Dimer-Monomer Equilibrium Constants for Acetic Acid and the Three Chloroacetic Acids in Benzene

By Yoichiro NAGAI and Osamu SIMAMURA

(Received May 23, 1961)

An accurate value of the equilibrium constant for the association of monomeric dichloroacetic acid to the dimeric form in benzene was required for a kinetic study being carried out in this laboratory. A search of the literature showed that a number of workers[1-5] had already been concerned with the problem of determining the association constants of acetic acid and the three chloroacetic acids in various non-polar solvents. In view of the lack of a reliable value for our present purpose, however, we have now determined, by infrared absorption measurement, the dimer-monomer equilibrium constant for dichloroacetic acid in benzene at 20°C, together with those for acetic, monochloroacetic, and trichloroacetic acid.

Experimental

Materials.—Benzene was shaken with concentrated sulphuric acid and with water, dried with calcium chloride and fractionated over sodium. Acetic acid was refluxed with potassium permanganate, distilled, and subjected to fractional crystallizations until a product with a constant freezing point, 16.5°C, was obtained; this material was distilled before use, b. p. 117°C. Monochloroacetic acid was recrystallized three times from benzene, dried over phosphorus pentoxide in an Abderhalden apparatus, m. p. 63.0°C, and distilled, b. p. 186°C. Dichloroacetic acid was prepared by Cope, Clark, and Connor's procedure[6] and fractionated three times under reduced pressure, b. p. 86.6∼87.0°C/13mmHg. Trichloroacetic acid was distilled four times, b. p. 195.5∼195.8°C.

Absorption Measurement.—The measurements were carried out at 20°C on benzene solutions of the acids in concentrations ranging from 0.01 to 1 mol./l., a Perkin-Elmer grating spectrophotometer Model 112G being used. A 1 mm. measuring cell was used for solutions of acetic, monochloroacetic, and dichloroacetic acid and an 0.1 mm. cell for solutions of trichloroacetic acid. The absorption spectra were measured in the region between 3250 and 3550 cm^{-1}, in which the peak of a band due to a free OH stretching vibration usually appears, with a spectral slit width of 1.0 cm^{-1} being used.

Results and Discussion

The absorption frequencies observed in benzene corresponding to the stretching mode of the free OH group of acetic acid and the three chloroacetic acids are listed in Table I, together with the values in carbon tetrachloride reported in the literature.

---

[1] J. T. Harris, Jr. and M. E. Hobbs, *J. Am. Chem. Soc.*, **76**, 1419 (1954).

[2] J. Wenograd and R. A. Spurr, ibid., **79**, 5844 (1957).

[3] C. P. Brown and A. R. Mathieson, *J. Chem. Soc.*, **1957**, 3625; C. P. Brown and A. R. Mathieson, *J. Phys. Chem.*, **58**, 1057 (1954).

[4] H. A. Pohl, M. E. Hobbs and P. M. Gross, ibid., **9**, 408 (1941); R. J. W. Le Fèvre and H. Vine, *J. Chem. Soc.*, **1938**, 1795.

[5] M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Phys.*, **6**, 755 (1938).

[6] A. C. Cope, J. R. Clark and R. Connor, "Organic Syntheses", Coll. Vol. II (1948), p. 181.

TABLE I. ABSORPTION FREQUENCIES (cm^{-1})

Acid	Present work in C_6H_6	Ref. 1 in CCl_4	Ref. 7 in CCl_4	pK_a[8] in H_2O
CH_3COOH	3472	3548	3533	4.76
$CH_2ClCOOH$	3438	3539	3522	2.86
$CHCl_2COOH$	3410	3529	3511	1.29
CCl_3COOH	3389	3526	3505	0.3

Table I shows that the free OH vibration frequency of the stronger acid is lower than that of the weaker one both in benzene and in carbon tetrachloride. There is a linear relation between the OH vibration frequencies in benzene and the pK_a values[8], as is shown in Fig. 1. A similar relation has also been observed in carbon tetrachloride solution[7].

