

Interaction between Phenol and Electron Donors in Cyclohexane and Carbon Tetrachloride

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Association constants, K_a , for the process phenol + electron donor \rightleftharpoons complex have been determined from absorbance measurements at a predetermined wavelength in the u.v. region for a series of solutions of phenol in cyclohexane-donor and carbon tetrachloride-donor mixtures of varying composition. Electron donors used are classified as ether- or alcohol-type and consist of 1,2-dimethoxyethane, tetrahydrofuran, dioxan, diethyl ether, di-isopropyl ether, di-n-butyl ether, methanol, ethanol, n-butanol, propan-2-ol, isoamyl alcohol, t-butyl alcohol, and dimethylformamide. It is found that (i) K_a is greater in cyclohexane than in carbon tetrachloride solution, (ii) K_a increases with increase in donor E_T value, and in the case of the ethers with $\Delta\nu_D$ the shift in the O-D stretching frequency of methan[²H]ol, defined as ν_D (benzene) - ν_D (ether), and (iii) variation in K_a arises principally from changes in the standard entropy of association, ΔS^\ominus .

In a recent study of the influence of solvent on the adsorption affinity between phenol and silica gel,¹ the logarithm of the affinity was found to decrease almost linearly with increasing solvent E_T value.²

This paper describes a related study involving the determination of phenol-electron donor association constants, K_a , in cyclohexane and carbon tetrachloride solution. The electron donors consisted of 1,2-dimethoxyethane, tetrahydrofuran, dioxan, diethyl ether,

Nagakura *et al.*,³ and then processed by the method of Rose and Drago⁴ to give values with standard deviation of the order of 5% (Table 1).

Additionally, shifts in the OH stretching frequency of phenol on hydrogen bonding to the donor molecules in carbon tetrachloride were observed using a Unicam SP 700 recording spectrophotometer. These shifts were used in the evaluation of changes in the standard enthalpy and entropy of complexation (Table 2).

TABLE I

Association constants for phenol-electron donor complexes, and E_T and $\Delta\nu_D$ values for the electron donors

Electron donors	$E_T/kJ\ mol^{-1}$	μ_D^*	$\Delta\nu_D/cm^{-1}$	$K_a/dm^3\ mol^{-1}$ at 298 K	
				C_6H_{12}	CCl_4
Dimethylformamide	183.3	3.82	107		42.5 ± 1.2
1,2-Dimethoxyethane	159.8	2.1	71	26.3 ± 1.1	14.0 ± 0.3
Tetrahydrofuran	156.5	1.75	90	23.1 ± 1.1	13.4 ± 0.2
Dioxan	150.6	0	77	15.1 ± 0.2	8.5 ± 0.1
Diethyl ether	144.8	1.26	78	11.4 ± 0.3	6.1 ± 0.3
Di-isopropyl ether	142.3	1.26	75	12.9 ± 0.4	8.2 ± 0.5
Di-n-butyl ether	139.7	1.26		7.9 ± 0.6	5.2 ± 0.2
Methanol	232.2	1.66			11.0 ± 0.4
Ethanol	217.2	1.66		27.8 ± 1.6	9.5 ± 0.3
n-Butanol	210.0	1.66		25.8 ± 0.3	8.6 ± 0.4
Propan-2-ol	203.3	1.67		24.2 ± 0.3	7.5 ± 0.4
Isoamyl alcohol	196.6			21.6 ± 0.5	6.8 ± 0.5
t-Butyl alcohol	191.2	1.66		27.3 ± 1.0	10.2 ± 0.5

* Values taken from J. W. Smith, 'Electric Dipole Moments,' Butterworths, London, 1955.

di-isopropyl ether, di-n-butyl ether, methanol, ethanol, n-butanol, propan-2-ol, isoamyl alcohol, t-butyl alcohol, and dimethylformamide and were purified by standard methods as were cyclohexane, carbon tetrachloride, and phenol.

The association constants for the process phenol (A) + electron-donor (D) \rightleftharpoons complex (C) were determined from absorbance measurements at a predetermined wavelength in the u.v. region for a series of solutions of phenol in cyclohexane-donor and carbon tetrachloride-donor mixtures of varying composition. Approximate values of K_a were first calculated by the method used by

¹ K. M. C. Davis, J. A. Deuchar, and D. A. Ibbitson, *J.C.S. Faraday I*, 1973, 117.

² K. Dimroth and C. Reichardt, Palette No. 11, Sandoz A.G., Basel, 1962, p. 28; K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Annalen*, 1963, 661, 1.

