for the chromatography of series of aromatic amines and hydrocarbons. The results obtained are discussed in terms of the available spectroscopic association constants for the complexes of these donors with 1,3,5-trinitrobenzene and it is suggested that such complexing is important in this system.

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