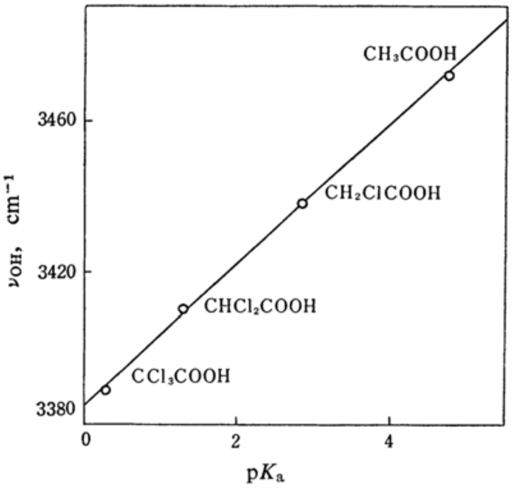

Fig. 1. Relation between the OH vibration frequency of the monomeric acid in benzene and the pK_a value.

Further, the observed frequencies are considerably lower in benzene than in carbon tetrachloride. This shift in the OH frequency is obviously attributable to an interaction, similar to hydrogen bond formation, between the hydroxyl of a carboxyl group and the π-electron system of a benzene nucleus. Since the relative affinity of the acid for benzene is considered to be parallel to the acid strength, it is expected that the more highly chlorinated acids interact more strongly with benzene, resulting in a larger shift in frequency; this has been borne out, as is shown in Fig. 1. Such a shift has also been observed for methanol-d[9] and phenols[10], and a similar one has been observed in the NH frequency for *N*-methylacetamide[11].

The dimer-monomer equilibrium constants were calculated from the change in the apparent molar extinction coefficient of the OH absorption band with the acid concentration by using the equations,

$$d=l\varepsilon C=lEM$$

$$K=2M^2/(C-M)$$

In these equations d is the optical density, l the absorption path length, ε the apparent molar extinction coefficient, E the molar extinction coefficient of the monomeric acid, C the concentration of the acid taken, M the concentration of the acid monomer, and K the equilibrium constant. Combination of the above equations and rearrangement gives

$$\varepsilon C=(KE^2/2)(1/\varepsilon)-KE/2$$

It follows from this equation that a graph of εC at the particular OH absorption frequency against $1/\varepsilon$ should give a straight line of slope $KE^2/2$ and intercept $KE/2$. The experimental data are shown numerically in Table II and graphically in Fig. 2. The apparent molar extinction coefficient ε increases with a decreasing concentration of the acid, showing that the frequencies which have been measured are due to the OH vibration of the monomeric acids. Since there are satisfactory linear relations between εC and $1/\varepsilon$, as is shown in Fig. 2, it is evident that the assumption of a dimer-monomer equilibrium is well-founded.

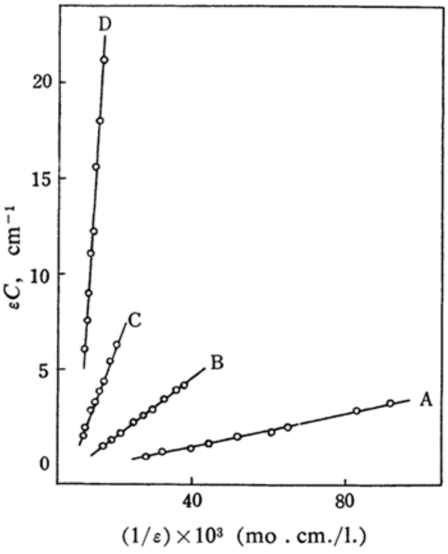

Fig. 2. Relation between εC and $1/\varepsilon$.

A: CH_3COOH B: $CH_2ClCOOH$
C: $CHCl_2COOH$ D: CCl_3COOH

---

[7] J. P. S. Goulden, *Spectrochim. Acta*, **6**, 129 (1954).

[8] E. J. P. Dippy, *Chem. Revs.*, **25**, 151 (1939).

