Kinetic Studies of the Dissociation and the Recombination Reaction in Aqueous Solutions of Monocarboxylic Acids by Means of Ultrasonic Absorption Measurements

Takayuki Sano, Tomohiro Miyazaki, Nobuhide Tatsumoto, and Tatsuya Yasunaga
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

(Received April 25, 1972)

The ultrasonic absorptions were measured in aqueous solutions of acetic, propionic, butyric, valeric, and chloroacetic acids as a function of the pH over the frequency range from 1.5 to 220 MHz at 25°C. From the dependences of $\mu'_{\max}$ and f_r on pH, it was deduced that the perturbation of the ionization equilibrium of acids was the cause of the excess absorptions in dilute aqueous solutions. The kinetic parameters thus calculated were compared with those obtained by other methods.

It is well known that the ionization equilibrium exists in aqueous solutions of carboxylic acids. Their equilibrium constants have thus far been determined by means of static methods. However, the reaction is so rapid that the kinetic studies of this process could not be done until the appearance of the relaxation methods.

In 1964, Nürnberg and his co-workers[1] determined the dissociation and the recombination rate constants for a number of carboxylic acids by a kind of the relaxation method, the high-level faradaic rectification method. Eigen and his co-workers[2] have also determined the rate constants for some acids by the electric-field method.

On the other hand, the ultrasonic absorption measurements in liquid carboxylic acids have been carried out by many investigators.[3] As a result, it has been concluded that the absorption in pure carboxylic acid is due to the perturbation of the equilibrium between the cyclic dimer and the open dimer. However another type of absorption different from that in the liquid of pure acids has been observed in comparatively dilute aqueous solutions. The perturbation of the ionization equilibrium[4] has been expected to be a cause of this type of absorption, but no thorough consideration has been done of this absorption. Therefore, it seems that it would be very interesting to clarify the mechanism of the absorption and to compare the kinetic parameters obtained by the ultrasonic method with those obtained by other methods.

Experimental

In aqueous solutions of monocarboxylic acids, the ultrasonic absorption was measured by means of the pulse technique[5] over the frequency range from 1.5 to 220 MHz at various concentrations and pH's. The sing-around[6] method operated at 1.92 MHz was used to measure the sound velocity. The concentrations of the hydrogen ion were determined with a Hitachi-Horiba F-5 type pH meter. The densities were measured using a pycnometer. All the measurements were made at 25°C.

The monocarboxylic acids used were acetic, propionic, butyric, and valeric acids, in which the alkyl group consists of hydrocarbon only, and monochloro-, dichloro-, and trifluoroacetic acids, which contain halogen atoms in the alkyl group. Guaranteed reagents were used throughout this study without further purification.

Results

The spectra of the ultrasonic absorption in the aqueous solutions of acetic acid are shown in Fig. 1. Double relaxations are observed in 3—6M solutions and are expressed by the following equation:

$$(\alpha\lambda)' = vf\left(\frac{\alpha}{f^2}-B\right) = vf\left[\frac{A_1}{1+(f/f_{r1})^2}+\frac{A_2}{1+(f/f_{r2})^2}\right], \quad (1)$$

where α is the ultrasonic absorption coefficient, λ is the wavelength of the acoustic wave, $(\alpha\lambda)'$ is the excess absorption per wavelength, v is the velocity of sound, f is the frequency of sound, A and B are the relaxational and classical absorptions respectively, and f_r is the relaxation frequency, and where the subscripts 1 and 2 refer to the absorption at the lower and higher fre-

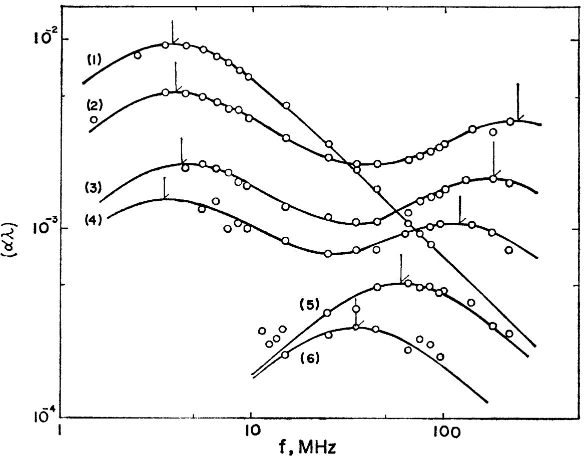

Fig. 1. Ultrasonic absorption spectra of acetic acid in aqueous solutions at 25°C. (1): 8.02M, (2): 6.01M, (3): 4.01M, (4): (4): 3.00M, (5): 1.45M, (6): 1.00M.

