220. *Hexamethylbenzene Complexes of Polynitrobenzenes.*

By R. FOSTER.

The apparent association constants of hexamethylbenzene complexes with the three trinitrobenzenes and with 1,2,3,5-tetranitrobenzene in solution have been determined spectrophotometrically. The stabilities are in the order: 1,2,3- $<$ 1,2,4- $<$ 1,3,5-trinitrobenzene $<$ 1,2,3,5-tetranitrobenzene.

1,3,5-TRINITROBENZENE is a well-known electron acceptor in molecular complexes. By contrast, little has been reported of 1,2,3- or 1,2,4-trinitrobenzene or 1,2,3,5-tetranitrobenzene in this rôle. Sinomiya [1] has reported that the stabilities of electron donors with 1,2,3- or 1,2,4-trinitrobenzene are less than the corresponding complexes with the 1,3,5-isomer, but the results, derived from melting-point determinations, are only qualitative.

The stabilities of a series of complexes involving these polynitrobenzenes have now been measured. Hexamethylbenzene was chosen as the electron donor because of ease of purification, low ionisation potential, low chemical reactivity, and high molecular symmetry. As a measure of the stability of these complexes the apparent association constant (K) of the components in solution has been used, where:

$$K = [\text{complex}]/[\text{nitro-compound}][\text{hexamethylbenzene}] \quad . \quad . \quad . \quad (1)$$

All concentrations are expressed as molarities, K having the dimensions l. mole^{-1}. The values of K are termed apparent rather than true association constants as defined by eqn. (1) for it is possible that the optical absorption is enhanced by contact charge-transfer processes.[2] For the same reason the extinction coefficients of the complexes are also termed apparent.

The method [3] of determining K enables it to be evaluated directly from the slope of a linear plot of two functions and avoids the necessity of evaluating a very small intercept, as is the case in the method of Benesi and Hildebrand.[4]

The association constants have been determined for these complexes in cyclohexane and in carbon tetrachloride. The stabilities in chloroform are considerably lower, and only the 1,3,5-trinitrobenzene complex was measured in this solvent.

EXPERIMENTAL

Materials.—Solvents. " AnalaR " chloroform was washed ten times with water, dried ($CaCl_2$), then refluxed over, and finally distilled from, phosphorus pentoxide; it was used the same day. Carbon tetrachloride and cyclohexane were B.D.H. " Spectroscopic Grade " reagents.

1,2,3-*Trinitrobenzene.* Prepared by Holleman and Van Haeften's method [5] and recrystallised twice from ethanol and once from carbon tetrachloride it had m. p. 126°.

1,2,4-*Trinitrobenzene.* Similarly prepared and purified it had m. p. 60°.

1,3,5-*Trinitrobenzene.* Recrystallised four times from ethanol and twice from carbon tetrachloride it had m. p. 123°.

1,2,3,5-*Tetranitrobenzene.* Prepared by Borsche's method [6] and recrystallised twice from chloroform it had m. p. 126°.

Hexamethylbenzene. Samples were from three sources: Kodak Ltd., by the methylation of xylene,[7] and by Cullinane and Chard's method.[8] The product in each case was recrystallised five times from ethanol and had m. p. 164°.

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[1] Sinomiya, *Bull. Chem. Soc. Japan*, 1940, **15**, 137.
[2] Orgel and Mulliken, *J. Amer. Chem. Soc.*, 1957, **79**, 4839.
[3] Foster, Hammick, and Wardley, *J.*, 1953, 3817.
[4] Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.
[5] Holleman and Van Haeften, *Rec. Trav. chim.*, 1921, **40**, 67.
[6] Borsche, *Ber.*, 1923, **56**, 1942.
[7] Smith and Dobrovolny, *J. Amer. Chem. Soc.*, 1926, **48**, 1413.
[8] Cullinane and Chard, *J.*, 1945, 821.

Analytical Methods.—The method used has been previously described.[3]

Two primary solutions were made up gravimetrically, one containing only hexamethylbenzene as solute (*ca.* 0·2M), the other containing both hexamethylbenzene (*ca.* 0·2M) and the polynitrobenzene (10^{-3}—10^{-4}M). From these two a set of solutions was made, each having the same concentration ([*a*]) of polynitrobenzene but a different concentration ([*b*]) of hexamethylbenzene, so that in all the solutions [polynitrobenzene] $\ll$ [hexamethylbenzene]. The optical densities of these solutions were measured at several wavelengths at which the polynitrobenzene showed no, and the hexamethylbenzene little or no, absorption. All determinations were made with either, or both, a Unicam S.P. 500 quartz-prism spectrophotometer and an Optica CF4 grating spectrophotometer. The same 1-cm. quartz cell was used in all determinations, the comparisons were made against air, and light was always passed through the cell in the same direction. An arithmetical correction was made for the absorption by the cell and solvent. This avoided errors due to mismatched cells. The optical-density scales of both instruments were checked by using solutions of potassium chromate in 0·05M-sodium hydroxide.

