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THE UNRELIABILITY OF ASSOCIATION CONSTANTS OF ORGANIC CHARGE-TRANSFER COMPLEXES DERIVED FROM OPTICAL ABSORPTION SPECTRA—II[1]

APPARENT ISOTOPE EFFECTS SHOWN BY THE TETRACYANOETHYLENE COMPLEXES OF BENZENE AND BENZENE-d_6

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Abstract—An attempt to compare optical and thermodynamic properties of the charge-transfer complex benzene–tetracyanoethylene in cyclohexane with those of the corresponding benzene-d_6 complex using an optical method has been made. Differences have been noted in the calculated intensity of the intermolecular charge-transfer band, but not in its position. Although the differences in the measured values of association constant at various temperatures are apparently accounted for by differences in the entropy change of complex formation, it is suggested that a failure of Beer's law gives a better account of all these differences.

THE only study which appears to have been made of the effect of isotopic replacement on the properties of charge-transfer complexes is that of Halevi and Nussim,[2] who have compared the association constants for the toluene-(α)d_3 and m-xylene-(α)d_3 complexes of chloranil with those of the corresponding undeuterated hydrocarbons. The measurements were made at a single temperature. An indirect competitive method[3] was used to calculate the association constant, this method does not permit the molar extinction coefficient of the complex to be calculated.

The relatively strong electron-accepting properties of tetracyanoethylene[4] suggested that there might be measurable isotopic effects in the properties of the complex with benzene-d_6 compared with the undeuterated benzene complex. In the present work the relatively low energies of the intermolecular transitions of tetracyanoethylene complexes[4] have enabled the apparent association constants, K_{exp}, to be determined from direct measurements on the optical charge-transfer band. From the variation of K_{exp} with temperature within the range 6·3–33° the apparent enthalpy (ΔH) and apparent entropy (ΔS) changes have been calculated for an assumed equilibrium:

$$A + D \rightleftharpoons AD \tag{1}$$

where A is the electron acceptor, tetracyanoethylene, and D is the electron donor, benzene or benzene-d_6. From the values of K_{exp}, the apparent molar extinction coefficients (ϵ_{exp}) and the apparent shapes of the intermolecular charge-transfer absorption bands have been obtained for the two complexes. For comparison values

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[1] Part I. P. H. Emslie, R. Foster, C. A. Fyfe and I. Horman, *Tetrahedron* 21 (1965).

[2] E. A. Halevi and M. Nussim, *J. Chem. Soc.* 876 (1963).

[3] R. Foster, *Nature, Lond.* **173**, 222 (1954); J. M. Corkhill, R. Foster and D. LL. Hammick, *J. Chem. Soc.* 1202 (1955).

[4] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.* **80**, 2775 (1958).

of K_{exp} of the corresponding 1,3,5-trinitrobenzene complexes have been determined from the NMR shifts[5] of the protons in 1,3,5-trinitrobenzene in equilibrium mixtures. Absence of protons in tetracyanoethylene prevented its use in this latter type determination. The *optical* determination of the 1,3,5-trinitrobenzene complexes of benzene and benzene-d_6 was not attempted since it was known that K_{exp} for such systems is very small[6] and the experimental error would have made any comparisons difficult.

RESULTS

Values of $K_{exp} = [AD]/[A][D]$ for the complexes of tetracyanoethylene with benzene and benzene-d_6 have been evaluated from optical data by a method described previously.[7] The results of the determinations are summarized in Table 1. The spectrum due to the complex alone has been calculated for each of the two complexes (Fig. 1). Values of K for the corresponding complexes of 1,3,5-trinitrobenzene using the NMR method[5] are given in Table 2.