---

[1] H. W. Nürnberg and H. W. Dürbeck, *Z. Anal. Chem.*, **205**, 217 (1964).

[2] M. Eigen and J. Schoen, *Z. Elektrochem.*, **59**, 483 (1955), M. Eigen and K. Tamm, *ibid.*, **66**, 93 (1962).

[3] B. Spakowski, *C. R. Acad. Sci. URSS.*, **18**, 169 (1938), J. Lamb and J. M. M. Pinkerton, *Proc. Roy. Soc., Ser. A*, **199**, 114 (1949), J. E. Piercy and J. Lamb, *Trans. Faraday Soc.*, **52**, 930 (1956).

[4] L. G. Jackopin and E. Yeager. Technical Report No. 35 (1969).

[5] N. Tatsumoto, *J. Chem. Phys.*, **47**, 4561 (1967).

[6] T. Yasunaga, N. Tatsumoto, and M. Miura, This Bulletin, **37**, 1655 (1964).

quencies respectively.

In 1, 1.5, and 8M solutions single relaxations are observed; they may be represented as follows:

$$(\alpha\lambda)' = vf\left(\frac{\alpha}{f^2}-B\right) = vf\frac{A}{1+(f/f_r)^2} \qquad (2)$$

The solid lines in Fig. 1 are theoretical curves which are expressed by either Eq. (1) or (2). The values of the parameters, the relaxation frequency (f_r), and the maximum absorption per wavelength ($\mu'_{\max}$) are listed in Table 1, together with the velocity of sound (v), and the density (ρ).

Table 1. The acoustical characteristics of acetic acid at various concentrations at 25°C

M	f (MHz)	$\mu'_{\max}$ (10^{-4})	pH	v (10^5 cm·sec^{-1})	ρ (g·cm^{-3})
8.02	3.8	95.0	1.43	1.4984	1.0494
6.02	4.0	51.9	1.67	1.5255	1.0392
	240	35.8			
4.01	4.3	21.3	1.85	1.5369	1.0270
	180	17.8			
3.00	3.5	13.9	1.93	1.5341	1.0147
	130	10.8			
1.45	60	5.2	2.23	1.5216	1.0066
1.00	35	3.1	2.26	1.5160	1.0047

As can be seen in Fig. 1, the excess absorption at the lower frequency decreases with a decrease in the concentration, and it entirely disappears in 1 and 1.5M solutions over the frequency range measured. This behavior of the spectra shows that the excess absorptions in 1 and 1.5M solutions correspond to those at the higher frequency in 3—6M solutions. On the other hand, the excess absorption in 8M, and that at the lower frequency in 3—6M solutions, seem to be identical with that in pure acetic acid. The mechanism of these absorptions has been discussed in detail by Atkinson and his co-workers.[7] Since our purpose in this paper is to investigate the mechanism of the absorption at higher frequencies, the measurements of the ultrasonic absorption were carried out in detail for a 1M solution, in which the absorption at lower frequencies disappears.

Now, assuming that the excess absorption is associated with the dissociation and the recombination reaction of the acetic acid, the best way to justify the above assumption is to measure the ultrasonic absorption at various pH's in the 1M solution, in which the excess absorption disappears at lower frequencies. Under these conditions, the results obtained are shown in Fig. 2, while the values of the ultrasonic parameters are listed in Table 2. It can be seen from Fig. 2 that both f_r and $\mu'_{\max}$ are dependent on the pH. This fact may imply the validity of the above assumption.

