The Dimerization of Benzoic Acid in Carbon Tetrachloride and Chloroform

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Although the dimerization equilibria of benzoic acid in various solvents have been spectroscopically studied by many authors,[1-6] the equilibrium constants obtained so far extend over a wide range. In the very dilute solutions which are often used for ultraviolet spectroscopy, the interaction of the carboxylic group of the acid with a small amount of water present in the solvents might have a considerable effect on the dimerization equilibrium.

We have studied the dimerization of benzoic acid in the concentration range from 0.0001 mol. to 0.1 mol. in carbon tetrachloride and chloroform by infrared spectroscopy, and have calculated the dimerization constant from the integrated intensities of the carbonyl-stretching vibration bands corresponding to the monomer and the dimer forms of benzoic acid. Barrow and Yerger[7] used the same infrared technique to obtain the dimerization constant of acetic acid in carbon tetrachloride and chloroform from the optical densities at the absorption maxima of the respective carbonyl absorption bands. Davies and Sutherland[1] obtained the dimerization constant of benzoic acid from the integrated intensity of the hydroxyl-stretching vibration band.

The purpose of the present paper is two-fold: to apply the integrated intensity technique for the determination of the monomer and dimer concentrations to the carbonyl-stretching band, using a high resolution infrared spectrometer, and to compare the effect of carbon tetrachloride upon acid dimerization with that of

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[1] M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Phys.*, **6**, 767 (1938).

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

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

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[5] M. Ito, *J. Mol. Spectry.*, **4**, 144 (1960).

[6] H. Hosoya, J. Tanaka and S. Nagakura, ibid., **8**, 257 (1962).

[7] G. M. Barrow and E. A. Yerger, *J. Am. Chem. Soc.*, **76**, 5248 (1954).

chloroform. Barrow and Yerger[7] assumed that a weak association of acetic acid with chloroform occurs through hydrogen bonding to the monomer carbonyl. The present paper will examine whether a like association exists in the benzoic acid - chloroform system.

Experimental

The Measurement of Dimerization Constants.—The basic equation from which infrared intensity measurements proceed is:

$$A=(Cl)^{-1}\int \ln(I_0/I)_\nu d\nu \qquad (1)$$

where A is the *true* integrated intensity; C, the molar concentration of an absorbing species; l, the optical path length, and I_0 and I, the incident and transmitted intensity of the monochromatic radiation of the frequency, ν, respectively. In practice, because of the use of a finite slit width, the radiation is not monochromatic and the intensity measured experimentally is not I but the apparent intensity, T. Therefore, Eq. 1 should be replaced by:

$$B=S/Cl, \text{ with } S=\int \ln(T_0/T)_\nu d\nu \qquad (2)$$

where B is the *apparent* integrated intensity. As Ramsay has shown,[8] the apparent band intensity, B, determined in this way is not the true physical constant of the absorbing species but depends upon the instrumental conditions employed. However, if one assumes that the $(T_0/T)_\nu/(I_0/I)_\nu$ ratio does not significantly depend upon the ratio of the apparent half-intensity band width to the slit width, one can reasonably determine the concentration of the absorbing species from Eq. 2 by putting an appropriate value into B. In fact, when this was checked by measuring the carbonyl band of ethyl methyl ketone, the deviation of the apparent integrated intensity from the true integrated intensity was found not to be significant, the decrease in peak intensity produced by the finite slit width being approximately compensated for by an increase in the half-intensity band width.

All measurements were made with a Koken DG 201 infrared spectrophotometer equipped with a grating or a rock-salt prism. Dry air was led into the instrument after it had passed through a column packed with a molecular sieve in order to remove the carbon dioxide and water present in the air. A set of rock salt cells was used; the cell thickness was 0.190 mm., as determined by interference patterns, and 1.20, 3.10, 9.9, and 20.0 mm., as determined by direct measurement with a micrometer.

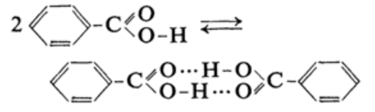
The acetic acid concentrations used were in the range from 7.35×10^{-2} to 3.03×10^{-4} mol. in carbon tetrachloride and 7.64×10^{-2} to 1.31×10^{-4} mol. in chloroform. The temperature of the samples was not specifically controlled but was between room temperature, 23°C, and that of the instrument, 25°C.

Materials.—Wako special-grade benzoic acid was recrystallized from water, dried under a vacuum, and sublimated in a flask. The carbon tetrachloride was Kanto Kagaku reagent grade, washed several times with concentrated sulfuric acid, a sodium hydroxide aqueous solution and water, dried over calcium chloride and then over phosphorus pentoxide, and finally passed through a column packed with aluminum oxide. It was stored in a brown desiccator placed in a dark and cool place and used within two day.

The chloroform was of the same grade and was purified in the same manner as carbon tetrachloride.

