

113. *Interaction of Lewis Acids with Aromatic Hydrocarbons and Bases. Part XVI.* The Association of Chloranil with Methylbenzenes in cycloHexane.*

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The degree of interaction of chloranil with a series of methylbenzenes in *cyclohexane* solution has been determined colorimetrically by using a competitive method described by Corkill, Foster, and Hammick.¹ The free energies of the interactions, evaluated from the association constants, are found to be linearly related to the ionisation potentials of the respective hydrocarbons, as are the energies of excitation of the complexes.

THE present work was undertaken to determine the effect of ring methylation of benzene on the stability of the complexes formed with a Lewis acceptor (acid) in solution. Mulliken² regards such complexes as the result of interaction of a Lewis donor (base) and a

* The series of papers entitled "Interaction of Polynitro-compounds with Aromatic Hydrocarbons and Bases" are regarded as previous parts of this series. Part XV, *J.*, 1955, 1202.

¹ Corkill, Foster, and Hammick, *J.*, 1955, 1202.

² Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 605; 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801.

Lewis acceptor, whereby a complex is formed which is a hybrid of unbonded structures of weak interactions of the component molecules with a contribution of a structure in which an electron has been transferred from the donor to the acceptor molecule. Thus the ground state of the complex may be represented as ψ_N where :

$$\psi_N = a\psi(A, B) + b\psi(A^- - B^+) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

An excited state ψ_E exists where :

$$\psi_E = a^*\psi(A^- - B^+) - b^*\psi(A, B) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

so that an electronic excitation, characteristic of the complex, exists corresponding to the transition $\psi_N \longrightarrow \psi_E$. This absorption is called the charge-transfer band of the complex, and the height of this band is presumably a measure of the charge-transfer interaction.

It is reasonable to expect a relation between such charge-transfer and the ionisation potentials of the aromatic donor molecules; since the present work was commenced, this expectation has been realised by Briegleb and Czekalla³ who have studied the interaction of methylbenzenes with *s*-trinitrobenzene. Keefer and Andrews⁴ have made a similar study of methylbenzene-iodine interactions. Our choice of chloranil as an acceptor was determined by the wish to extend the scanty systematic knowledge of this Lewis acid in interactions of the type we are studying. Our results will be seen to run parallel to those of the authors mentioned above.

The determinations by both Andrews and Briegleb depend on direct measurements of the enhancement of absorption due to charge transfer when the components are mixed. In the present work, a different method for determining the association constants has been employed. It depends on the measurement of the depression of charge-transfer absorption of a complex by adding a third substance which will compete with one of the components in the complex for the second component of the complex. A full account of the method has already been given.^{1,5} It has the advantage that optical measurements can be made at a wavelength at which the components of the complex do not absorb, by choosing a suitable acid or base against which the other base or acid can compete. The method has already been justified by comparison of the association constant of *s*-trinitrobenzene-benzene determined by this competitive method,¹ with the result obtained by direct measurement of the *s*-trinitrobenzene-benzene charge-transfer band.⁶

Two corrections have had to be applied in the determinations. The first is a compensation for instrumental error. Vandenbelt, Forsyth, and Garrett⁷ show that, with a Beckman DU spectrophotometer, the plot of extinction coefficient against optical density is only linear from $D = 0.45$ to $D = 1.9$; indeed, even over this central range a slight variation persists. This non-linearity occurred also with the Unicam SP 600, the instrument used in the present work, and was discovered from check measurements with aqueous potassium chromate solutions. All values of D given are corrected to compensate for this instrumental error. Where possible, optical densities have been kept above 0.45 to minimise such effects. It was also found that the values of K obtained by the competition method were dependent on the concentration of the methylbenzene; the association constants can however be extrapolated to zero concentration of methylbenzene. This extrapolation gives consistent results, which agree with the values obtained from the direct measurement of the charge-transfer absorption of the complex by the method of Foster, Hammick, and Wardley.⁸

Experimental.—Materials. cycloHexane was purified by passing it through silica gel (30/120 mesh; 50 cm. \times 3.5 cm.) which had been heated to 250°, subsequently washed with water and

³ Briegleb and Czekalla, *Z. Electrochem.*, 1955, **59**, 184.

⁴ Keefer and Andrews, *J. Amer. Chem. Soc.*, 1955, **77**, 2164.

⁵ Foster, *Nature*, 1954, **173**, 222.

⁶ Lawrey and McConnell, *J. Amer. Chem. Soc.*, 1952, **74**, 6174.

⁷ Vandenbelt, Forsyth, and Garrett, *Ind. Eng. Chem. Anal.*, 1945, **17**, 235.

⁸ Foster, Hammick, and Wardley, *J.*, 1953, 3817.

sodium carbonate solution, and finally dried and fractionated. The purity was checked spectroscopically. Other materials were purified by standard procedures.

Analytical. Full details of the method employed are given in an earlier paper.¹ It depends on the relation between the association constants, K' and K'' , of two Lewis bases which are allowed to compete for one Lewis acid (or *vice versa*) in charge-transfer complex formation. If B' and B'' are the two bases, then it may be shown that :

$$K' = \frac{D_0 - D_1}{D_1} \left(1 + \frac{[B'']K''}{[B']} \right) \quad \dots \quad (3)$$

where D_0 is the optical density at, or near, the absorption maximum of the complex AB'' , of a solution containing B'' , at a concentration $[B'']$, and A , at a concentration $[A]$, where $[A] \ll [B'']$. D_1 is the optical density at the same wavelength of a solution containing B'' at a concentration $[B'']$, A at $[A]$, and B' at $[B']$, where $[A] \ll [B']$. If K'' is known, K' can be evaluated.

In the present work B'' is *NN*-diethylaniline. The value of K'' for the *NN*-diethylaniline-chloranil complex in *cyclohexane* is 3.5 l./mole at 18–20°, between which temperatures all optical measurements were made. Data of a typical determination are given in Table 1.

TABLE 1. Association constant (K') for hexamethylbenzene-chloranil in *cyclohexane* solution. The symbols refer to the terms in equation 3.

$[B']$ (M)	$[B'']$ (M)	D_0	D_1	K' (l./mole)	K'' (l./mole)
0.1053	0.01122	0.287	0.235	3.5	27.0
0.1053	0.02245	0.287	0.203	3.5	25.2
0.1053	0.03370	0.287	0.180	3.5	24.2

Extrapolation of the plot of K'' against $[B'']$ to the value $[B''] = 0$ results in a value of $K'' = 28.6$ l./mole.

The results of the determinations are summarised in Table 2. The extrapolated values of the association constant (K) are the average of at least three separate determinations. The second column gives values of the free energy of formation of the complexes referred to the standard state in which activity is equal to molarity at infinite dilution. Values of the wave-number of the centre of the charge-transfer band are given in the column headed ν .

TABLE 2. Methylbenzene-chloranil complexes in *cyclohexane*.

	K (l./mole)	ΔG (cals./mole)	ν (cm. ⁻¹)		K (l./mole)	ΔG (cals./mole)	ν (cm. ⁻¹)
Benzene ...	0.56	+ 340	28,900	Durene	10.4	-1360	22,100
Toluene ...	1.7	- 310	27,400	Pentamethylbenzene	16.5	-1630	21,000
<i>m</i> -Xylene	2.9	- 613	25,600	Hexamethylbenzene	28.9	-1960	19,800
Mesitylene	5.9	-1030	24,500	Hexaethylbenzene...	1.3	- 152	too weak to be measured

Discussion.—Our results show that the free energy of interaction of chloranil with methylbenzenes up to hexamethylbenzene increases linearly in magnitude with the decreasing ionisation energies of the methylbenzenes.⁹ Chloranil thus shows the same Lewis acid characteristics as *s*-trinitrobenzene³ and iodine⁴ in their interactions with these aromatic hydrocarbons (Fig. 1). The same order of free energy of interaction is shown in the iodine monochloride-methylbenzene complexes,¹⁰ but here the linear correlation with the ionisation potentials of the benzene homologues is not very satisfactory. This relationship between the free energy of interaction and the ionisation potential of the methylbenzene may be expected if the interactions with which we are dealing are of charge-transfer type. The low value of the association constant of hexaethylbenzene-chloranil is almost certainly due to the steric interference of the ethyl groups hindering the approach of the chloranil molecule. This is the reason suggested for the corresponding low constant for the hexaethylbenzene-iodine association.^{10,11}

⁹ Franklin, *J. Chem. Phys.*, 1954, **22**, 1304.

¹⁰ Andrews and Keefer, *J. Amer. Chem. Soc.*, 1952, **74**, 4500.

¹¹ Tamres, Vizi, and Searles, *ibid.*, 1953, **75**, 4358.

The energy of the excited state will mainly depend on the function $a^*\psi(A^- - B^+)$ in eqn. 2. This will be proportional, for a given Lewis acid, to the ionisation potential of the Lewis base. Consequently the energy of excitation of the complex may be expected to be a function of the ionisation potential of the electron donor. In fact, the mean energy of excitation represented by the centre of the charge-transfer band of each interaction (which

FIG. 1. Relation between the ionisation potentials of methylbenzenes and the free energies of complex formation ($-\Delta G$) of these methylbenzenes with (A) chloranil in cyclohexane, (B) *s*-trinitrobenzene in carbon tetrachloride (see ref. 3), (C) iodine in carbon tetrachloride (see ref. 4).

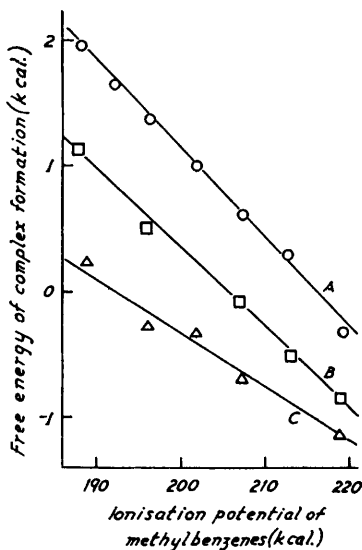
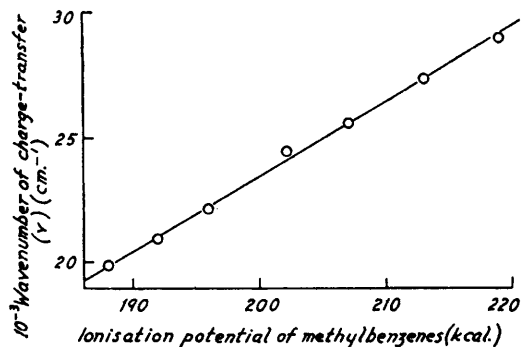


FIG. 2. Relation between the ionisation potentials of methylbenzenes and the wave-numbers of the charge-transfer bands of the respective complexes with chloranil in cyclohexane.



may consist of more than a single absorption) has been found to be directly proportional to the ionisation energy of the respective methylbenzenes (Fig. 2). A similar relation has been found for the methylbenzene-*s*-trinitrobenzene interactions by Briegleb and Czekalla,³ and for electron donor-iodine interactions by McConnell, Ham, and Platt.¹²

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¹² McConnell, Ham, and Platt, *J. Chem. Phys.*, 1953, **21**, 66.