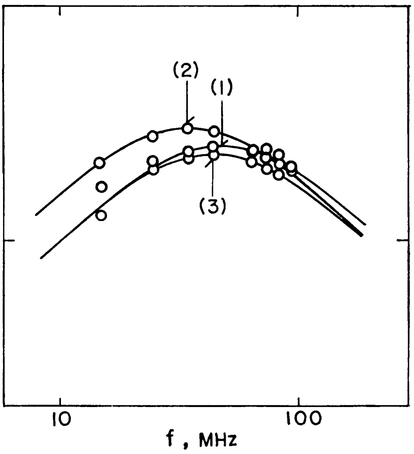

Fig. 2. Ultrasonic absorption spectra in 1.00M solution of acetic acid at 25°C. (1): pH 1.76, (2): pH 2.26, (3): pH 3.20.

In the dissociation and the recombination reaction of acid, which is generally represented by the following equation:

$$\mathrm{AH} \underset{k_r}{\overset{k_d}{\rightleftarrows}} \mathrm{A^-} + \mathrm{H^+}$$

the relaxation time, τ, and $\mu'_{\max}$ are given by the following equations:

$$\frac{1}{\tau} = 2\pi f_r = k_d + k_r(A^- + H^+) = k_r(K + A^- + H^+) \qquad (3)$$

Table 2. The acoustical characteristics of carboxylic acids at various pH's at 25°C

	M	pH	f_r (MHz)	$\mu'_{\max}$ (10^{-4})	v (10^5 cm·sec^{-1})	ρ (g·cm^{-3})
Acetic acid	1.00	1.76	49±3	2.6	1.5156	1.0059
		2.26	35±2	3.1	1.5160	1.0047
		2.75	40±5	2.8	1.5169	1.0062
		3.20	45±5	2.4	1.5189	1.0070
Propionic acid	1.01	2.42	62±5	4.4	1.5275	1.0025
		3.16	40±5	1.9	1.5294	1.0030
		3.40	58±10	2.6	1.5307	1.0026
Butyric acid	0.507	1.90	50±3	1.5	1.5198	0.9992
		2.21	40±3	2.7	1.5197	0.9977
		2.55	45±2	3.1	1.5197	0.9966
		2.76	56±2	2.3	1.5199	0.9979
		3.00	65±5	1.8	1.5577	0.9982
Valeric acid	0.103	2.95	43±2	1.8	1.5034	0.9959
		2.67	28±2	1.4	1.5400	0.9958

---

7) R. D. Corsaso and G. Atkinson, *J. Chem. Phys.*, **55**, 1971 (1971).

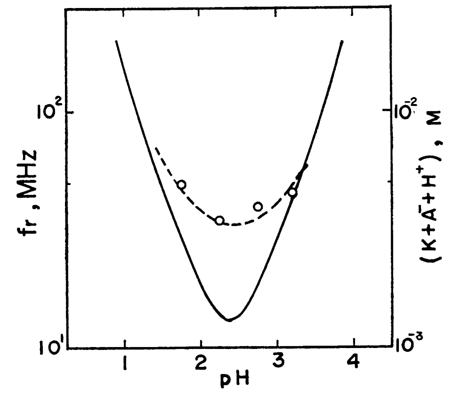

Fig. 3. Plot of the relaxation frequency *versus* pH; the experimental values of f_r are indicated by circles, and solid line shows the dependence of the calculated concentration term on pH.

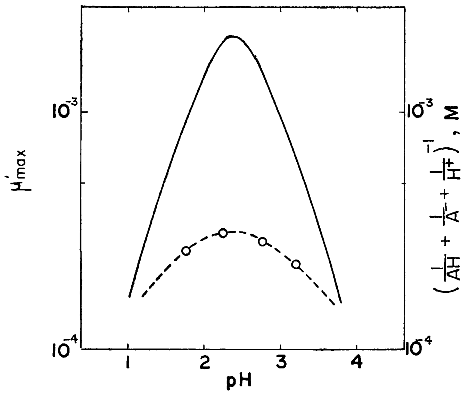

Fig. 4. Plot of maximum of the absorption per wavelength *versus* pH; the experimental values of μ'_{max} are indicated by circles, and the solid line shows the calculated concentration terms.

$$\mu'_{max} = \frac{(\Delta V)^2}{2\beta_0 \boldsymbol{R}T}\left[\frac{1}{AH}+\frac{1}{A^-}+\frac{1}{H^+}\right]^{-1} \tag{4}$$

where k_d and k_r are the rate constants of the dissociation and the recombination respectively, K is the equilibrium constant, β_0 is the adiabatic compressibility, $\boldsymbol{R}$ is the gas constant, T is the absolute temperature, and ΔV is the volume change per mole for the reaction.