DISCUSSION

Many criticisms of the evaluation of association constants of charge-transfer complexes from optical spectrophotometric measurements have been made in recent years. It is appropriate to consider these criticisms in relation to the more strongly hydrogen-bonded complexes studied in this work. Person⁵ has argued that the most accurate values for formation constants of a complex are obtained when $e_{CC} \sim e_{CA}$, the symbols having their usual significance. For complexes measured by the Benesi-Hildebrand method or one of its many variations, this

³ S. Nagakura and H. Baba, *J. Amer. Chem. Soc.*, 1952, 74, 5693; S. Nagakura, *ibid.*, 1954, 76, 3070; S. Nagakura and M. Souterman, *J. Chem. Phys.*, 1957, 26, 881.

⁴ N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, 1959, 81, 6138.

⁵ W. B. Person, *J. Amer. Chem. Soc.*, 1965, 87, 157.

condition requires that the donor concentration in the most concentrated solution must be greater than 0.1 ($1/K_c$). In the present study this condition is readily

TABLE 2

Enthalpy, entropy changes, and OH stretching frequency shifts on complexation of phenol

	$\Delta\nu(\text{OH})/\text{cm}^{-1}$	$-\Delta H^\circ/\text{kJ mol}^{-1}$	$-\Delta S^\circ/\text{J K}^{-1} \text{mol}^{-1}$
Dimethylformamide	293	25.1	53.0
1,2-Dimethoxyethane	244	23.0	55.3
Dioxan	242	22.8	58.7
Tetrahydrofuran	290	25.0	62.4
Diethyl ether	280	24.5	67.1
Di-isopropyl ether	297	24.8	67.4
Di-n-butyl ether	285	25.3	69.4
Methanol	214	21.5	52.0
Ethanol	229	22.2	55.7
n-Butanol	233	22.4	57.3
Propan-2-ol	236	22.5	58.7
Isoamyl alcohol	236	22.5	60.0
t-Butyl alcohol	253	23.3	58.4

satisfied with K_c values ranging from 5 to 28 $\text{dm}^3 \text{mol}^{-1}$ and c_D values from 0.1 to 0.7M.

The effect of various concentration scales on the evaluation of ϵ_c has been considered by Scott⁶ and by Trotter and Hanna.⁷ In this work because of the magnitude of the values of K_c recorded, the choice of concentration scale is not critical.

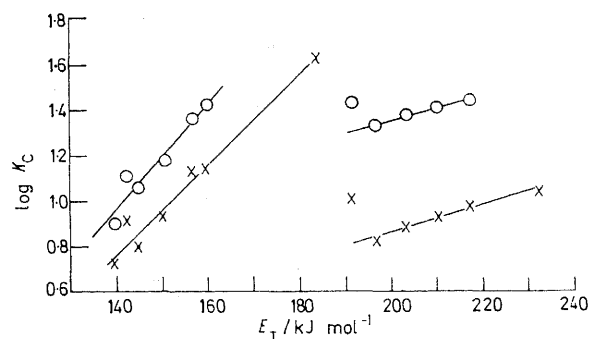
Again, for a given system, optical methods yield values of K_c and ϵ_c which are often dependent on the concentration conditions.⁸ Above the ratio $c_D/c_A = 10/1$ however, changes in K_c are less than the experimental error in this work, the ratio is exceeded with all systems.

It has been suggested^{8b} that deviations from Beer's law of the optical absorption characteristic of the complexes may result in anomalies in the evaluation of K_c . In this connection it is interesting to note that Epley and Drago⁹ have determined the enthalpies of reaction and association constants of complexation of phenol with several Lewis bases in carbon tetrachloride by a calorimetric method. A value for K_c of $13.5 \pm 0.5 \text{ dm}^3 \text{mol}^{-1}$ is reported for the system phenol-tetrahydrofuran which is in good agreement with the value of 13.4 ± 0.2 obtained in this study.

From the data in Table 1 it is noted that K_c , as anticipated, is greater in cyclohexane than in carbon tetrachloride for all the electron donors used in this study.

In the case of charge-transfer complexes of a given acceptor with a series of electron donors, K_c values have been related to Taft σ^* constants,¹⁰ Hammett σ values,¹¹ and donor basicities.¹² In the present investigation $\log K_c$ is seen to increase with increase in E_T value of the

donor, and in the case of the ether-type donors, with the i.r. frequency shift $\Delta\nu_D$ of the O-D vibrational band of methan[²H]ol¹³ (Table 1). The plots in the Figure of $\log K_c$ against E_T are interesting in that the slopes appropriate to the ether-type donors are much greater than those for the alcohol-type donors. Speculating on the reason for this it is first of all pertinent to comment on the relative magnitudes of the E_T values of the two types of donor. Pyridinium *N*-phenolate is a dye with a predominantly polar ground state in which oxygen and nitrogen atoms within the molecule have negative and positive charge respectively. Excitation is associated with an intramolecular charge-transfer giving rise to a comparatively less polar excited state. Enhanced solvent stabilisation of the ground state then leads to a hypsochromic shift which increases with increase in solvent polarity. In this connection it is noted that the dipole moments of the ether-type donors broadly parallel the E_T values. In the case of dioxan, whereas the resultant moment of the molecule is zero, two equal and opposing group moments exist, the two oxygen atoms being



Plots of $\log K_c$ against E_T values of electron-donors: O, cyclohexane; X, carbon tetrachloride

fractionally negatively charged. That the E_T values of the alcohol-type donors are greater than those of the ether-type is due presumably to additional ground state stabilisation of the dye molecule by hydrogen bonding. Now, let us consider the relationship between $\log K_c$ and E_T . It is experimentally observable that electronic transitions are shifted to the blue when the chromophore is involved in hydrogen bonding as proton acceptor, and shifted to the red when serving as proton donor. In the present study, the OH group of phenol is the chromophore and hydrogen bonding to all the electron donors used produces the anticipated bathochromic shifts. The tendency for hydrogen bonding to occur (ΔG°) between the ether-type donors and phenol may, in general, be expected to increase with increase in polarity of the donor molecule. This expectation is realised and the wide

⁶ R. L. Scott, Proc. Internat. Conference on Co-ordination Compounds, Amsterdam, 1955, p. 265; *Rec. Trav. chim.*, 1956, **75**, 787.

⁷ P. J. Trotter and M. W. Hanna, *J. Amer. Chem. Soc.*, 1966, **88**, 3724.

⁸ (a) G. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.*, 1957, **79**, 76; (b) P. H. Emslie, R. Fosh, C. A. Fyfe, and I. Horman, *Tetrahedron*, 1965, **21**, 2843; (c) P. H. Emslie, R. Foster, and R. Pickles, *Canad. J. Chem.*, 1966, **44**, 9.

⁹ T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, 1967, **89**, 5770.

¹⁰ W. B. Person, W. C. Golton, and A. I. Popor, *J. Amer. Chem. Soc.*, 1963, **85**, 891.

¹¹ R. L. Carlson and R. S. Drago, *J. Amer. Chem. Soc.*, 1963, **85**, 505.

¹² R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, 1965, **61**, 1626; N. M. D. Brown, R. Foster, and C. A. Fyfe, *J. Chem. Soc. (B)*, 1967, 406.

¹³ T. Kagiya, T. Sumida, and T. Inoue, *Bull. Chem. Soc. Japan*, 1968, **41**, 767.

variation in dipole moment, μ , of the electron donors could explain the pronounced slope of the plot of $\log K_c$ against E_T . In the case of the alcohol-type donors, the variation of K_c may be, as before, a consequence of the change in tendency of the hydrogen-bonding process to occur, but the slope of the plot of K_c against E_T is much smaller. Factors which may contribute to this are (1) the approximate constancy of the dipole moments of the alcohols and (2) variations in steric hindrance to the interactions between dye and alcohol on the one hand, and phenol and alcohol on the other.

To assess the relative importance of the contributions of the enthalpy and entropy changes to the free energy change on complexation, it is necessary to study the variation of association constant with temperature or to evaluate enthalpy changes directly by calorimetric methods. Because of inconsistencies of reported values of equilibrium constants and enthalpies for a multitude of proton donor-acceptor complexes¹⁴ obtained by the use of several spectroscopic techniques, the latter method is becoming increasingly favoured. Epley and Drago⁹ have determined the enthalpies of reaction of phenol with several Lewis bases in carbon tetrachloride solution by a calorimetric procedure, and have used these values to re-examine the sometimes disputed relationships between enthalpy of reaction and the change in the O-H stretching frequency. These authors conclude that

their calorimetric data does indicate considerable error in the spectrophotometric evaluation of ΔH° for the weaker acid-base adducts. They find that ΔH° is linearly related to $\Delta\nu(\text{O-H})$ by equation (1) in which ΔH° is

$$-\Delta H^\circ = (0.046\Delta\nu + 11.66) \pm 0.08 \quad (1)$$

expressed in kJ mol^{-1} and $\Delta\nu$ in cm^{-1} .

In consequence of the above it was decided to evaluate the enthalpy changes on complexation for the systems studied in this work by application of equation (1), and the corresponding ΔS° values by the use of equation (2).

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

Frequency shifts, $\Delta\nu(\text{O-H})$, and values of ΔH° and ΔS° are recorded in Table 2. It is seen that the ΔH° values show a maximum variation of only *ca.* 3 kJ mol^{-1} over the whole range of phenol-electron donor systems studied. It thus appears that the variation in K_c and hence in ΔG° arises principally from changes in the standard entropy of association, ΔS° .

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¹⁴ S. Singh, A. S. N. Murthy, and C. N. Rao, *Trans. Faraday Soc.*, 1966, **62**, 1056 and references cited therein.