TABLE 1. APPARENT THERMODYNAMIC AND SPECTROSCOPIC VALUES FOR THE COMPLEXES TETRACYANOETHYLENE–BENZENE AND TETRACYANOETHYLENE–BENZENE-d_6 IN CYCLOHEXANE

Donor	Temp °C	K_{exp} (l.mol.$^{-1}$)	ϵ_{exp} ($\times 10^{-3}$)	ΔH kcal.mol.$^{-1}$	TΔS kcal.mol^{-1}	ΔS e.u.	$K_{exp}\,\epsilon$ ($\times 10^{-3}$)
C_6H_6	6·3	$2{\cdot}7_8$	$1{\cdot}8_2$		$3{\cdot}0_5$	$10{\cdot}_9$	5·07
	22·0	$2{\cdot}0_0$	$1{\cdot}6_9$		$3{\cdot}2_1$	$10{\cdot}_9$	3·38
	22·0	$2{\cdot}0_6$	$1{\cdot}6_0$	$-3{\cdot}6_1$	$3{\cdot}1_9$	$10{\cdot}_8$	3·30
	32·9	$1{\cdot}6_5$	$1{\cdot}6_9$		$3{\cdot}3_1$	$10{\cdot}_8$	2·79
C_6D_6	6·8	$2{\cdot}1_2$	$2{\cdot}3_7$		$3{\cdot}2_4$	$11{\cdot}_6$	5·02
	22·0	$1{\cdot}5_0$	$2{\cdot}2_4$	$-3{\cdot}6_6$	$3{\cdot}4_2$	$11{\cdot}_6$	3·36
	22·0	$1{\cdot}4_6$	$2{\cdot}2_3$		$3{\cdot}4_4$	$11{\cdot}_6$	3·26
	33·0	$1{\cdot}2_2$	2·2		$3{\cdot}5_8$	$11{\cdot}_6$	2·80

DISCUSSION

In the first part of the discussion it is assumed that the determined values of the association constant (K_{exp}) represent the equilibrium constant for the interaction expressed in Eq. 1. The apparent secondary isotope effect observed, $K_{exp}(D)/K_{exp}(H) = 0{\cdot}73$ at 22° is significantly greater than that observed[2] for the chloranil complexes of toluene-(α)d_3 where $K_{exp}(D)/K_{exp}(H) = 0{\cdot}93$ and for the corresponding *m*-xylene-(α)d_3 where $K_{exp}(D)/K_{exp}(H) = 0{\cdot}92$. If the apparent free energy of formation of the complex is a measure of the Lewis base strength of the electron donor molecule then in all these systems the deuterated hydrocarbon is the weaker base.

Several workers[8] have suggested that electron release is easier from C—D than from C—H. This may in part be due to the greater repulsion between non-bonded D . . . D atoms in molecules containing CD_2 or CD_3 groups compared with repulsion

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[5] R. Foster and C. A. Fyfe, *Trans. Faraday Soc.* **61**, 1626 (1965).

[6] D. M. G. Lawrey and H. McConnell, *J. Amer. Chem. Soc.* **74**, 6175 (1952).

[7] R. Foster, D. LL. Hammick and A. A. Wardley, *J. Chem. Soc.* 3817 (1953).

[8] E. A. Halevi, *Tetrahedron* **1**, 174 (1957); E. S. Lewis, *Ibid.* **5**, 143 (1959); V. J. Shiner, *Ibid.* **5**, 243 (1959); E. A. Halevi, M. Nussim and A. Ron, *J. Chem. Soc.* 866 (1963); and Refs therein.

between H. . . H atoms in corresponding undeuterated molecules.[9] Nevertheless the observation that C_6D_5OH is a weaker Bronsted acid than phenol,[10] that 2,4,6-trideuteroaniline is a stronger nucleophile than aniline,[11] and that deuterocarbonium ions are more stable than the undeuterated species[12] substantiates the thesis that the C—D bond is polarized in the sense of a +I substituent. This should result in benzene-d_6

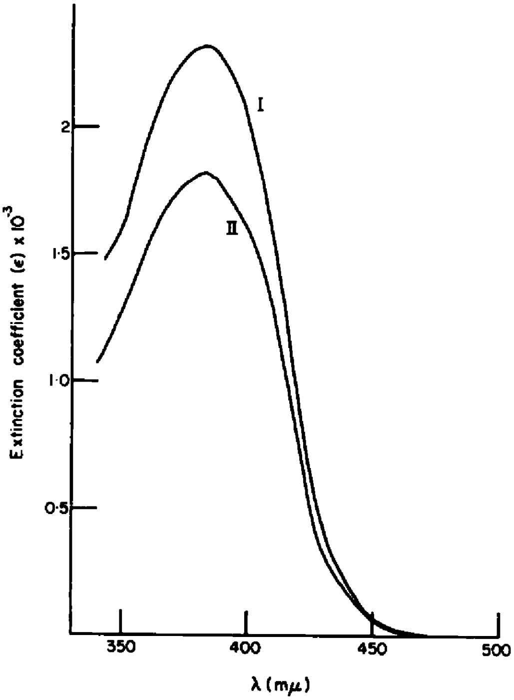

FIG. 1. Calculated absorption spectra of: (I) tetracyanoethylene-benzene-d_6; II tetracyanoethylene-benzene complexes in cyclohexane, based on the values of apparent association constants (K_{exp}).

TABLE 2. ASSOCIATION CONSTANTS (K_c) FOR THE COMPLEXES OF BENZENE AND BENZENE-d_6 WITH 1,3,5-TRINITROBENZENE IN CARBON TETRACHLORIDE AT 33·5° EVALUATED FROM THE NUCLEAR MAGNETIC PROTON SHIFTS OF THE ACCEPTOR MOLECULE; Δ_0 = CALCULATED SHIFT FOR PURE COMPLEX AND Δ_{max} = MAXIMUM OBSERVED SHIFT FOR THESE PROTONS (at 60 mc/s)

Donor	Δ_{max} c/s	Δ_0 c/s	K_c l.mole⁻¹
C_6H_6	46·8	75·5	$0{\cdot}31_8 \pm 0{\cdot}015$
C_6D_6	47·0	75·5	$0{\cdot}31_6 \pm 0{\cdot}015$

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[9] R. Pauncz and E. A. Halevi, *J. Chem. Soc.* 1967 (1959); E. A. Halevi and R. Pauncz, *Ibid.* 1974 (1959); A. Ron, E. A. Halevi and R. Pauncz, *Ibid.* 630 (1960).

[10] H. S. Klein and A. Streitweiser, Jr., *Chem. & Ind.* 180 (1961).

[11] J. J. Elliott and S. F. Mason, *Chem. & Ind.* 488 (1959).

[12] A. J. Kresge, K. N. Rao and N. N. Lichtin, *Chem. & Ind.* 53 (1961).

being a stronger Lewis base (electron donor) than benzene. The observed converse in the case of the chloranil complexes was explained[2] in terms of over-compensation by the diminished hyperconjugation in changing the substituent from —CH_3 to —CD_3. Obviously such an explanation cannot be applied to the benzene complexes.

For the complex tetracyanoethylene–benzene there appears to be no difference in the enthalpy of formation of the complex after isotopic replacement in the benzene moiety. The absence of an isotope effect is also shown in the energy of excitation of the complex ($\nu_{max} = 26{,}300\ cm^{-1}$), and in the virtually identical ionization potentials of benzene-d_6 and benzene.[13]

We suggest that *all* the apparent differences between the two complexes arise from deviations from Beer's law by the species (AD) as has been described in the preceding paper.[1] In particular the deviations from Beer's law for tetracyanoethylene–benzene in solutions of cyclohexane containing varying amounts of benzene are different from the deviations for tetracyanoethylene–benzene-d_6 in solutions of cyclohexane containing varying amounts of benzene-d_6. It has been shown[1] that deviations ~5% from Beer's law in absorptions of the complex species (AD) in 0·2M solutions of donor can easily give rise to differences in K_{exp} of ~20%.

Although such deviations affect K_{exp} and ϵ_{exp} separately, it has been shown[1] that the product $K_{exp} \cdot \epsilon_{exp}$ should not be affected. Comparison of this product for the two complexes shows them to be equal at a given temperature (Table 1).

A theory of solvation of the various species in Eq. 1 described by Murrell *et al.*[14] also results in the conclusion that the product $K_{exp} \cdot \epsilon_{exp}$ will be identical with that which would obtain if the system could be represented simply by Eq. 1 and the Beer's law be obeyed.[1] However in the system similar to the one under discussion, namely the 1,3,5-trinitrobenzene complexes of benzene and benzene-d_6 in carbon tetrachloride, no isotope effect is detectable when a sensitive *non*-optical NMR method[5] is used (Table 2). This observation supports the thesis[1] that the differences in K_{exp} and in ϵ_{exp} between the two isotopically different complexes determined by the optical method are due to deficiencies in using optical absorption as a direct measure of [AD], rather than that Eq. 1 is not tenable, as is required by the solvation theory. If this latter condition were to obtain, then it would also apply to non-optical determinations. Such does not appear to be the case (Table 2).