[9] M. Tamres, *J. Am. Chem. Soc.*, **74**, 3375 (1952).

[10] M. Ōki, H. Iwamura and Y. Urushibara, this Bulletin, **31**, 769 (1958); R. West, ibid., **81**, 1641 (1959).

[11] I. Suzuki, M. Tsuboi, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **31**, 1437 (1959); I. Suzuki, M. Tsuboi and T. Shimanouchi, ibid., **32**, 1263 (1960).

TABLE II. THE APPARENT MOLAR EXTINCTION COEFFICIENTS (ε IN l. mol^{-1} cm^{-1}) AT VARIOUS ACID CONCENTRATIONS (C IN mol./l.)

CH_3COOH		$CH_2ClCOOH$		$CHCl_2COOH$		CCl_3COOH	
C	ε	C	ε	C	ε	C	ε
0.309	10.9	0.159	26.3	0.124	50.4	1.174	42.8
0.247	12.0	0.143	27.7	0.0993	54.2	0.587	52.3
0.129	15.5	0.123	29.3	0.0931	54.5	0.528	55.5
0.124	15.9	0.114	30.1	0.0827	57.4	0.440	56.4
0.103	16.4	0.0858	33.2	0.0744	58.6	0.411	57.7
0.0772	19.2	0.0715	36.2	0.0620	62.5	0.352	60.2
0.0515	22.5	0.0572	39.5	0.0558	65.4	0.261	65.2
0.0483	23.2	0.0476	40.9	0.0496	66.9	0.235	66.5
0.0322	24.9	0.0357	46.2	0.0414	72.3	0.176	69.3
0.0215	30.8	0.0286	47.9	0.0372	73.4	0.147	75.7
0.0129	35.7	0.0238	52.6	0.0248	79.4	0.117	76.7
		0.0159	59.2	0.0186	82.8	0.0978	77.7
				0.0165	86.5	0.0733	83.2

The values of E and K calculated from the slopes and intercepts of the lines in Fig. 2 determined by the method of least squares are given in Table III. Harris and Hobbs[1] have estimated, by means of infrared absorption measurement, the equilibrium constants in carbon tetrachloride at 25°C at 2.5×10^{-4}, 6.2×10^{-4}, 9.3×10^{-4}, and 19×10^{-4} mol./l. for acetic, monochloroacetic, dichloroacetic, and trichloroacetic acid, respectively. Comparison with the present values indicates that these acids are very much more associated in carbon tetrachloride than in benzene. The larger dissociation in the latter solvent is evidently attributable to the same cause that has been adduced above to account for the shift in the hydroxyl frequency in benzene from that in carbon tetrachloride; the stabilizing interaction of a hydroxyl group with a molecule of benzene tends to bring about the dissociation of the dimeric form.

TABLE III. MOLAR EXTINCTION COEFFICIENTS AND DIMER-MONOMER EQUILIBRIUM CONSTANTS IN BENZENE AT 20°C

Acid	E l.mol^{-1} cm^{-1}	K mol./l.
CH_3COOH	50.8	0.036
$CH_2ClCOOH$	87.7	0.041
$CHCl_2COOH$	110.9	0.092
CCl_3COOH	92.2	0.91

Summary

Acetic, monochloroacetic, dichloroacetic, and trichloroacetic acid in benzene show an infrared absorption band due to the OH stretching vibration of the monomeric form at 3472, 3438, 3410, and 3389 cm^{-1}, respectively. The dimer-monomer equilibrium constants for these acids in benzene at 20°C have been evaluated, from the change in intensity of these bands with the acid concentration, to be 0.036, 0.041, 0.092, and 0.91 mol./l., respectively.

The observed shift in frequency indicates that there is an interaction, similar to hydrogen bond formation, between the hydroxyl of a carboxyl group and the π-electron system of a benzene nucleus and that the stronger acid interacts more strongly with benzene, resulting in a larger shift in frequency.

The authors are indebted to Professor Takehiko Shimanouchi for valuable suggestions.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo