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THE RELATIONSHIP BETWEEN THE ASSOCIATION CONSTANTS OF PHENOL WITH ETHERS AND THOSE OF TRICHLOROACETIC ACID WITH ETHERS

ESTIMATION OF ASSOCIATION CONSTANTS OF TRICHLOROACETIC ACID WITH OXIRANE

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Abstract—The association constants, K_p, of phenol with ethers (tetrahydrofuran, tetrahydropyran, dibutyl ether, dipropyl ether, 1,4-dioxane) and those, K_T, of trichloroacetic acid with ethers were measured in CCl_4 over a temperature range 20°–40° using near IR spectra. A linear relationship between K_p and K_T was found. On the basis of this relationship the association constants of trichloroacetic acid with propylene oxide were estimated from those of phenol with propylene oxide.

Oxirane has considerable ring-opening reactivity due to both the ring strain and the basicity of the O atom in the ring. There are many reports on the ring-opening of oxirane with either nucleophiles or electrophiles.[1] A kinetic study is useful in the investigation of the ring-opening of oxirane. Kinetic studies have been carried out in the protonic-acid catalyzed ring-opening of oxirane in which there is known to be an equilibrium between the O atom in the ring and the protonic acid followed by the ring-opening of the protonated oxirane. In such a reaction a ring cleavage is a rate-determining step, but it has not been clarified whether the protonated oxirane opens by bimolecular attack of a gegen ion on the ring (S_N2 type) or unimolecular via a carbonium ion intermediate (S_N1 type).[2] In each case the overall rate constant of the ring-opening contains the above equilibrium constant, evaluation of which is believed necessary to clarify the mechanism. However, it is impossible to measure directly the association constant of a strong acid with oxirane owing to the great reactivity of oxirane.

The purpose of this paper is to estimate indirectly the association constant of a strong carboxylic acid with oxirane on the basis of the relationship between the association constants of phenol with ethers and those of the strong carboxylic acid with ethers. Trichloroacetic acid (TCA) was used as the strong acid.

EXPERIMENTAL

Reagents. All ethers were commercial products and purified by the usual method just before use. Phenol was distilled, transferred into a preweighed 50-ml volumetric flask and dried in a desiccator over P_2O_5 until a constant weight was reached. TCA was a commercial product, distilled twice under reduced pressure, and dried in a disiccator over H_2SO_4 in the same manner as the phenol. CCl_4 was purified according to the method of Yerger[3] and distilled over P_2O_5 just before use.

Measurements of the association constants of phenol with ethers. All spectral measurements were made in CCl_4 under flushing dry air by use of a Hitachi Model 230 double beam IR spectrophotometer with water-jacketed cells of path-length 20 mm. In all cases the spectral slit widths were controlled automatically within 5% of the half-intensity band widths and *ca.* 1.0 cm^{-1} in the neighborhood of 3600 cm^{-1}. The scanning speeds were 24 cm^{-1}/min. The temp. of the cell could be varied by passing through the jacket water from a thermostat and was kept within ±0.2°. Both cells were filled with the soln without phenol and a base line spectrum (100% transmittance curve) was taken. The soln in the sample beam was then replaced by the soln containing phenol and the spectrum of free phenol in *ca.* 3608 cm^{-1} was measured. In all cases, after the temp. had become constant, at least 15 min were allowed for equilibration. Measurements were made at five temps., 20°, 25°, 30°, 35° and 40°. At least two photometric recordings were made at each temp. For each phenol–ether system, more than two solns were measured. The concentration of free phenol was calculated from the extinction coefficient for the monomeric O–H stretching vibration peak in *ca.* 3608 cm^{-1}, on the basis of the temp. dependence of molecular extinction coefficients of phenol which were measured independently. The association constants, K_p, were calculated from eqn (1).

$$K_p = \frac{[AB]_t}{[A]_t[B]_t} = \frac{[A_0]_t - [A]_t}{[A]_t\{[B_0]_t - [A_0]_t + [A]_t\}} \qquad (1)$$

where $[AB)_t$, $[A]_t$ and $[B]_t$ are the concn of phenol–ether 1:1 complex, free phenol and ether, respectively, and $[A_0]_t$ and $[B_0]_t$ are the initial formal concn of phenol and ether corrected for density changes (eqn 2), respectively.

$$[A_0]_t = \frac{\rho_t}{\rho_s}[A_0]_s, \quad [B_0]_t = \frac{\rho_t}{\rho_s}[B_0]_s \qquad (2)$$

where ρ is the density of the soln and subscript t and s express the temp. at which measurements were made and one at which the soln was prepared, respectively. The density of the soln was calculated on the basis of the assumption that the CCl_4-ether solution is ideal.

Measurements of IR spectra in the trichloroacetic acid-ethers systems. The associations of the TCA–ethers were measured by the same apparatus as in the phenol–ethers system. Carboxylic acids are well known to exist as equilibrium mixtures of monomer and dimer molecules even in dilute solns in nonpolar solvents. In such a case the plot of the integrated absorption intensity of TCA vs its formal concn does not obey the Lambert–Beer law. Then the integrated intensity of the monomer band was calculated by the method of Wenograd and Spurr[4] in the following way.

The integrated intensity, A, of a band is given by eqn (3) according to the method of Ramsay.[5]

$$A = \frac{1}{Cl}\int \ln\left(\frac{I_0}{I}\right) d\nu = \frac{K}{Cl}\ln\left(\frac{I_0}{I}\right)_{\nu_{max}} \Delta\nu_{1/2} \tag{3}$$

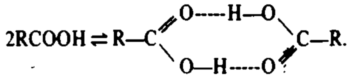
where C is the concn of a solute, l the path length, I_0/I the transmittance of the soln, ν the frequency and $\Delta\nu_{1/2}$ the half-intensity band widths. K is a constant and approximately $\pi/2$ if the spectral slit widths is within 5% of the half-intensity band widths. The integrated intensity, D, of a band independent of the concn of a solute is expressed as follows,

$$D = K \ln\left(\frac{I_0}{I}\right)_{\nu_{max}} \Delta\nu_{1/2}. \tag{4}$$

Combining eqns (3) and (4).

$$A = D/Cl. \tag{5}$$

The equilibrium between the monomer and the dimer of carboxylic acids in nonpolar solvent is as follows.



(6)

The dissociation constant, K_d, for the dimer of carboxylic acid is given by eqn (7)

$$K_d = \frac{2C^2}{(C_0 - C)} \tag{7}$$

where C_0 is the initial formal concn of carboxylic acid and C is the concn of monomer molecules. Equation (8) is obtained by the combination of eqns (5) and (7).

$$D = \frac{1}{2}A^2l^2K_d\frac{C_0}{D} - \frac{1}{2}AlK_d. \tag{8}$$

The integrated intensities, A, of the free O–H band of carboxylic acid and dissociation constants are obtained from D vs C_0/D plots.

In this paper the initial formal concns of TCA were in the range of *ca.* 5×10^{-4} to 5×10^{-3} M and at least ten solutions were measured for each temperature. The spectral slit widths were *ca.* 2.6 cm^{-1} near 3500 cm^{-1}.

In the equilibria of TCA with ethers the concns of the monomeric TCA were obtained from eqn (3) and association constants, K_T, were calculated from eqn (9)

$$K_T = \frac{[C_{0,t} - C_t - (2C_t^2/K_d)]}{[C_t][B_{0,t} - C_{0,t} + C_t + (2C_t^2/K_d)]} \tag{9}$$

where B_0 and C_0 are the initial formal concns of ethers and TCA, and the subscript t designates the temperature at which measurements were made. In all cases the initial formal concns of ethers and TCA were *ca.* 10^{-2} and 10^{-3} M, respectively, and corrected only for density changes of CCl_4 in the same manner as in the phenol–ether soln, as the contribution of ethers and TCA to density changes could be neglected. For each TCA-ether pair, 2–4 solutions were measured. At least two scannings were made at each temp.

RESULTS AND DISCUSSION

Measurements of the association constants of the phenol–ethers system. The molecular extinction coefficient, ϵ_{max}, of phenol was obtained from eqn (10) on the basis of the free OH stretching band at *ca.* 3612 cm^{-1}

$$\epsilon_{max} = \frac{1}{Cl}\log_{10}\left(\frac{I_0}{I}\right)_{\nu_{max}} \tag{10}$$

Its temperature dependence was expressed by eqn (11) over a temperature range 17.5°–40° and decreased regularly with increase in temp.

$$\epsilon_{max} = 322.5 - 1.038\,t \tag{11}$$

where t was a Celsius temperature (°C).

The concn of free phenol in the phenol–ethers system was calculated from eqn (11) and the association constants were obtained from eqn (1). Thermodynamic parameters were calculated by the usual method. The results in the phenol–ethers system are collected in Table 1. The ethers used were tetrahydrofuran THF, tetrahydropyran THP, dibutyl ether (BuE), dipropyl ether (PrE), 1,4-dioxane (1,4-Dox) and propylene oxide (PO). In PO-phenol pair, measurements were made in the temperature range 17.5°–30° because of the volatility of PO. The associations of phenol with ethers have been systematically studied by Lippert and Prigge[6] and West *et al.*[7] The study of the former was made on the asso-

Table 1. Association constant and thermodynamic parameters for phenol–ethers system

ether	K_p (M^{-1})	$-\Delta H$ (Kcal/mol)	$-\Delta F$ (Kcal/mol)	$-\Delta S$ (e.u.)	K_p[a] (M^{-1})	$-\Delta H$[a] (Kcal/mol)	K_p[b] (M^{-1})	$-\Delta H$[c] (Kcal/mol)
THF	11.94±0.38	5.04±0.27	1.47±0.02	11.98±0.95	7.53	4.25	16.2	5.29
THP	9.33±0.51	5.43±0.46	1.32±0.03	13.77±1.66	7.07	4.32	7.0	5.19
OX[d]	—	—	—	—	9.82	4.97	15.8	5.16
PO	6.33±0.08	4.14±0.11	1.09±0.01	10.21±0.40	4.70	3.75	—	—
BuE	5.00±0.30	5.45±0.43	0.95±0.04	15.09±1.58	—	—	6.25	5.71
PrE	5.16±0.16	5.61±0.27	0.97±0.02	15.56±0.96	—	—	—	—
1.4-Dox	4.46±0.16	4.36±0.27	0.89±0.02	11.65±0.98	5.14	4.23	—	—

[a] Ref.6 at 30°C. [b] At 25°C. Calculated from ref.7 on the basis of thermodynamic parameters. [c] Ref.7. [d] Oxetane.

ciation of phenol with 3- to 6-membered heterocycles. The data in this paper have been compared with previously reported data in Table 2. However, there is clearly no agreement. The association constant of phenol with cyclic ethers decreased in the following order, 4-, 5-, 6- and 3-membered rings. The association behavior of phenol with BuE was almost identical to that of phenol with PrE.

Measurements of the association constants of the trichloroacetic acid–ethers system. The integrated intensity, A, of the free O–H band of TCA in *ca.* 3508 cm^{-1} was calculated by the least-squares method from D vs C_0/D plot of eqn (8) which is shown in Fig. 1. Table 2 shows integrated intensities, A, the dissociation constants of the TCA dimer, K_d, and the temperature dependence of half-intensity band widths, $\Delta\nu_{1/2}$. The integrated intensity was found to be approximately constant. And then association constants were calculated on the basis of the average value of integrated intensities, 3.95×10^4. The half-intensity band widths increased regularly with increased temp. The temp. dependence of dissociation constant of the TCA dimer, K_d, was obtained by the least-squares method and expressed by the following equation

$$\log_{10} K_d = 5.07 - 2.37 \times 10^3 (1/T) \tag{12}$$

where T is an absolute temp. (°K).

Table 2. Integrated intensities of monomer band, A, half-intensity band widths, $\Delta\nu_{1/2}$ and dissociation constants, of the TCA dimer

temp. (°C)	20	25	30	35	40
$A \times 10^{-4}$ (intens. unit)	4.08	3.92	3.87	3.90	3.96
$\Delta\nu_{1/2}$ (cm^{-1})	52.7	53.4	54.0	55.2	55.4
$K_d \times 10^3$ (M)	0.934	1.37	1.86	2.47	3.04

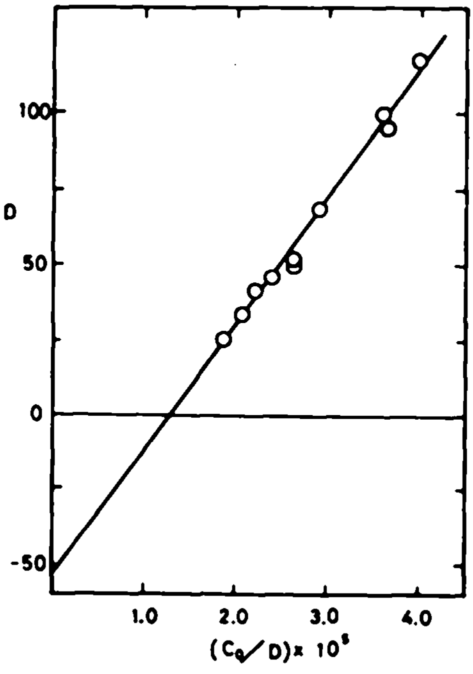


Fig. 1. D vs C_0/D plot at 25°.

