Interaction of Polynitro-compounds with Aromatic Hydrocarbons and Bases. Part XV.* The Association Constants for the Equilibria in the Systems: s-Trinitrobenzene–Benzene and Chloranil–Benzene.

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The competitive method described by Foster (*Nature*, 1954, **173**, 222) for the determination of equilibrium constants has been applied to the systems mentioned in the title. In each case, a series of *N*-alkylanilines was made to compete with the Lewis base benzene for the respective Lewis acids in *cyclo*hexane. Incidental to the work has been the evaluation of equilibrium constants for the equilibria between the *N*-alkylanilines and chloranil.

COLORIMETRIC methods for the study of equilibria in solution of complex systems of the type $A + B \rightleftharpoons AB$, where AB is coloured, have the obvious advantage of directness compared with such a method as partition (Moore, Shepherd, and Goodall, *J.*, 1931, 1447; Anderson and Hammick, *J.*, 1950, 1089). However, in cases where A and B are coloured and where their absorption curves overlap to any extent with that of the product AB, calculations of equilibrium constants from optical data become complicated and tedious (cf., *e.g.*, Landauer and McConnell, *J. Amer. Chem. Soc.*, 1952, **74**, 1221; Lawrey and McConnell, *ibid.*, p. 6175). Moreover, since they involve differences between the total absorption and those of the separate components in the equilibrium, considerable inaccuracy may be inevitable. Thus, when determining the association constant of benzene–*s*-trinitrobenzene Lawrey and McConnell (*loc. cit.*) used solutions in which, at certain wave-lengths, benzene accounted for 90% of the total absorption.

A method has been suggested by one of us (Foster, *Nature*, 1954, **173**, 222) by which these difficulties can in certain circumstances be overcome. Suppose we wish to investigate the interaction of a substance A with a substance B′ by measuring the colour densities of the complex AB′, but find that the absorption of AB′ overlaps that of B′. We then seek an alternative substance to B′, say B″, having an absorption for the complex AB″ that does not overlap with that of any of the other species present. The equilibrium constant K'' for $A + B'' \rightleftharpoons AB''$ can easily be found by, say, the method of Foster, Hammick, and Wardley (*J.*, 1953, 3817). We can now add some B′ to the system $A + B'' \rightleftharpoons AB''$ and measure the diminution of the colour density of AB″ due to the shift of equilibrium in the system $A + B'' \rightleftharpoons AB''$ as a result of the interaction of B′ with some A, and hence arrive at the equilibrium constant K' for $A + B' \rightleftharpoons AB'$. This is essentially the principle of the Thomson and the Ostwald method for finding " acid strengths " by causing two acids to compete for a single base.

We can put this principle in an analytical form as follows : consider a solution containing a Lewis acid A and a pair of Lewis bases B′ and B″ which interact with A. For 1 : 1 interactions we have :
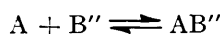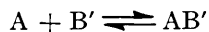
$$A + B' \rightleftharpoons AB'$$

$$A + B'' \rightleftharpoons AB''$$

A pair of equilibrium constants may be defined as :

$$K' = \frac{[AB']}{([\mathbf{A}] - [AB'] - [AB''])([\mathbf{B}'] - [AB'])}{}^{\dagger} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

$$K'' = \frac{[AB'']}{([\mathbf{A}] - [AB'] - [AB''])([\mathbf{B}''] - [AB''])} \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

where [AB′] and [AB″] are the equilibrium concentrations of AB′ and AB″. [**A**], [**B′**], and [**B″**] represent the total concentrations of these species respectively, namely, the sum of the

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* Part XIV, *J.*, 1955, 89.

† Concentration terms which are determined analytically are printed in bold type.

amounts appearing in the free and in the "complexed" forms. If $[\mathbf{B'}] \gg [\mathbf{A}]$ and $[\mathbf{B''}] \gg [\mathbf{A}]$, then equations (1) and (2) become :

$$K' = \frac{[AB']}{[\mathbf{B'}]([\mathbf{A}] - [AB'] - [AB''])} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

$$K'' = \frac{[AB'']}{[\mathbf{B''}]([\mathbf{A}] - [AB'] - [AB''])} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

from which :
$$[AB''] = \frac{K''[\mathbf{B''}][\mathbf{A}]}{K'[\mathbf{B'}] + K''[\mathbf{B''}] + 1} \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

For a wave-length at which the species A, B', B'', and AB' have negligible absorptions, but at which AB'' absorbs, let the extinction coefficient of AB'' be ε. If D_0 is the optical density at this wave-length for a solution containing A at a concentration $[\mathbf{A}]$, and B'' at a concentration $[\mathbf{B''}]$, but containing no B'; also if D_1 is the optical density of a solution containing A and B'' at concentrations $[\mathbf{A}]$ and $[\mathbf{B''}]$, and B' at a concentration $[\mathbf{B'}]$, then :

$$D_0 = \varepsilon \cdot [AB'']_0, \qquad D_1 = \varepsilon \cdot [AB'']_1$$

and
$$\frac{D_0}{D_1} = \frac{[AB'']_0}{[AB'']_1} = \frac{K'[\mathbf{B'}] + K''[\mathbf{B''}] + 1}{K''[\mathbf{B''}] + 1} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

whence
$$K' = \frac{D_0 - D_1}{D_1}\left(\frac{1 + [\mathbf{B''}]K''}{[\mathbf{B'}]}\right) \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

Thus if K'' is known, a value of K' may be found.

Experimental.—To determine the association constants for the interactions of benzene with *s*-trinitrobenzene and with chloranil, alkylanilines were made to compete with the benzene for the respective Lewis acid, the charge-transfer band of the former fulfilling the conditions of equations (6) and (7).

The optical densities were measured in *cyclo*hexane at the wave-length corresponding to the maximum absorption in the charge-transfer bands of the respective Lewis acid–alkylaniline complexes, and are shown in the Tables (p. 1204). The instrument used in all the determinations was a Unicam SP 600 spectrophotometer, equipped with 4-cm. cells. Materials have been purified by methods described previously (Foster and Hammick, *J.*, 1954, 2685).

Discussion.—The degree of association of benzene with *s*-trinitrobenzene has been determined by Lawrey and McConnell (*loc. cit.*), using a direct photometric method. They give a value for an association constant defined as $k = [ab]/[a]$ (b), where [ab] is the equilibrium concentration of the complex, [a] is the equilibrium concentration of *s*-trinitrobenzene, and (b) is the mole fraction of benzene in equilibrium. Their value of $k = 4\cdot02 \pm 0\cdot02$ for benzene–*s*-trinitrobenzene in *n*-heptane corresponds to an association constant expressed in l./mole of $0\cdot60 \pm 0\cdot03$. This is in fair agreement with the value obtained in the present work, namely, $0\cdot77 \pm 0\cdot12$ l./mole. However, it is known that there is an increase of about 15% in the value of the association constant for NN-dimethyl-aniline–*s*-trinitrobenzene on changing the solvent from *n*-heptane to *cyclo*hexane (Foster and Hammick, *loc. cit.*). If the effect of this change of solvent is comparable in benzene–*s*-trinitrobenzene interaction, then a value of $0\cdot70 \pm 0\cdot04$ l./mole for the association of benzene–*s*-trinitrobenzene in *cyclo*hexane would be expected from the results of Lawrey and McConnell.

The association constant for chloranil and benzene is less than for *s*-trinitrobenzene–benzene. This is also true of the corresponding N-alkylaniline complexes (K'' in Tables 1

and 2). However, the maxima of the charge-transfer bands measured are at longer wave-lengths in the chloranil complexes with N-alkylanilines than in the respective s-trinitro-benzene complexes (λ in Tables 1 and 2).

TABLE 1. *The association constant for benzene–s-trinitrobenzene in* cyclohexane. [A] = *ca.* 6 × 10⁻⁴M. Temp. 19° ± 1°.

Competing base (anilines)	B′ (M)	B″ (M)	D_0	D_1	K″ (l./mole) [1]	λ (mμ) [1]	K′ (l./mole)
N-Methyl-	0·614	0·478	0·114	0·0990	7·8	435	0·96
,, ...	0·920	0·478	0·114	0·0948	7·8	435	0·90
,, ...	1·23	0·478	0·114	0·0940	7·8	435	0·72
NN-Dimethyl-	0·581	0·242	0·0752	0·0660	9·5	475	0·69
,, ...	1·02	0·242	0·0752	0·0610	9·5	475	0·76
,, ...	1·46	0·242	0·0752	0·0562	9·5	475	0·81
N-Ethyl-	0·615	0·447	0·107	0·100	8·4	445	0·54
,, ...	0·942	0·447	0·107	0·0958	8·4	445	0·60
,, ...	1·23	0·447	0·107	0·0912	8·4	445	0·67
NN-Diethyl-	0·615	0·148	0·116	0·0938	6·5	500	0·76
,, ...	0·942	0·148	0·116	0·0848	6·5	500	0·77
,, ...	1·23	0·148	0·116	0·0765	6·5	500	0·82
NN-Di-n-butyl- ...	0·291	0·0655	0·0472	0·0412	7·4	510	0·74
,, ...	0·437	0·0655	0·0472	0·0360	7·4	510	1·06
,, ...	0·727	0·0655	0·0472	0·0335	7·4	510	0·84

Mean : $K' = 0.77 \pm 0.13$ l./mole.

[1] Foster and Hammick, *J.*, 1954, 2685.

TABLE 2. *The association constant for benzene–chloranil in* cyclohexane. [A] = *ca.* 6 × 10⁻⁴M. Temp. 19° ± 1°.

Competing base (anilines)	B′ (M)	B″ (M)	D_0	D_1	K″ (l./mole)	λ (mμ)	K′ (l./mole)
N-Methyl-	0·390	0·209	0·0762	0·0687	5·0	590	0·56
,, ...	0·587	0·209	0·0762	0·0652	5·0	590	0·58
,, ...	0·782	0·209	0·0762	0·0625	5·0	590	0·57
NN-Dimethyl-	0·415	0·263	0·136	0·127	5·4	635	0·41
,, ...	0·623	0·263	0·136	0·120	5·4	635	0·52
,, ...	0·831	0·263	0·136	0·113	5·4	635	0·57
NN-Diethyl-	0·348	0·190	0·0317	0·0287	4·1	710	0·48
,, ...	0·695	0·190	0·0317	0·0260	4·1	710	0·56
,, ...	1·044	0·190	0·0317	0·0247	4·1	710	0·52
N-Butyl-	0·348	0·240	0·0212	0·0200	6·4	590	0·47
,,	0·590	0·240	0·0212	0·0185	6·4	590	0·64
,, ...	0·695	0·240	0·0212	0·0175	6·4	590	0·71
NN-Di-n-butyl- ...	0·347	0·223	0·0225	0·0205	3·8	720	0·52
,, ...	0·522	0·223	0·0225	0·0195	3·8	720	0·60
,, ...	0·695	0·223	0·0225	0·0185	3·8	720	0·58

Mean : $K' = 0.56 \pm 0.07$ l./mole.

Mulliken (*J. Amer. Chem. Soc.*, 1950, **72**, 605; 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801) has expressed the ground state of charge-transfer complexes as :

$$\psi_N = a\psi(A,B) + b\psi(A^- - B^+) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $\psi(A,B)$ is a " no-bond " function involving such terms as van der Waals, multi-pole, and London forces : $\psi(A^- - B^+)$ is a dative function in which the base molecule B has donated an electron to the acceptor molecule A. The corresponding excited state is :

$$\psi_E = a^*\psi(A^- - B^+) - b^*\psi(A,B) \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Excitation is the transition $\psi_N \longrightarrow \psi_E$.

The energies of the ground states of the complexes are small compared with the energies of excitation. Therefore the energies of the excited states must mainly account for the wave-length maxima of the charge-transfer bands. In equation (9) the coefficient a^* is very much greater than b^* (*idem, locc. cit.*). Thus it is the dative function which mainly

determines the energy of the excited state, and consequently the wave-length maximum of the charge-transfer band. The results suggest that this function is larger in chloranil than in the corresponding *s*-trinitrobenzene complexes (*i.e.*, chloranil is the stronger Lewis acid).

The association constant, on the other hand, is a measure of the function ψ_N. Because *a* is very much greater than *b* in equation (8) (*idem, locc. cit.*; Landauer and McConnell, *loc. cit.*) the lower values for the association constants of the chloranil complexes must presumably be due to the effect of the no-bond function.

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