Cationic Micellar Effect on the Kinetics of the Protolysis of Aromatic Carboxylic Acids studied by the Ultrasonic Absorption Method

Teruyo Isoda,† Miyuki Yamasaki and Hiroshige Yano*

Daiichi College of Pharmaceutical Sciences, 22-1, Tamagawa-cho, Minami-ku, Fukuoka 815, Japan Takayuki Sano

Department of Materials Science, Faculty of Science, Hiroshima University, Higashi-hiroshima 724, Japan

Shoji Harada

Hiroshima Bunkyo Women's College, Kabehigashi, Asakita-ku, Hiroshima 731-02, Japan

The protolysis of carboxylic acids has been kinetically studied by the ultrasonic absorption method in the presence of tetradecyltrimethylammonium bromide (TTAB) micelles in aqueous solution. The carboxylic acids studied were classified into two categories, one capable of formation of intramolecular hydrogen bond, namely the salicylic acid derivatives (SAD) and the other which cannot form the bond, namely the benzoic acid derivatives (BAD). The rate constant ($\gamma^2 k_f$, k_b), the apparent dissociation constant (K_a), and the volume change of the reaction (ΔV) were obtained. Different K_a dependences of the rate constants observed for SAD and BAD are discussed in relation to the effect of intramolecular hydrogen bond. pK_a dependences were also observed for ΔV of SAD and BAD. These dependences are larger than those in aqueous solution. This result was attributed to the change of arrangement of water molecules around the solute in micellar solution and aqueous solution.

A number of intramolecular hydrogen bonds in the protein are contributing not only to the stabilization of its structure, but also to the control of the reactions of the dissociative groups. We can generally admit that the intramolecular hydrogen bond increases the dissociation of acid¹ and decreases the volume change of the reaction² (ΔV) in aqueous solution. By the ultrasonic absorption method, we have reported that the micelles promote the dissociation of acids and bases, and catalyse their rapid ionization reactions³⁻⁶ in the same manner as in the slow reactions, *e.g.* the hydrolysis of esters, amides, and Schiff bases.⁷⁻⁹ In the present work, we measured the ultrasonic relaxation absorption based on the protolysis of BAD and SAD in TTAB micellar solutions and aimed to examine the effect of intramolecular hydrogen bonds on the rate constants and ΔV in the micellar solution.

Experimental

Benzoic acid (BA), m-nitrobenzoic acid (m-NO2BA), mchlorobenzoic acid (m-ClBA), p-hydroxybenzoic acid (p-OHBA), p-toluic acid (p-CH₃BA), salicylic acid (SA), 4methylsalicylic acid (4-CH₃SA), 5-methylsalicylic acid (5-CH₃SA), 5-chlorosalicylic acid (5-ClSA) and 5-bromosalicylic acid (5-BrSA) purchased from Nakarai and 3-methylsalicylic acid (3-CH₃SA) and 3-hydroxy-4-methylbenzoic acid (3-OH-4-CH₃BA) from Aldrich, and TTAB from Tokyo Kasei were all reagent grade and used without further purification. Ultrasonic absorption measurements were performed with the pulse technique over the frequency range 5-105 MHz. Details of the apparatus have been described elsewhere.¹⁰ The velocity of sound was measured by the sing-around method at 1.92 MHz. Density was measured by a pycnometer. The pH and ultrasonic measurements for the solutions were carried out under a dry nitrogen gas atmosphere. All the measurements were performed at 30.0 °C.

Results and Discussion

The acids used in this work are only slightly soluble in water and the ultrasonic relaxation absorption was not observed even in the saturated solution. When the acids were solubilized in the TTAB micelles, however, the ultrasonic absorption was observed in spite of their low concentrations. All of the spectra were characterized by a single relaxation equation $^{11-13}$

$$\alpha/f^2 = A/\{1 + (f/f_r)^2\} + B \tag{1}$$

where α is the absorption coefficient, f is the frequency, f_r is the relaxation frequency, and A and B are the relaxation and non-relaxation absorptions, respectively. The absorption parameters, f_r , A and B, were determined by a least-squares fit of the experimental data to eqn. (1). Experimental errors were within 9, 6 and 6% of the corresponding values, respectively. Representative ultrasonic absorption spectra are shown in Fig. 1. Experimental conditions and the absorption parameters obtained are summarized in Table 1. The concentration, acidity of acids and pH in the solution, greatly affect the ultrasonic absorption; similar dependences have been observed for the protolysis of carboxylic acids in cationic micellar systems in our previous works.^{3,4} All of the results



Fig. 1 Representative ultrasonic absorption spectra of acid aqueous solution (0.05 mol dm⁻³) in the presence of TTAB (0.30 mol dm⁻³) at 30.0 °C : 3-methylsalicylic acid (\bigcirc , pH = 1.93) and p-methylbenzoic acid (\bigcirc , pH = 2.78)

[†] Née Yamashita.

Table 1 Ultrasonic absorption parameters for various pH of acids (0.05 mol dm⁻³) in the presence of TTAB (0.30 mol dm⁻³) at 30.0 °C

pН	$A/10^{-17} \text{ s}^2 \text{ cm}^{-1}$	$B/10^{-17} \text{ s}^2 \text{ cm}^{-1}$	f _r /MHz	pН	$A/10^{-17} \text{ s}^2 \text{ cm}^{-1}$	$B/10^{-17} \mathrm{s}^2 \mathrm{cm}^{-1}$	f <mark>r</mark> ∕MHz			
w NO BA					5-BrSA					
1.99	45	31	15.0	1.20	29	32	35.6			
1.00	71	30	11.3	1.38	37	31	30.3			
2.04	76	30	10.8	1.60	47	31	26.7			
2.17	63	31	11.6	1.00	44	30	23.5			
2.30	42	31	13.2	2 52	15	30	25.4			
2.57	42	51	15.2	2.52	10	50	23.4			
m-CIBA			5-CISA							
1 80	28	30	13.5	1.19	20	33	35.6			
2.11	44	29	10.5	1.29	29	33	30.0			
2.11	68	29	83	1.42	36	33	25.2			
2.30	08	30	97	1.64	45	32	22.3			
2.00	48	30	12.7	1.94	33	32	20.0			
2.82	29	50	12.7	2.11	26	32	21.4			
D.A				2.35	16	32	23.0			
BA 1.00	17	27	18.0		*					
1.99	22	28	13.0	3-CH35	A	•				
2.23	32	20	10.3	1.11	14	29	43.1			
2.63	46	20	10.5	1.50	53	29	21.0			
3.01	36	28	12.0	1.93	102	31	13.9			
3.30	16	29	10.8	2.33	62	29	14.8			
10114				2.54	36	31	16.8			
3-OH-4-	Сп ₃ ба 17	30	20.0	5-CH-S	A					
2.10	17	32	20.0	1.07	18	31	30.7			
2.67	45	51	11.4	1.54	10	30	20.0			
2.99	44	31	10.5	1.07	42	21	20.0			
3.30	25	31	14.6	1.52	83	21	15.4			
3.54	12	31	21.7	2.27	44	31	15.9			
				2.74	27	30	18.0			
p-OHBA	1	20	20.0	4-CH ₃ S	Α					
2.09	11	30	20.0	1.15	13	31	38.4			
2.23	27	29	12.5	1.57	50	31	20.0			
2.99	46	29	9.4	2.04	94	31	14.5			
3.19	26	30	12.6	2.42	50	30	18.0			
3.39	15	30	16.8	3.21	14	30	25.0			
CIL D				54						
<i>p</i> -CH ₃ B	A 16	20	155	5A 1 22	17	22	22.5			
2.28	10	29	15.5	1.23	1/	32	33.7			
2.49	28	29	11.2	1.01	41	32	21.8			
2.78	48	29	8.5	1.97	88	31	14.6			
3.14	26	28	11.2	2.44	45	30	17.8			
3.39	18	29	13.4	2.72	28	30 ·	20.0			

(3)

mentioned above suggest that the relaxation absorption can be ascribed to the protolysis of carboxylic acid solubilized in the TTAB micelles.

$$\operatorname{RCO}_2^- + \mathrm{H}^+ \xleftarrow[k_b]{k_b} \operatorname{RCO}_2 \mathrm{H}$$
 (I)

where R is incorporated into the micelle core. For reaction (I), the relaxation frequency and the maximum relaxation absorption per wavelength, $(\alpha' \lambda)_{max}$, are expressed by the following equations¹¹⁻¹³

$$2\pi f_{\rm r} = \gamma^2 k_{\rm f} \left\{ \frac{C_0}{K_{\rm a}^{-1} [{\rm H}^+] + 1} + [{\rm H}^+] \right\} + k_{\rm b} \qquad (2)$$
$$(\alpha' \lambda)_{\rm max} = \frac{\pi \rho U^2}{2RT} (\Delta V)^2 \Gamma^{-1} \qquad (3)$$

$$\Gamma = [RCO_2^-]^{-1} + [H^+]^{-1} + [RCO_2H]^{-1}$$
(4)

$$=\frac{K_{a}^{-1}C_{0}[\mathrm{H}^{+}]}{K_{a}^{-1}C_{0}+(K_{a}^{-1}[\mathrm{H}^{+}]+1)^{2}}$$
(5)

where C_0 is the total concentration of acid, α' is the excess absorption coefficient, λ the wavelength, ρ the density, U the sound velocity, ΔV the volume change of the reaction, and the subscript max means the maximum value. When $K_a^{-1}C_0 > 1$ is satisfied, as in the present experiments, these equations predict that the minimum and the maximum of $(2\pi f_r)$ and Γ^{-1} [then $(\alpha'\lambda)_{max}$], respectively, appear at the definite value of pH, i.e. pH*;

$$pH^* = -(\log C_0 + \log K_a)/2$$
 (6)

Since C_0 is known, the value of K_a can be determined from pH*. As shown representatively in Fig. 2 and 3, experimental data are in agreement with eqn. (2) and (3). The values of K_a , $\gamma^2 k_{\rm f}$, $k_{\rm b}$ and ΔV were determined so as to give best fits for the experimental values of $(2\pi f_r)$ and $(\alpha' \lambda)_{max}$. All the values obtained are summarized in Table 2.

As an index of the catalysis, the differences of the pK_a values in aqueous solution and micellar solutions, denoted by $\Delta p K_a$, are listed in Table 2 together with those in the DAC and DPC solutions.⁴ In order to evaluate this, the electrostatic effect and the polarity effect of the micelle should be examined. Since the cationic atmosphere of the micelle stabilizes the carboxylate anion, the electrostatic effect promotes the dissociation of the acids. The polarity of the micelle was evaluated from the ratio of ketonic and enolic forms of benzoylacetoanilide¹⁴ solubilized in the micelles. Fig. 4 shows the UV spectra of benzoylacetoanilide in the micellar solutions together with that in the aqueous solution. This figure shows that the polarity of the micelle is lower than that in water, and the TTAB micelle provides the most hydrophobic field. The decrease of polarity induces the depression of the dissociation, then the two opposite factors affect the pK_a of acid in the TTAB micellar solution. All the $\Delta p K_a$ values are



Fig. 2 Plots of $2\pi f_r$ vs. pH for acid aqueous solution (0.05 mol dm⁻³) in the presence of TTAB (0.30 mol dm⁻³) at 30.0 °C : 3-methylsalicylic acid (\bigcirc) and p-methylbenzoic acid (\bigcirc)



Fig. 3 Plots of $(\alpha'\lambda)_{max}$ vs. pH for acid aqueous solution (0.05 mol dm⁻³) in the presence of TTAB (0.30 mol dm⁻³) at 30.0 °C : 3-methylsalicylic acid (\bigcirc) and p-methylbenzoic acid (\bigcirc)

positive and indicate that the dissociation is promoted in micellar solution, which means that the electrostatic effect is superior to the hydrophobic effect. The largest value of $\Delta p K_a$ in DAC solution is easy to understand from a consideration of the largest electrostatic effect induced by the exposure of the charged centre outside of the Stern layer. The equivalent value of $\Delta p K_a$ in the TTAB and DPC micellar solutions and the superior hydrophobicity in the former, known from the UV spectra, indicates that the electrostatic effect is larger in the TTAB solution.

The acids in this work can be divided into two groups, one capable of formation of intramolecular hydrogen bond, namely the salicylic acid derivatives (SAD) and the other which cannot form a bond, namely the benzoic acid derivatives (BAD). The values of $\Delta p K_a$ of SAD are about two times larger than those of BAD; this can be attributed to the stabilization of CO_2^- by intramolecular hydrogen bond formation in the hydrophobic environment of the TTAB micelle.^{15,16}

Acidity dependences of the rate constants for BAD are plotted in Fig. 5A and the relationships are expressed by eqn. (7) and (8) for the aqueous solution, and eqn. (9) and (10) for the micellar solution.

$$\gamma^2 k_{\rm f}/{\rm dm^3 \ mol^{-1} \ s^{-1}} = 10^{10.6}$$
 (7)

$$k_{\rm b}/{\rm s}^{-1} = 10^{10.6}K_{\rm a} \tag{8}$$

$$\gamma^2 k_{\rm f}/{\rm dm^3~mol^{-1}~s^{-1}} = 10^{8.3} K_{\rm a}^{-0.44}$$
 (9)

$$k_{\rm b}/{\rm s}^{-1} = 10^{8.3} K_{\rm a}^{0.56} \tag{10}$$

In the micellar solution, the rate constants at $pK_a = 0$ are more than two orders of magnitude smaller than that in aqueous solution. This indicates that the TTAB micelle causes the reaction mechanism to vary widely from that in aqueous solution. Another feature is the lack of dependence of $\gamma^2 k_f$ on K_a in aqueous solution while both rate constants are dependent on K_a in micellar solution.

The protolysis of carboxylic acids has often been interpreted by the following mechanism

$$\phi' - \operatorname{CO}_{2}^{-} + \operatorname{H}^{+} \xleftarrow{k_{12}}_{k_{21}} \left[\phi' - \operatorname{C}_{O}^{-} + \operatorname{H}^{+} \operatorname{O}^{+} + \operatorname{O}^{+}_{O} \right]$$
(i)
(i)
(i)
(ii)
(ii)
(iii)
(iii)
(iii)
(iii)

Table 2 Kinetic parameters for the protolysis of acids (0.05 mol dm⁻³) in the presence of TTAB micelle at 30.0 °C

				pK,	ΔpK_{\bullet}		
	$\gamma^2 k_{\rm f} / 10^9 {\rm dm^3 \ mol^{-1} \ s^{-1}}$	$k_{\rm b}/10^6 {\rm s}^{-1}$	$\Delta V/cm^3 mol^{-1}$		ТТАВ	DAC	DPC
BAD							
m-NO,BA	5.1	4.7	11.8	3.03	0.5	1.2	0.4
m-C1BA	6.0	2.4	12.1	3.40	0.4	1.2	0.3
BA	12	1.2	17.3	4.01	0.2	1.2	0.2
3-OH, 4-CH ₃ BA	16	1.0	17.0	4.19	0.2		
p-OHBA	14	0.93	17.8	4.21	0.4		
p-CH ₃ BA	17	0.85	17.0	4.31	0.1		
SAD							
5-BrSA	2.9	36	9.4	1.90	0.7		
5-CISA	2.7	30	8.1	1.94	0.7		
3-CH ₃ SA	3.2	11	12.2	2.44	0.6		
5-CH ₃ SA	3.3	10	11.6	2.49	0.7		
4-CH ₃ SA	3.7	10	12.6	2.56	0.6		
SA	3.9	9.9	12.5	2.60	0.4		