In Eqs. (3) and (4), k_r, k_d, and $\pi(\Delta V)^2/2\beta_0\boldsymbol{R}T$ may be taken as constant, so both f_r, and μ'_{max} are directly proportional to the concentration. The concentration terms at various pH's can be calculated by using the equilibrium constant listed in the literature.[8] From the calculation of the terms in Eqs. (3) and (4), it is found that these terms have a maximum and a minimum at the corresponding pH. The results are presented in Figs. 3 and 4, together with the experimental values of f_r and μ'_{max} respectively. In view of the similarity of the behavior of the experimental values to that of the calculated terms against the pH, the assumption that the excess absorption in aqueous acetic acid is to be attributed to the perturbation of the ionization equilibrium of acid is strongly supported.

Table 3. The kinetic parameters for the dissociation and recombination reaction of carboxylic acids at 25°C

	k_d (10^5 sec^{-1})	k_r (10^{10} M$^{-1}\cdot$sec^{-1})	ΔV[a] (cc$\cdot$mol^{-1})
Acetic acid	3.1±1.3	1.8±0.8	12.9±2.9 (12.5)
Propionic acid	3.4±2.8	2.6±2.1	15.8±2.1 (13.7)
Butyric acid	6.4±2.6	4.3±1.7	12.3±1.1 (13.7)
Valeric acid	5.8±3.2	3.9±2.2	13.9±0.5
Monochloro-acetic acid	260±30	1.9±0.2	7.9±0.2 (9.2)

a) The values presented in parentheses have been repoted by Kauzman.[6]

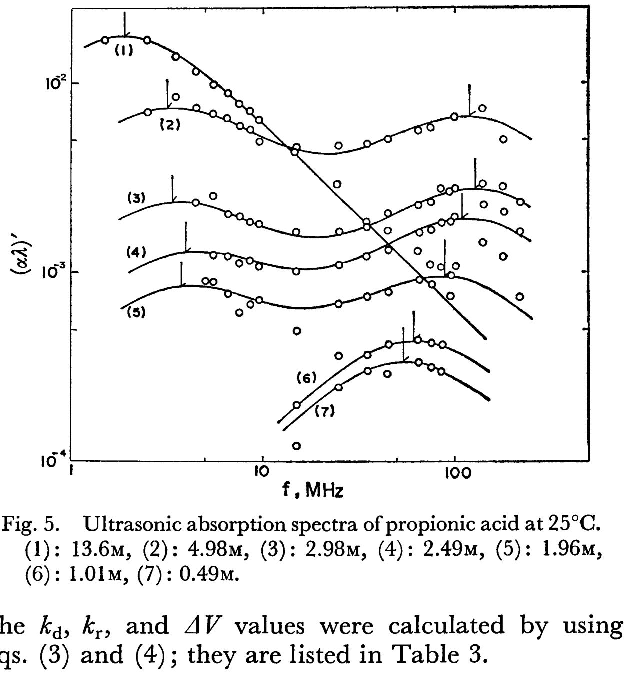

Fig. 5. Ultrasonic absorption spectra of propionic acid at 25°C. (1): 13.6M, (2): 4.98M, (3): 2.98M, (4): 2.49M, (5): 1.96M, (6): 1.01M, (7): 0.49M.

The k_d, k_r, and ΔV values were calculated by using Eqs. (3) and (4); they are listed in Table 3.

Secondly, in aqueous solutions of propionic, butyric, and valeric acids, the ultrasonic absorption were measured by the same procedure as was used in the acetic acid. The ultrasonic absorption spectra of the propionic acid at various concentrations are represented in Fig. 5. It may be seen from the figure that the excess

Table 4. The acoustical characteristics of propionic acid at various concentrations at 25°C

M	f_r (MHz)	μ'_{max} (10^{-4})	pH	v (10^5 cm$\cdot$sec^{-1})	ρ (g$\cdot$cm^{-3})
13.6	2.2	148	—	1.1524	0.9886
4.98	3.2	71.1	1.94	1.5142	1.0187
	120	6.4			
2.98	3.4	22.4	2.13	1.5453	1.0119
	130	2.7			
2.49	4.0	11.8	2.19	1.5463	1.0108
	110	1.6			
1.96	3.8	7.4	2.26	1.5434	1.0089
	90	8.8			
1.01	62	4.4	2.43	1.5275	1.0025
9.49	55	3.4	2.58	1.5139	0.9986

---

[8] Landolt-Börnstein, "Physikalish-Chemische Tabellen," Springer (1936).

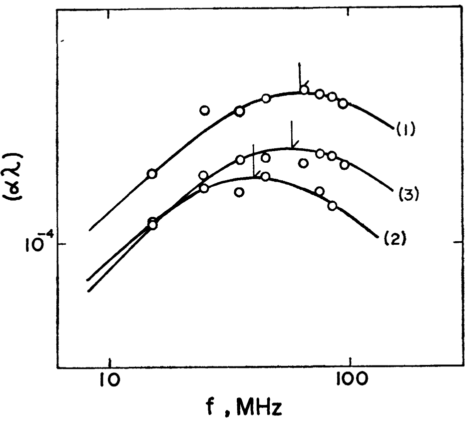

Fig. 6. Ultrasonic absorption apectra of 1.01M solution of propionic acid at 25°C. (1): pH 2.42, (2): pH 3.16, (3): pH 3.40.

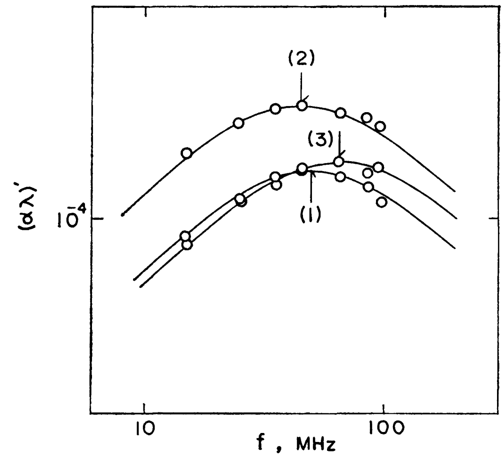

Fig. 7. Ultrasonic absorption spectra of 0.507M solution of butyric acid at 25°C. (1): pH 1.90, (2): pH 2.55, (3): pH 3.00.

absorptions at the lower frequency correspond to those in pure propionic acid, and that the absorptions in 0.5 and 1M solutions, represented by the single relaxation curves are identical with those at higher frequencies in solutions more concentrated than 2M. The relaxation parameters are listed in Table 4.

Next, Fig. 6 shows the ultrasonic absorption spectra in a 1M solution of the propionic acid at various pH's. Similarly, as is shown in Fig. 7, the ultrasonic absorptions were observed in 0.5M solutions of butyric acid at various pH's. In the butyric acid, however, the low solubility prevented the measurement of the dependence of the absorption on the concentration of the acid. Valeric acid is less soluble than butyric acid, so it is very difficult to investigate the dependence of the absorption not only on the acid concentration, but also on the pH. As the result of our great effort, however, the absorptions were measured in a 0.1M solution of the valeric acid at the values of pH, 2.69 and 2.75. The spectra are shown in Fig. 8. The relaxation parameters for propionic, butyric, and valeric acids are presented in Table 2.

As can be seen in Figs. 6—8, both f_r and μ'_{max} are dependent on the pH. The mechanism of these absorptions, therefore, may be due to the dissociation and recombination reaction of acid, as in the acetic acid. The kinetic parameters based on the reaction for each acid are calculated in a manner similar to the case of the acetic acid; they are listed in Table 3. The kinetic parameters for the acetic and propionic acids at various concentrations are presented in Table 5.