Results and Discussion

The dimerization equilibrium of benzoic acid in non-dissociating solvents is assumed to be:



(3)

The infrared absorption spectrum of benzoic acid has been fairly well established.[9] The O–H stretching vibration band was found at 3525 cm^{-1}, which corresponds to that of monomer benzoic acid, and the out-of-plane O–H deformation, at 945 cm^{-1}. The C=O stretching vibration bands used to determine the monomer and dimer concentrations were found at 1737 cm^{-1} for the monomer and at 1692 cm^{-1} for the dimer in carbon tetrachloride, and at 1725 and 1690 cm^{-1} for the

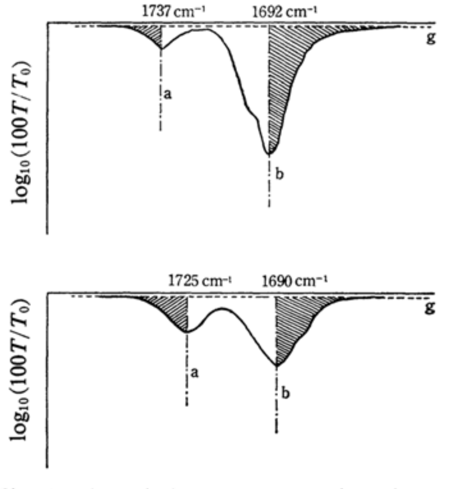


Fig. 1. $\log_{10}(T/T_0)_\nu$ versus ν plot of the C=O stretching vibration bands of benzoic acid. Above: 0.0073 M benzoic acid in CCl_4; Below: 0.0076 M benzoic acid in $CHCl_3$ The cell length is 1.20 mm.

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[8] D. A. Ramsay, ibid., 74, 72 (1952).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London (1957), p. 139ff.

TABLE I. THE EQULIBRIUM CONSTANT FOR THE DIMERIZATION OF BENZOIC ACID IN CARBON TETRACHLORIDE

M mol. l^{-1}	l mm.	S_m cm^{-1}	S_d cm^{-1}	C_m mol. l^{-1}	C_d mol. l^{-1}	$K\times10^{-3}$ l.mol^{-1}
0.07349	0.190	0.907	37.240	3.33×10^{-3}	3.08×10^{-2}	2.78
0.05060		0.898	28.483	3.29	2.36	2.18
0.02530		0.584	13.454	2.14	1.11	2.42
0.01012	1.20	2.131	32.374	1.24	4.24×10^{-3}	2.76
0.007349		1.975	23.209	1.15	3.04	2.30
0.005060	3.10	4.211	38.853	9.46×10^{-4}	1.97	2.20
0.004048		3.780	32.960	8.49	1.67	2.32
0·003036		3.198	24.483	7.19	1.24	2.40
0.002024		2.685	15.790	6.03	8.01×10^{-4}	2.20
0.001515		2.103	10.301	4.73	5.22	2.33
0.001012	9.9	5.499	21.110	3.87	3.35	2.24
0.0007349		4.417	13.165	3.11	2.09	2.16
0.0005060	20.0	6.805	15.108	2.37	1.19	2.12
0.0003036		5.070	8.808	1.77	6.92×10^{-5}	2.21
						(average 2.33)

TABLE II. THE EQUILIBRIUM CONSTANT FOR THE DIMERIZATION OF BENZOIC ACID IN CHLOROFORM

M mol. l^{-1}	l mm.	S_m cm^{-1}	S_d cm^{-1}	C_m mol. l^{-1}	C_d mol. l^{-1}	$K\times10^{-3}$ l. mol^{-1}
0.07644	0.190	6.314	34.912	9.36×10^{-3}	3.11×10^{-2}	3.55
0.04375		4.408	21.743	6.54	1.94	4.53
0.02188		3.263	9.270	4.84	8.26×10^{-3}	3.53
0.008750	1.20	11.424	21.660	2.68	3.05	4.25
0.007644		10.820	17.880	2.54	2.52	3.91
0.004375	3.10	20.386	25.234	1.85	1.38	4.03
0.003500		16.748	17.775	1.52	9.70×10^{-4}	4.20
0.002625		14.723	12.290	1.34	6.71	3.74
0.001750		10.920	6.759	9.92×10^{-4}	3.69	3.75
0.001313	9.9	26.930	13.206	7.66	2.26	3.85
0.000875		19.310	7.281	5.50	1.24	4.10
0.0007644		18.790	6.583	5.35	1.13	3.95
0.0004375	20.0	21.706	4.147	3.06	3.51×10^{-5}	3.75
0.0002625		12.028	1.778	2.19	2.02	4.20
0.0001313		6.351	0.587	1.29	6.65×10^{-6}	4.02
						(average 3.96)

monomer and dimer, respectively, in chloroform. These assignments are consistent with those already reported.

