780. *Interaction of Polynitro-compounds with Aromatic Hydrocarbons and Bases. Part XI.* A New Method for determining the Association Constants for Certain Interactions between Nitro-compounds and Bases in Solution.*

By R. FOSTER, D. LL. HAMMICK, and (MISS) A. A. WARDLEY.

A new relation between the optical density *D* and the association constants of the coloured products of the reaction in solution between nitro-compounds and bases is developed. The relation is limited to cases where the absorption of the interactants does not significantly overlap that of the products. The value of *n* in the formula AB_n for the product of interaction is also readily obtained, and a check on the validity of the relation is made by a comparison of *n* for the interaction between *s*-trinitrobenzene and (1) diphenylamine, (2) dimethylamine. The compositions of the complexes, 1 : 1 and 1 : 4, respectively, are confirmed by the method of continuous variations (Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437).

THE extent of interaction between nitro-compounds and bases (amines and "generalised" bases such as aromatic hydrocarbons) has frequently been estimated from measurements of the intensity of the colour developed on mixing them in inert solvents. An inherent defect in the methods used to derive dissociation or association constants for the coloured complexes has been the impossibility of a direct determination of their extinction coefficients. Attempts have been made to overcome this difficulty by temperature variation, the assumption being that the extinction coefficients are not appreciably temperature-variant (Hammick and Young, *J.*, 1936, 1463; Hamilton and Hammick, *J.*, 1938, 1356; Hammick and Yule, *J.*, 1940, 1539). More recently, Edmonds and Birnbaum (*J. Amer. Chem. Soc.*, 1941, **63**, 1471), corrected by Amis (*ibid.*, 1952, **74**, 1340), Hildebrand, Benesi, and Mower (*ibid.*, 1950, **72**, 1017), Landauer and McConnell (*ibid.*, 1952, **74**, 1221), and Andrews and Keefer (*ibid.*, 4500), have obtained general expressions directly connecting the association constants with the extinction coefficients of the reactants and the optical densities of the products of the interaction. However, in systems where the reactants do not absorb at the same wave-lengths as the product, it is possible to derive a much simpler relation from which the association constant may be readily obtained.

For complex formation between a molecule of a substance A and a species of molecule B,

* Part X, *J.*, 1950, 1089.

involving an equilibrium in solution, we have $A + nB \rightleftharpoons AB_n$ (where AB_n is the complex). The association constant is defined as:

$$K = [AB_n]/[A][B]^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If A represents one species of molecule and *a* its initial concentration, B representing the second species of molecule and *b* its original concentration, and *c* the concentration of the complex, then equation (1) becomes:

$$K = c/(a - c)(b - c)^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If *b* is made very much larger than *a*, then *c* is small compared with *b* and $(b - c) \approx b$, whence equation (2) becomes:

$$K = c/(a - c)b^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If the optical density *D* of the solution containing the complex is measured at a wave-length at which the extinction coefficients of A and B are negligible, ε being the extinction coefficient of the complex at that wave-length, then assuming that only one species of molecule is present and bearing in mind that $c = D/\varepsilon$, we have by equation (3):

$$K = D/(a\varepsilon - D)b^n \text{ or } Ka\varepsilon - KD = D/b^n \quad . \quad . \quad . \quad . \quad . \quad (4)$$

A plot of D/b^n against *D* should be linear, the gradient being equal to $-K$, the intercept with the *x*-axis being $a\varepsilon$.

This relationship has been tested for the interaction of diphenylamine and *s*-trinitrobenzene in chloroform and also for the interaction of dimethylamine and *s*-trinitrobenzene in dioxan.

Experimental

All concentrations are expressed in mole/l., the association constants having the dimensions of $(l./mole)^n$.

Analytical Methods.—All solutions were made up by weight, except those of dimethylamine which were standardised by titration. The optical densities were measured by using a Beckman Quartz Spectrophotometer (model DU) with 10 mm. cells.