EXPERIMENTAL

Materials. Cyclohexane, B.D.H. "Pure for spectroscopy" was used without further treatment. CCl_4 B.D.H. "Special for spectroscopy" was used without further treatment. B.D.H. Benzene "pure for mol. wt. determinations" was used in some experiments. In other determinations, reagent grade material, dried over Na, and fractionated, was used. This latter showed no impurities when analysed by GLC. Ciba "99·9% pure" benzene-d_6 was used without further treatment. Tetracyanoethylene[15] was recrystallized from chlorobenzene, and thrice sublimed, m.p. 198°. 1,3,5-Trinitrobenzene recrystallized once from EtOH and twice from CCl_4, m.p. 123°.

Analytical. The method used for determining K_{exp} optically is a variant of the Benesi–Hildebrand[16] method; it has been described previously.[7] For a series of solutions of constant acceptor concentration [A] and varying donor concentration [D], where [D] $\gg$ [A], a plot of d/[D] against d (where d is

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[13] P. G. Wilkinson, *J. Chem. Phys.* **24**, 917 (1956); *Canad. J. Phys.* **34**, 596 (1956).

[14] S. Carter, J. N. Murrell and E. J. Rosch, *J. Chem. Soc.* 2048 (1965).

[15] T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Englehardt, R. E. Heckert, E. L. Little, E. G. McGreer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, *J. Amer. Chem. Soc.* **80**, 2775 (1958).

[16] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.* **71**, 2703 (1949).

the optical density for a 1 cm path length due to the charge-transfer complex) should be linear with gradient equal to $-K_{exp}$. All solutions were made up at 20°, corrections for solvent expansion or contraction were made using an expansion coefficient $\alpha = 0{\cdot}00120$ for cyclohexane.[17] Optical densities were measured using an Optica CF4 spectrophotometer. Typical plots are shown in Fig. 2. The method of evaluation of K_c using NMR shifts is described elsewhere.[6] A Perkin–Elmer R. 10 Spectrometer operating at 60 mc/s, 33·5° was used for these latter determinations.

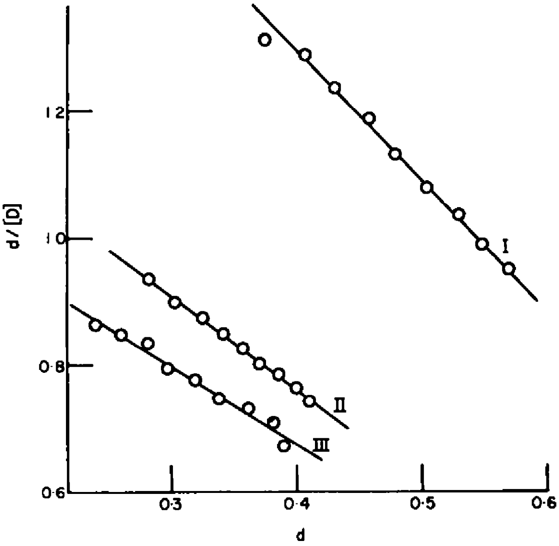

FIG. 2. Plots of d/[D] against [D] for solutions of benzene-d_6-tetracyanoethylene in cyclohexane: (I) $[A] = 4{\cdot}294 \times 10^{-4}$ M, $[D] = 0{\cdot}6008 - 0{\cdot}2875$ M, temp = 6·8°; (II) $[A] = 4{\cdot}043 \times 10^{-4}$ M, $[D] = 0{\cdot}5540 - 0{\cdot}3029$ M, temp = 22°; (III) $[A] = 4{\cdot}162 \times 10^{-4}$ M. $[D] = 0{\cdot}5822 - 0{\cdot}2786$ M, temp = 33°; all optical densities measured at 380 mμ.

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[17] G. Steensholt, *Phil. Mag.* 37, 357 (1946).