In Fig. 1 plots of $\log_{10}(T_0/T)_\nu$ versus the frequency, ν, are shown for the C=O stretching vibration bands of benzoic acid in carbon tetrachloride and chloroform. In this frequency region, benzoic acid does not show any absorption except for the two C=O stretching bands of the free and associated species, so one may regard the g shown in the figure as the base line. The broken lines, a and b, show the position of the absorption maxima corresponding to the monomer and dimer forms. The area intensity, S_m, is taken to be twice the shaded area to the left of line a in Fig. 1; similarly, S_d is taken to be twice the shaded area to the right of line b. This procedure was utilized because the two absorption bands overlapped in the region between lines a and b in Fig. 1. (Hereafter the suffixes m and d will be used to specify quantities concerning the monomer and dimer respectively). The shaded parts of the figure were then cut off and weighed. The area intensities thus obtained for a set of experiments are shown in Table

TABLE III. THE APPARENT INTEGRATED INTENSITIES OF THE CARBONYL STRETCHING BANDS OF THE BENZOIC ACID MONOMER AND DIMER (l. mol.$^{-1}$)

	in CCl_4	in $CHCl_3$
$B_m\times10^{-4}$	1.44	3.55
$B_d\times10^{-4}$	6.36	5.91

I for the carbon tetrachloride solution and in Table II for the chloroform solution.

To obtain the apparent integrated intensity, B_m (or B_d), it is necessary to make an extrapolation of the (S_m/lM or $2S_d/lM$) measured for a series of different concentrations to a zero (or finite) concentration, M being the total concentration of benzoic acid in carbon tetrachloride and chloroform. A difficulty lies in the fact that these extrapolations are very sensitive to measurements of the area intensities at small concentrations, where the experimental errors in determining band areas are quite large. In fact, the approximate values of the extrapolated (S_m/lM) and ($2S_d/lM$) as obtained for the carbon tetrachloride solution, for example, range from 0.9 to 1.5×10^4 and from 5.8 to 6.5×10^4 $1.\,mol^{-1}\,cm^{-2}$ respectively. These uncertainties can not be eliminated by even the inclusion of more experimental data gathered at small concentrations.

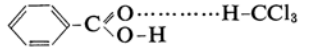
Therefore, it is advisable to determine the apparent integrated intensities, B_m and B_d, by the method of least squares so as to satisfy the stoichiometrical relations:

$$S_m/lB_m + 2S_d/lB_d = M \qquad (4)$$

for a set of different concentrations. The values of B_m and B_d thus obtained are listed in Table III. With these values of B_m and B_d and with the observed area intensities listed in the third and fourth columns of Table I and Table II, the monomer and dimer concentrations of benzoic acid are calculated from Eq. 1 for a set of benzoic acid concentrations. The equilibrium constants, K, for the dimerization of benzoic acid are then obtained. The results are shown in the fifth, sixth, and the last columns of Tables I and II.

The equilibrium constants for both carbon tetrachloride and chloroform solutions are satisfactorily constant; the value as averaged over a set of benzoic acid concentrations is 2300 $1.\,mol^{-1}$ for the former and 400 $1.\,mol^{-1}$ for the latter. These values of K seem to be more reliable than those obtained by Harris and Hobbs(2) or even by Barrow and Yerger,(7) who showed the concentration dependence of the equilibrium constant, in particular, at high dilutions. For instance, Barrow and Yerger gave, for the dimerization equilibrium of acetic acid in carbon tetrachloride, values between 1000 and 2650 $1.\,mol^{-1}$ for concentrations in the range from 0.17 mol. to 0.000112 mol. (Note that they treated not the integrated intensity but the optical density of the carbonyl stretching band maxima.) The values of the equilibrium constant obtained in the present paper are smaller than those previously reported by several authors; for example, Davies and Sutherland(1) gave the values of 13700 $1.\,mol^{-1}$ at 19.5°C and 220 $1.\,mol^{-1}$ at 76.5°C for the carbon tetrachloride solution, while Harris and Hobbs obtained a value of about 7000 $1.\,mol^{-1}$ at room temperature for the same solution.

The equilibrium constant in chloroform is smaller than that in carbon tetrachloride by a factor of about ten. This trend is parallel with the results obtained by Barrow and Yerger for acetic acid. As is shown in Fig. 1, the position of the carbonyl-stretching vibration band of the monomer in carbon tetrachloride is considerably different from that in chloroform. Moreover, the band width of the monomer band is broader in chloroform than in carbon tetrachloride, while the dimer bands have almost the same width in the two solvents. This agrees with the general observations that the position of a stretching vibration band of a hydrogen-bonded chromophore tends to shift to the lower frequency side and that the band width becomes broader than that of a free species. Therefore, one might expect a weak association in the chloroform solution.



The values of the apparent integrated intensity give further support to this conclusion; as Table III shows, B_d is about the same in magnitude in both solvents, while the B_m in chloroform is larger than that in carbon tetrachloride by a factor of 2.5.

Summary

The dimerization equilibrium of benzoic acid has been studied by high resolution infrared spectroscopy over a wide range of acid concentrations. The concentrations of the monomer and the dimer fractions have been determined from the integrated intensities of the respective carbonyl-stretching vibration bands. The calculated equilibrium constant is 2300 $1.\,mol^{-1}$ for carbon tetrachloride and 400 $1.\,mol^{-1}$ for chloroform, both values being considered more reliable than that determined by peak intensity measurements. A weak association of chloroform with benzoic acid has been suggested as occurring through hydrogen bonding to the monomer carbonyl.

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