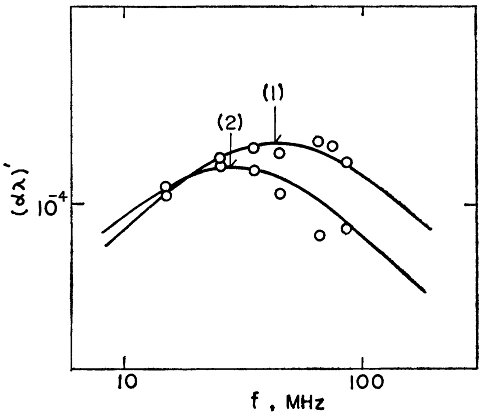

Fig. 8. Ultrasonic absorption spectra of 0.103M solution of valeric acid at 25°C. (1): pH 2.75, (2): pH 2.69.

TABLE 5. THE KINETIC PARAMETERS FOR THE DISSOCIATION AND RECOMBINATION REACTION OF ACETIC AND PROPIONIC ACIDS AT VARIOUS CONCENTRATIONS AT 25°C

	M	k_d (10^6 sec^{-1})	k_r (10^{10} M^{-1}·sec^{-1})	ΔV (cc·mol^{-1})
Acetic acid	6.02	9.3	5.5	25.0
	4.01	10	5.9	17.9
	3.00	8.6	5.1	15.0
	1.45	6.3	3.7	11.9
	1.00	4.3	2.6	10.2
Propionic acid	4.98	5.7	4.4	33.8
	2.98	8.3	6.4	23.8
	2.49	7.8	6.0	19.1
	1.96	7.2	5.5	15.1
	1.01	7.0	5.4	12.7
	0.49	8.8	6.8	13.5

Thirdly, it is very interesting to study the variation in the kinetic parameters of monocarboxylic acids with the change in molecular structure. For this purpose, the ultrasonic absorptions were measured in aqueous solutions of halogeno carboxylic caids, which have quite different electronegativities from the above acids. The single relaxation curves obtained from the measurements of the absorption in 0.5 and 1M solutions of monochloro acetic acid are graphed in Fig. 9. The relaxation parameters are listed in Table 6. As the values of f_r, 180, and 220 MHz are near the end of the frequency range measured, it is thought that the experimental error may be larger than that of other acids. In this case, the kinetic parameters were also calculated on the basis of the expectation that the absorptions are associated with the perturbation of the ionization equilibrium of acid. The results are listed in Table 3. The ultrasonic absorptions were measured in 1M solutions of dichloro- and trifluoroacetic acids, but in both acids no excess absorption was observed in the fre-

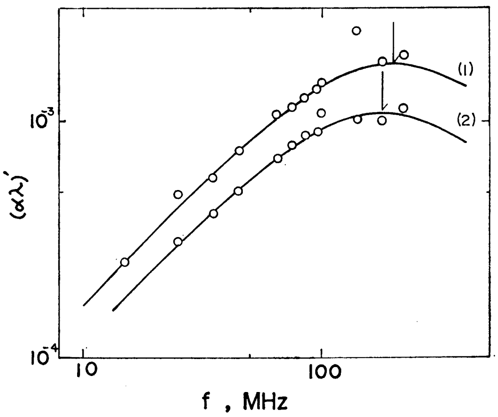

Fig. 9. Ultrasonic absorption spectra of 1.00M and 0.503M solutions of monochloroacetic acid at 25°C.

Table 6. The acoustical characteristics of chloroacetic acid at 25°C

M	pH	f_r (MHz)	$\mu'_{\max}$ (10^{-4})	v (10^5 cm·sec^{-1})	ρ (g·cm^{-3})
0.50	1.56	180	10.9	1.5079	1.0131
1.00	1.36	200	17.5	1.5175	1.0299

quency range from 15 to 95 MHz. The values of α/f^2 are 31×10^{-17} and 36×10^{-17} cm^{-1}sec^2 in solutions of dichloro- and trifluoroacetic acids respectively, so the f_r values associated with the ionization equilibrium of acid can be expected to be higher than the frequency measured in this work.