All plots were straight lines and it was assumed that only 1 : 1 complexes were present. The data of one determination are given. The results of all the determinations are summarised in Table 2.

*The Apparent Association Constant of Hexamethylbenzene–*1,3,5-*Trinitrobenzene in Cyclohexane.*—From the two basic solutions, I (0·1801M with respect to hexamethylbenzene and 1·340 × 10^{-3}M with respect to 1,3,5-trinitrobenzene) and II (0·1839M with respect to hexamethylbenzene), the set of solutions indicated in Table 1 was obtained, each solution being made up to 10·00 ml. with pure solvent. From optical densities (D') measured at 420 mμ on a CF4 spectrophotometer (slit 0·02 mm.) and corrected for the absorption due to the hexamethylbenzene (ΔD), a plot of $D/[b]$ against D gives a line of negative gradient 13·5 l. mole^{-1}.

TABLE 1.

Soln. I (ml.)	Soln. II (ml.)	[*b*] (M)	[*a*] (M)	D'	ΔD	$D = (D' - \Delta D)$	$D/[b]$
5·00	5·00	0·1819	6·70 × 10^{-4}	0·866	0·006	0·860	4·73
,,	4·50	0·1727	,,	0·850	0·006	0·844	4·89
,,	4·00	0·1636	,,	0·836	0·005	0·831	5·08
,,	3·50	0·1544	,,	0·821	0·005	0·816	5·28
,,	3·00	0·1452	,,	0·806	0·005	0·801	5·52
,,	2·50	0·1360	,,	0·781	0·004	0·777	5·71
,,	2·00	0·1268	,,	0·772	0·004	0·768	6·06
,,	1·60	0·1194	,,	0·738	0·004	0·734	6·15
,,	1·20	0·1121	,,	0·729	0·004	0·725	6·47
,,	0·90	0·1065	,,	0·711	0·003	0·708	6·65
,,	0·60	0·1010	,,	0·696	0·003	0·693	6·86
,,	0·40	0·0974	,,	0·686	0·003	0·683	7·01
,,	0·00	0·0900	,,	0·666	0·003	0·663	7·37

TABLE 2. *Apparent association constants* (K), *wavelengths of maximum absorption* ($\lambda_{max.}$) *and apparent maximum molar extinction coefficients* ($\varepsilon_{max.}$) *of hexamethylbenzene complexes in carbon tetrachloride, cyclohexane* (*CXA*), *and chloroform, all at* 20°.

Tri- or tetra-nitro-	K (l. mole^{-1})			$\lambda_{max.}$ (mμ)			$\varepsilon_{max.}$ (l. mole^{-1} cm.$^{-1}$)			$K_{CXA}/$
benzene	CCl_4	CXA	$CHCl_3$	CCl_4	CXA	$CHCl_3$	CCl_4	CXA	$CHCl_3$	K_{CCl_4}
1,2,3-	1·5 ± 0·2	3·9 ± 0·3	—	350	—	—	1500 ± 200	—	—	2·6
1,2,4-	2·0 ± 0·2	5·0 ± 0·3	—	395	—	—	1200 ± 200	—	—	2·5
1,3,5-	5·7 ± 0·3	13·5 ± 0·4	0·76 ± 0·05	395	387	390	2500 ± 100	2500 ± 50	2600 ± 200	2·4
1,2,3,5-	9·4 ± 0·3	24·6 ± 0·5	—	425	420	—	2300 ± 50	2200 ± 50	—	2·6

DISCUSSION

The values of K, $\lambda_{max.}$, and $\varepsilon_{max.}$ of only two of the systems studied have been previously recorded. The results for hexamethylbenzene–1,3,5-trinitrobenzene in chloroform are in good agreement with those obtained by Castro, Andrews, and Keefer[9] (K = 0·80 l. mole^{-1}, $\lambda_{max.}$ = 390 mμ, $\varepsilon_{max.}$ = 2·4 × 10^3). However these constants for this complex in carbon

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[9] Castro, Andrews, and Keefer, *J. Amer. Chem. Soc.*, 1958, **80**, 2322.

tetrachloride are reported by Briegleb and Czekalla[10] to be $K = 7{\cdot}10$ l. mole^{-1}, $\lambda_{\text{max.}} =$ 395 mμ, $\varepsilon_{\text{max.}} = 2150$. Thus while there is reasonable agreement for $\lambda_{\text{max.}}$ and $\varepsilon_{\text{max.}}$, there is an inexplicable difference in the values of K. The value of K quoted in the present work, *viz.* $5{\cdot}7 \pm 0{\cdot}3$ l. mole^{-1}, has been obtained by using hexamethylbenzene from three sources (cf. Experimental section). Different samples of 1,3,5-trinitrobenzene have also been used, and measurements have been made on both spectrophotometers. The result is not affected by using either Benesi and Hildebrand's[4] or Briegleb and Czekalla's[11] method of evaluating K.

The values of $\varepsilon_{\text{max.}}$ and to a lesser extent those of $\lambda_{\text{max.}}$ are determined by the accuracy of the respective values of K (apart from their being "apparent values" because of the possibility of contact charge-transfer). This is particularly the case of the complexes with 1,2,3- and 1,2,4-trinitrobenzene, where large corrections, due to the absorption of the components, have to be applied to evaluate these constants. In this connection, because of the low solubility of the polynitrobenzenes alone in cyclohexane, it has not been possible to assign values $\varepsilon_{\text{max.}}$ and $\lambda_{\text{max.}}$ for these two complexes. To determine the absorption of the hexamethylbenzene–1,3,5-trinitrobenzene and –1,2,3,5-tetranitrobenzene complexes in cyclohexane, values of ε for the respective polynitrobenzenes in carbon tetrachloride have been used. This is justified by the smallness of the corrections which have to be applied.

The stabilities are in the expected order. Sinomiya's observation[1] that the complexes of 1,3,5-trinitrobenzene are more stable than those of 1,2,3- or 1,2,4-trinitrobenzene is confirmed. That the 1,2,3-isomer forms less stable complexes than 1,2,4-trinitrobenzene may be explained by the greater difficulty of intermolecular packing of the *vic*-substituted molecule with hexamethylbenzene, because of the particular orientation of the groups about the ring and also because of the conformation of the 2-nitro-group which cannot lie in the plane of the ring, thus increasing the steric impedance of the approach of the hexamethylbenzene molecule. This lack of planarity of at least one group with the plane of the ring will reduce the mesomeric effect of that group and so decrease the Lewis acidity of the molecule. This will decrease the stability of the complex and may also account for the high frequency of the charge-transfer band relative to that of the corresponding 1,2,4- and 1,3,5-trinitrobenzene complexes.

The change in solvent appears to have little effect on $\varepsilon_{\text{max.}}$ and only a small, but consistent, influence on $\lambda_{\text{max.}}$. The bands are 200—500 cm.$^{-1}$ lower in carbon tetrachloride than in cyclohexane. This is also true of the hexamethylbenzene–chloranil complex and the dimethylaniline–1,3,5-trinitrobenzene complex (Table 3).

TABLE 3. *Apparent association constants* (K), *wavelengths of maximum absorption* ($\lambda_{\text{max.}}$), *and apparent maximum molar extinction coefficients* ($\varepsilon_{\text{max.}}$) *of other molecular complexes in carbon tetrachloride and cyclohexane* (CXA).

	K (l. mole^{-1})		$\lambda_{\text{max.}}$ (mμ)		$\varepsilon_{\text{max.}}$ (l. mole^{-1} cm.$^{-1}$)			
	CCl_4	CXA	CCl_4	CXA	CCl_4	CXA	$K_{\text{CXA}}/K_{\text{CCl}_4}$	Ref.
Hexamethylbenzene–chloranil...	10·3	28·9	518	512	2550	—	2·8	*a, b*
Dimethylaniline–1,3,5-trinitrobenzene	3·4	9·5	484	475	1340	1300	2·8	*c*

[a] Foster, Hammick, and Placito, *J.*, 1956, 3881. [b] Foster, Hammick, and Parsons, *J.*, 1956, 555. [c] Foster and Hammick, *J.*, 1954, 2685.

The influence of solvent on K also appears to be consistent. The ratio of $K_{\text{cyclohexane}}/K_{\text{carbon tetrachloride}}$ is in all cases *ca.* 2·5. This includes the complexes in Table 3.

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QUEEN'S COLLEGE, DUNDEE, UNIVERSITY OF ST. ANDREWS. [*Received, August 5th*, 1959.]

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[10] Briegleb and Czekalla, *Z. Electrochem.*, 1955, **59**, 184.
[11] Briegleb and Czekalla, *Z. Electrochem.*, 1954, **58**, 249.