Materials.—*s-Trinitrobenzene.* This was recrystallised four times from alcohol; it had m. p. 122°.

Dimethylamine. Obtained by decomposing recrystallised dimethylamine hydrochloride with sodium hydroxide, the gas being subsequently dried by passage through a quick-lime tower and condensed in a trap cooled with "Drikold."

Diphenylamine. A specimen, m. p. 53°, twice recrystallised from alcohol was used.

Dioxan. Purified by the method described by Vogel, "A Textbook of Practical Organic Chemistry," Longmans, London, 1948, p. 175, it had n_D^{20} 1·4224. Hess and Frahm (*Ber.*, 1938, **71**, 2627) give n_D^{20} 1·42241.

Chloroform. This was washed six times with half its volume of water, dried ($CaCl_2$), and distilled; it had n_D^{20} 1·4457. Gorke, Koppe, and Staiger (*Ber.*, 1908, **41**, 1156) give n_D^{20} 1·4455.

Results

Diphenylamine and s-*Trinitrobenzene in Chloroform Solution.*—The optical densities *D* of a series of solutions were measured at 460 mμ at 19°. All the solutions were 0·00192M with respect to *s*-trinitrobenzene, the concentration of diphenylamine, *b*, ranging from 0·0413M to 0·4127M, in accordance with the conditions of equation (4). The wave-length (460 mμ) at which the measurements were made is that of maximum absorption of the complex; in this region both the components have negligible extinction coefficients.

Table 1.

$[NHPh_2]$ (*b*), mole/l.	*D*	D/b	D/b^2	$[NHPh_2]$ (*b*), mole/l.	*D*	D/b	D/b^2
0·4127	0·457	1·017	2·682	0·2063	0·250	1·212	5·875
0·3714	0·419	1·128	3·037	0·1650	0·204	1·236	7·491
0·3301	0·378	1·145	3·469	0·1238	0·155	1·252	10·11
0·2889	0·337	1·166	4·036	0·0825	0·106	1·281	15·53
0·2476	0·295	1·191	4·810				

The linearity of the plot of D/b against *D* as opposed to the plot of D/b^2 against *D* (Table 1) suggests that the complex is of the type AB rather than AB_2. The gradient gives an association constant of $0{\cdot}5_1$ l./mole for a 1 : 1 complex.

Because of the solubility of *s*-trinitrobenzene in chloroform it was possible to repeat the determination, varying the *s*-trinitrobenzene concentration (*b*), with the amine concentration constant (at 0·00243M) throughout a series of solutions. The results (Table 2) again indicate that the complex is 1 : 1, the plot of D/b against D being linear and that of D/b^2 against D non-linear. [In this latter case *a* refers to the base, in conformity with the symbols used in deriving equation (4).] From the gradient of the plot of D/b against D the association constant is $0{\cdot}4_9$ l./mole.

TABLE 2.

$[C_6H_3(NO_2)_3]$ (*b*), mole/l.	D	D/b	D/b^2	$[C_6H_3(NO_2)_3]$ (*b*), mole/l.	D	D/b	D/b^2
0·2792	0·496	1·776	6·361	0·1675	0·313	1·869	11·16
0·2513	0·452	1·799	7·159	0·1396	0·265	1·898	13·60
0·2234	0·406	1·817	8·159	0·1117	0·214	1·916	17·15
0·1954	0·359	1·837	9·401	0·0838	0·163	1·945	23·21

FIG. 1.