Discussion

As can be seen in Table 3, the values of ΔV are in close agreement with those determined from the density measurements by Kauzman and his co-workers.[9] The values of the recombination rate constant, $\sim10^{10}$M^{-1}sec^{-1}, may be of an adequate order of magnitude as the rate of the diffusion-controlled reaction. As for the acetic acid, the values of the parameters may be comparable to those obtained from the ultrasonic absorption measurement by Yeager,[4] $k_r=5.5\times10^{10}$ M^{-1}sec^{-1}, $k_d=1.0\times10^6$ sec^{-1}, and $\Delta V=12.2$ cc·mol^{-1}.

Next, the Taft rule[10] can be applied to the relationship between the rate constants and the polar substituent constants. Taft's equation is given by:

$$\log k = \rho^*\sigma^*$$

where k is the rate constant, ρ^* is the constant characterized by only the type of the reaction, and σ^* is the polar substituent constant. In Fig. 10, the plots of $\log k_d$ and $\log k_r$ against σ^* are presented, together with the values for formic and benzoic acids obtained by Eigen and his co-workers.[2] $\log k_d$ is linearly correlated with σ^*, whereas $\log k_r$ is nearly constant within the experimental error. From the linear relationship between $\log k_d$ and σ^*, ρ^* was determined to be 1.7.

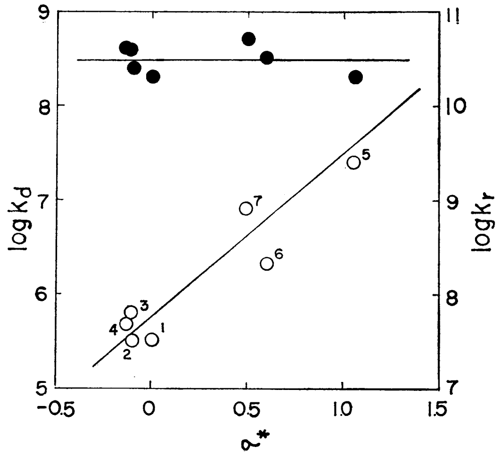

Fig. 10. Plot of $\log k_d$ (open circles) and $\log k_r$ (solid circles) *versus* polar substituent parameter σ^* for the various carboxylic acids. 1: acetic, 2: propionic, 3: butyric, 4: valeric, 5:monochloroacetic, 6: benzoic, 7: formic acids.

The value[11] of ρ^* found in the literature, estimated from the relationship between the ionization equilibrium constants of the carboxylic acids and σ^*, is 1.721 ± 0.025; this is in good agreement with that obtained for the recombination rate constants in the present work. This result suggests that the difference in the values of the equilibrium constants among the various carboxylic acids results not from the recombination rate constant, but from the dissociation rate constant. From these discussions, it can reasonably be concluded that the excess absorptions in dilute aqueous solutions of the carboxylic acids measured in the present work are associated with the perturbation of the ionization equilibrium of acids.

Finally, the kinetic parameters obtained from the ultrasonic absorption measurements of the acetic and propionic acids at various concentrations are listed in Table 5. As is shown in this Table, the rate constants for both the acids may be considered to be independent of the concentration, but the values of ΔV increase with an increase in the concentration of the solutions for each acid. For this result, the following three causes may be considered as the origin of the change in ΔV: 1) the experimental error, 2) the neglect of the activity coefficient, and 3) the change in the state of carboxylic acids in the solutions. The change in ΔV with the concentration, however, is far greater than the effects of 1) and 2). On the other hand, in the case of the ionization reaction of carboxylic acids it seems that the difference in the amount of hydration between the two species gives rise to the volume change, ΔV. The carboxylic acids form dimeric and polymeric molecules by intermolecular hydrogen bonding in concentrated solutions, and become electrically more neutral than the monomeric molecule. Therefore, the amount of hydrating water may decrease in the following order: ionic>monomeric>dimeric molecules, and the volume change between ionic and nonionic molecules may increase with an increase in the concentration. Consequently, the above feature in ΔV seems to result from the 3) effect, although this conclusion cannot be confirmed quantitatively at present.

---

9) W. Kauzman, A. Bodanszky, and J. Rasper, *J. Amer. Chem. Soc.*, **84**, 1777 (1962).

10) R. W. Taft, Jr., *ibid.*, **74**, 2729 (1952).

11) A. L. Henne and C. J. Fox, *ibid.*, **76**, 479 (1954).