

43. Interaction of Lewis Acids with Aromatic Hydrocarbons and Bases. Part XVIII.* Aromatic Hydrocarbon Picrates in Chloroform.

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Stability constants of fourteen hydrocarbon picrates in chloroform solution have been determined by a partition method. The stabilities have been related to the frequencies of the charge-transfer bands of the molecular complexes of the same hydrocarbons with chloranil.

MULLIKEN¹ has described the ground state of an intermolecular charge-transfer complex as ψ_N where:

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

a and b represent the electron acceptor and the electron donor respectively, $\psi(a,b)$ is a no-bond function and $\psi(a^- - b^+)$ is a dative function in which an electron has been donated from b to a . An excited state ψ_E exists where:

$$\psi_E = x\psi(a^- - b^+) - y\psi(a,b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The energy of the excitation $\psi_N \longrightarrow \psi_E$ can be expressed approximately as:²

$$h\nu_{CT} = I_p - E - W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

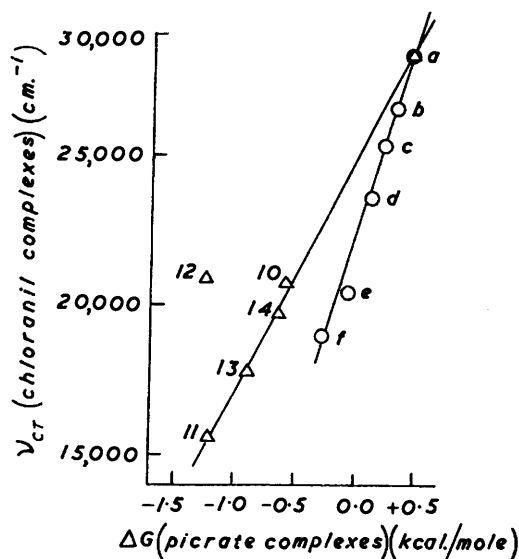
where ν_{CT} is the frequency of the charge-transfer absorption band, I_p is the ionisation

* Part XVII, *J.*, 1956, 3881.

¹ Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801.

potential of b , E is the electron affinity of a , and W is the dissociation energy of the charge-transfer excited state. If W can be taken as approximately constant for a series of complexes with the same acceptor molecule, then ν_{CT} is proportional to I_p .

In the ground state of the molecule (eqn. 1) normally $x \gg y$. Nevertheless the free energies of formation (ΔG) of the complexes between a series of donors and a particular acceptor are generally proportional to the corresponding I_p values provided that the donors are of the same type and there are no excessive steric factors.^{2,3,4,5} Combination of these two relationships leads to the expectation of a proportionality between the corresponding



Plot of the free energies of formation of hydrocarbon picrate complexes against the frequencies of the charge-transfer bands of the corresponding hydrocarbon complexes with chloranil.

a Benzene, b toluene, c *m*-xylene, d mesitylene, e durene, f hexamethylbenzene. The numbers refer to the hydrocarbons given in the Table.

values of ΔG and ν_{CT} for such a series of complexes.³ Likewise there should be a linear relationship between ν_{CT} for a series of donors with a particular acceptor against ν_{CT} for complexes of the same series of donors with a second acceptor. This has also been verified.⁶ Hence we should expect a linear relationship between ν_{CT} for complexes of a series of donors with a given acceptor and ΔG for complexes of the same series of donors with a second acceptor—provided that the donors have the same type of structure and that no excessive steric effects are involved. This we find to be approximately the case.

Details of the experimental determination of ΔG by a partition method are now given for a series of hydrocarbon picrates. For the series involving the planar condensed aromatic donors benzene, naphthalene, anthracene, phenanthrene, acenaphthene, and fluorene values of ΔG for the picrate complexes are compared with the values of ν_{CT} for the corresponding chloranil complexes (Figure). On the Figure are also plotted points for complexes involving methylbenzenes, for which values of ΔG have been calculated from the stability constants quoted by Anderson and Hammick.⁷ There is good agreement except for phenanthrene. Here the stability of the picrate is comparable with that of anthracene, as might be expected, but ν_{CT} for the chloranil complex is relatively high. Nevertheless this value of ν_{CT} might be expected from the ionisation potential of phenanthrene as calculated by Pople.⁸

² McConnell, Ham, and Flatt, *J. Chem. Phys.*, 1953, **21**, 66.