The dissociation constant of the TCA dimer in CCl$_4$ at 25° was measured by using IR spectra,[8–11] but the data did not give concordant results, being of the same order.

The association constant of TCA with ethers was calculated from eqn (9). It was assumed that the dissociation constant of the TCA dimer was not influenced in the presence of ethers and that the species of the TCA–ether association existed as a 1 : 1 complex in excess of ether. The results in the TCA–ether systems are collected in Table 3. The association of TCA with ethers has not been reported.

A relationship between the association constants of the phenol–ethers system and those of the trichloroacetic acid–ethers system. Figure 2 shows a relationship of the association constant, K_p, of phenol with ethers and those, K_T, of TCA with ethers in CCl$_4$. The plot of the logarithm of K_p vs the logarithm of K_T shows a linearity, where both K_p and K_T contain all the values measured on all the ethers used except 1,4-Dox in the temp. range 20°–40°. The relationship is expressed by the following equation and its correlation coefficient is 0.994.

$$\log_{10} K_T = 1.460 \log_{10} K_p - 1.726. \tag{13}$$

The association constant of TCA with PO was estimated from eqn (13) on the basis of the association constant of phenol with PO. The estimated association constants of the TCA–PO system are shown in Table 3.

The above relationship was independent of the structure of ethers, cyclic or aliphatic, and even in the dibutyl ether system which has some steric hindrance around the O atom due to the Bu group. It was considered reason-

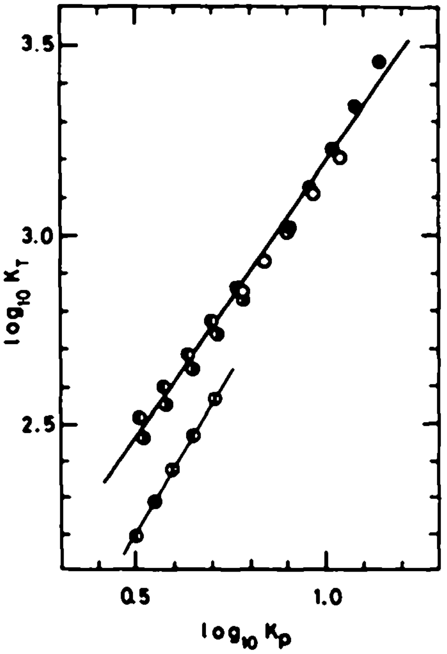


Fig. 2. The relationship between the association constants of phenol with ethers, K_p and those of TCA with ethers, K_T: ● THF; ○ THP; ◐ BuE; ◑ PrE; ○ 1.4-Dox.

Table 3. Association constants and thermodynamic parameters for TCA–ethers system

ether	$K_T \times 10^{-2}$ [a] (M^{-1})	$-\Delta H$ (Kcal/mol)	$-\Delta F_{298}$ (Kcal/mol)	$-\Delta S_{298}$ (e.u.)
THF	21.87 ± 0.75	9.21 ± 0.23	4.46 ± 0.02	15.59 ± 0.84
THP	12.83 ± 0.57	7.39 ± 0.30	4.24 ± 0.03	10.57 ± 1.09
BuE	5.93 ± 0.27	7.25 ± 0.27	3.78 ± 0.03	11.64 ± 1.01
PrE	5.48 ± 0.14	7.85 ± 0.22	3.74 ± 0.02	13.82 ± 0.78
1.4-Dox	2.95 ± 0.18	7.90 ± 0.46	3.37 ± 0.04	15.19 ± 1.66
PO	7.87 [b]	6.04 [b]	3.95 [b]	7.02 [b]

[a] At 25°C. [b] Estimated values.

able to estimate the association constant of TCA with PO on the basis of the relationship of eqn (13), because PO has no steric hindrance around the O atom in the ring. The data in 1,4-Dox deviated from the linearity as shown in Fig. 2. The fact may be explained as follows: in this study 1,4-Dox which has two ether groups in a molecule was treated as two functionality by the usual method,[9] but another of 1,4-Dox may not be able to behave independently when one ether group of 1,4-Dox is associated with one molecule of TCA.

In conclusion, the association constant of TCA with such a reactive cyclic ether as oxirane was estimated from eqn (13) if the association constant of phenol with the ether could be obtained from the molecular extinction coefficient of free OH group of phenol.

The estimated value of the association constant of a strong carboxylic acid with reactive cyclic ethers gave important information on the preliminary equilibrium constant in the protonic-acid-catalyzed ring-opening reaction of oxirane. Then it could serve as a useful tool in the clarification of reaction mechanism in the acid-catalyzed ring-opening of oxirane.

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