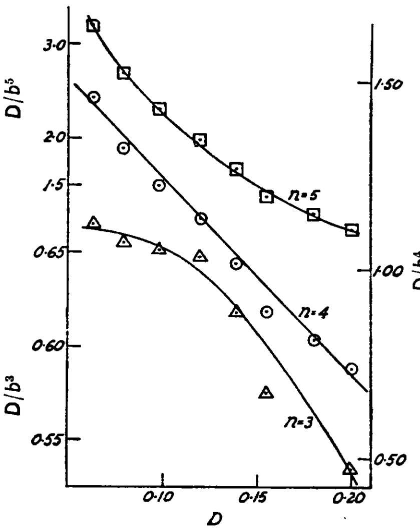
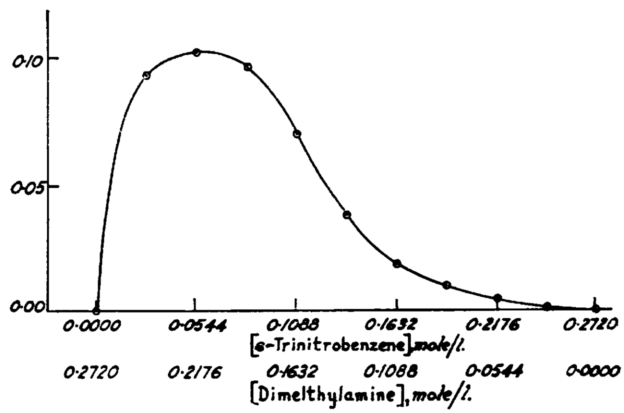


FIG. 2.



The conclusion that diphenylamine and *s*-trinitrobenzene form, at least mainly, a 1 : 1-complex in chloroform solution, is supported by the result of applying the method of continuous variations (Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437), to the system (see Table 3). However, the solid which crystallises from chloroform is a complex of 1 molecule of diphenylamine and 2 molecules of *s*-trinitrobenzene (Pfeiffer, "Organische Molekulverbindungen," Enke, Stuttgart, 1927, p. 243).

TABLE 3.

$C_6H_3(NO_2)_3]$, mole/l.	$[NHPh_2]$, mole/l.	D (460 mμ)	$[C_6H_3(NO_2)_3]$, mole/l.	$[NHPh_2]$, mole/l.	D (460 mμ)	$[C_6H_3(NO_2)_3]$, mole/l.	$[NHPh]_2$, mole/l.	D (460 mμ)
0·0315	0·0035	0·121	0·0210	0·0140	0·318	0·0105	0·0245	0·275
0·0280	0·0070	0·218	0·0175	0·0175	0·330	0·0070	0·0280	0·213
0·0245	0·0105	0·275	0·0140	0·0210	0·318	0·0035	0·0315	0·121

Dimethylamine and s-*Trinitrobenzene in Dioxan.*—The optical densities of a series of solutions were measured at 475 mμ and 19°. The solutions were 0·0018M with respect to *s*-trinitrobenzene, and from 0·456M to 0·721M with respect to dimethylamine. Plots of D/b^n against D, where $n = 1, 2, 3, \ldots 6$ (Table 4) suggest, by the linearity of the D/b^4 against D curve (Fig. 1), that the complex is 1 molecule of *s*-trinitrobenzene to 4 of dimethylamine. The gradient then

TABLE 4.

$[NHMe_2]$ (*b*), mole/l.	*D*	*D*/*b*	D/b^2	D/b^3	D/b^4	D/b^5	D/b^6
0·721	0·200	0·277	0·385	0·534	0·740	1·026	1·423
0·685	0·180	0·263	0·384	0·560	0·817	1·193	1·742
0·646	0·155	0·240	0·371	0·575	0·890	1·378	2·133
0·608	0·139	0·229	0·376	0·618	1·017	1·673	2·752
0·570	0·120	0·210	0·369	0·648	1·137	1·995	3·500
0·532	0·098	0·184	0·346	0·651	1·223	2·299	4·321
0·494	0·079	0·160	0·324	0·655	1·326	2·684	5·433
0·456	0·063	0·138	0·303	0·665	1·458	3·197	7·011

gives an association constant of 0·53 (mole/l.)$^{-4}$. The multiplicity of the complex is confirmed by the method of continuous variations (Fig. 2).

One of us (R. F.) acknowledges a grant from the Department of Scientific and Industrial Research.

THE DYSON PERRINS LABORATORY,
SOUTH PARKS ROAD, OXFORD.

[*Received, June* 24*th*, 1953.]