³ Foster, Hammick, and Parsons, *J.*, 1956, 555.

⁴ Briegleb and Czekalla, *Z. Electrochem.*, 1955, **59**, 184.

⁵ Keefer and Andrews, *J. Amer. Chem. Soc.*, 1955, **77**, 2164.

⁶ Foster, *Nature*, 1958, **181**, 337.

⁷ Anderson and Hammick, *J.*, 1950, 1089.

⁸ Pople, *J. Phys. Chem.*, 1957, **61**, 1.

EXPERIMENTAL

The stabilities of the picrates in chloroform at 18° were measured by Anderson and Hammick's⁷ partition method. This, a modification of that described by Moore, Shepherd, and Goodall,⁹ depends on the change in the partition of picric acid between water and chloroform when an aromatic hydrocarbon is added to the system. Allowance is made for the depressive effect of the hydrocarbon on the solubility of picric acid in the chloroform. The association of the hydrocarbon with the picric acid is expressed as:

$$K = [\text{complex}]/[\text{hydrocarbon}][\text{picric acid}] \quad (4)$$

Anderson and Hammick showed that if K and the effect of the solubility depression are small, then:

$$K = K_1 + k \quad (5)$$

where K_1 is a parameter obtained directly from the experimental data, and k is a solubility depression constant. Because the values of K measured in the present work are in some cases four to five times the highest values obtained by Anderson and Hammick,⁷ a more accurate relationship has been used in place of eqn. (5).

Consider the distribution of picric acid between water and chloroform, in the latter of which the solution has a molarity P . Addition of an aromatic substance depresses the molarity of picric acid to y by the amount $(P - y)$. At the same time the total molarity of picric acid (free and complexed) in the chloroform is increased to y_1 by the amount $(y_1 - P)$ owing to complex formation. If Y is the experimentally found molarity of picric acid in the chloroform, then

$$Y = y + y_1 - P \quad (6)$$

The solubility depression constant being:

$$k = (P - y)/yZ \quad (7)$$

where Z is the molarity of the aromatic substance in the chloroform layer and P is the initial molarity of the picric acid, then from eqn. (7):

$$y = P/(1 + kZ) \cong P(1 - kZ + k^2Z^2)$$

Substitution of this value of y in eqn. (6) gives:

$$y_1 - P = Y - P + PkZ - Pk^2Z^2 \quad (8)$$

The stability constant

$$K = \frac{y_1 - P}{P[Z - (y_1 - P)]} \quad (9)$$

whence, since $(y_1 - P)$ is small compared with Z :

$$K = (y_1 - P)/[PZ(1 - KP)] \quad (10)$$

Eliminating y_1 from eqns. (8) and (10) we have:

$$K(1 - KP) = (Y - P)/PZ + k - k^2Z \quad (11)$$

or

$$K = (K_1 + k - k^2Z)/(1 - KP) \quad (12)$$

where $K_1 = (Y - P)/PZ$ (the "apparent" stability constant). Anderson and Hammick showed that $k = 0.0038V$ where V is the molecular volume of the hydrocarbon. This relationship has been used to determine k and hence K by eqn. (12). The molecular volumes determined by Tyrer¹⁰ do not vary greatly for small changes in temperature or for certain solvent changes. The values used, obtained from standard data, are quoted in the Table.

The absorption maxima of the chloranil complexes were obtained from the spectra of chloroform solutions in which the concentration of chloranil $\approx 10^{-3}M$ and the concentration of the hydrocarbon $\approx 10^{-1}M$. In all the cases the maxima were observed in the mixtures. No attempt was made to resolve the absorption bands of the various species present.

⁹ Moore, Shepherd, and Goodall, *J.*, 1931, 1447.

¹⁰ Tyrer, *J.*, 1910, 97, 2620.

TABLE.

Hydrocarbon	Molecular volume			Ref.	K_1 (l./mole)	K	ΔG (kcal./mole)
	V (ml.)	Solv.	Temp.				
1. Diphenyl	148	CHCl ₃	25°	(a)	0.41	0.97	0.02
2. Diphenylmethane	167	C ₆ H ₆	25	(b)	0.09	0.66	0.24
3. Triphenylmethane	226	CHCl ₃	25	(a)	-0.27	0.52	0.38
4. Dibenzyl	183	—	—	(c)	0.08	0.70	0.21
5. Stilbene	174	C ₆ H ₆	18	(d)	1.10	1.80	-0.34
6. Tolan	179	C ₆ H ₆	18	(d)	0.83	1.54	-0.25
7. Tetraphenylethane ...	302	C ₆ H ₆	25	(e)	-0.24	0.83	0.11
8. Tetraphenylethylene ...	298	C ₆ H ₆	25	(e)	-0.63	0.22	0.87
9. Diphenyldiacetylene ...	200	C ₆ H ₆	25	(e)	0.51	1.22	-0.11
10. Naphthalene	123	CHCl ₃	18	(f)	2.03	2.68	-0.57
11. Anthracene	201	C ₆ H ₆	20	(g)	5.00	7.56	-1.17
12. Phenanthrene	157	C ₆ H ₅ ·CH ₃	20	(a)	5.41	8.04	-1.20
13. Acenaphthene	142	CHCl ₃	25	(a)	3.46	4.36	-0.85
14. Fluorene	152	C ₆ H ₆	25	(e)	2.09	2.87	-0.61

* Tyrer, *J.*, 1910, **97**, 2620. * Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1934, *A*, **143**, 147.
 ° Computed from molecular volume of diphenylmethane by adding 16 ml. for the extra methylene group; Cohn, McMeeekin, Edsall, and Blanchard, *J. Amer. Chem. Soc.*, 1934, **56**, 784. ° Smythe and Dornte, *ibid.*, 1931, **53**, 1296. ° Present work. † Forch, *Ann. Physik*, 1905, **17**, 1012. ‡ Tyrer, *J.*, 1910, **97**, 1778.

Analytical Methods and Apparatus.—These are as described by Anderson and Hammick.⁷ Spectra were measured on a Unicam S.P. 500 Spectrophotometer.

Materials.—Picric acid, recrystallised once from very dilute sulphuric acid, then four times distilled water and dried (P₂O₅), had m. p. 122.5°. Chloranil, recrystallised four times from benzene, had m. p. 289° (sealed tube). Chloroform was washed five times with water, four times with concentrated sulphuric acid, once with 5% sodium hydroxide solution, and finally thrice with ice-cold water, care being taken to avoid direct light, dried (CaCl₂), refluxed, and fractionated over P₂O₅ and stored away from the light in dark bottles completely filled. Hydrocarbons were prepared and purified by standard methods.

Results.—These are summarised in the Table. To illustrate the method of computation a single example is quoted in full, *viz.*, the stability constant K for anthracene picrate in chloroform at 18°:

Concentration of thiosulphate = 0.03372 mole/kg.; concentration of anthracene in the chloroform layer $Z = 0.05209M$; concentration of picric acid in the chloroform layer: three titrations gave:

Density of chloroform layer	1.4912	1.4912	1.4914 g./ml.
Wt. of Na ₂ S ₂ O ₃ soln./wt. of CHCl ₃ layer	0.8021	0.8029	0.8030

Average density = 1.492 g./ml. Average ratio = 0.8027. Hence concentration of picric acid in the chloroform layer, $Y = (1.492 \times 0.8027 \times 0.03372) = 0.04036M$. Concentration of picric acid in the water layer: two determinations gave:

Density of water layer	1.004	1.0046 g./ml.
Wt. of Na ₂ S ₂ O ₃ soln./wt. of water layer	0.7121	0.7136

Average density = 1.0045 g./ml. Average ratio = 0.7128. Hence concentration of picric acid in the water layer, $X = (1.0045 \times 0.7128 \times 0.03372) = 0.02414M$.

From a graphical interpolation of the partition coefficient of picric acid between water and chloroform, the concentration P of picric acid in pure chloroform corresponding to a concentration 0.0241M in water is 0.03201M, whence the apparent stability constant:

$$K_1 = (Y - P)/PZ = 0.00835/(0.03201 \times 0.05209) = 5.00 \text{ l./mole.}$$

The molecular volume of anthracene in benzene at 20° is 201 ml.,¹¹ whence $K = (201 \times 0.0038) = 0.76 \text{ l./mole}$, and from (12) $K = 5.73/(1 - 0.032K)$, whence $K = 7.56 \text{ l. mole}$.

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¹¹ Tyrer, *J.*, 1910, **97**, 1778.