The smaller k_f of SAD compared with eqn. (8) is explained in the following way. The reaction species of the protolysis is the non-bonding CO_2^- group (open form) which is in rapid equilibrium with the bonding one (closed form) as expressed by the following equation.

$$\begin{array}{cccc} \mathbf{RCO}_2^- & \xrightarrow{k_3} & \mathbf{RCO}_2^- & \xrightarrow{\mathbf{H}_1^+ k_t} & \mathbf{RCO}_2\mathbf{H} & (\mathbf{III}) \\ (\mathbf{i}') & (\mathbf{i}) & (\mathbf{ii}) & (\mathbf{ii}) \end{array}$$

where (i') is the closed form and (i) is the open form. Since (i)' \rightleftharpoons (i) is much faster than (i) \rightleftharpoons (ii), the relaxation equation for the overall reaction is given by

$$2\pi f_{\rm r} = \gamma^2 k_{\rm f} \left(\frac{[{\rm H}^+]}{1 + K_{43}} + [{\rm i}] \right) + k_{\rm b}$$
$$= \gamma^2 \left(\frac{k_{\rm f}}{1 + K_{43}} \right) ([{\rm H}^+] + [{\rm i}] + [{\rm i}']) + k_{\rm b}$$
$$= \gamma^2 k_{\rm f}' ([{\rm H}^+] + \Sigma [{\rm RCO}_2^-]) + k_{\rm b}$$
(13)

Here, the value of k_f might be similar to those of ordinary acids and of the order of 10^{10} dm³ mol⁻¹ s⁻¹. Since K_{43} is much larger than 1, however, the apparent rate constant $\gamma^2 k'_f$ becomes much smaller than the rate constant of protolysis of ordinary carboxylic acids.

 K_{a} dependences of the rate constants of SAD in the TTAB micellar solution are plotted in Fig. 5B and given by

$$\gamma^2 k_{\rm f}/{\rm dm^3 \ mol^{-1} \ s^{-1}} = 10^{9.1} K_{\rm a}^{-0.18}$$
 (14)

$$k_{\rm b}/{\rm s}^{-1} = 10^{9.1} K_{\rm a}^{0.82} \tag{15}$$

As seen in the figure, the values of the intercept and the slopes are very close to those in aqueous solution. These results indicate that the reaction mechanism and the energy levels of the protolysis of SAD are not much different from those in aqueous solution; then, in reaction (II), (i) \rightleftharpoons (ii)



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1.0

Fig. 4 Absorption spectra of benzoylacetoanilide in aqueous solution (-----), in the solutions of TTAB (----), DAC (----) and DPC (....)

where (i) \rightleftharpoons (ii) is a diffusion process and (ii) \rightleftharpoons (iii) is a protontransfer process and (ii) is a steady-state intermediate. Since the index of K_a in eqn. (7)-(10) indicates the degree of proton transfer at a transition state,¹⁸ it is concluded that the ratedetermining step is the diffusion process in aqueous solution and the proton-transfer process in micellar solution. These results are similar to those of BAD in DAC and DPC solutions,^{3,4} but the catalytic effect is much larger in TTAB solution.

In the case of SAD, the situation is a little different. Summarizing a small amount of kinetic information on the intramolecular hydrogen bonding acids in aqueous solution,^{19,20} following K_a dependences of the rate constant of SAD were obtained and shown by the dotted line in Fig. 5B.

$$\gamma^2 k_c / \mathrm{dm}^3 \ \mathrm{mol}^{-1} \ \mathrm{s}^{-1} = 10^{9.6}$$
 (11)

$$k_{\rm s}/{\rm s}^{-1} = 10^{9.6}K_{\rm s} \tag{12}$$





Fig. 6 pK_a dependence of ΔV of the ionization of acid in the presence of 0.30 mol dm⁻³ TTAB (\bigcirc , SAD; \bigcirc , BAD system) and in the absence of micelle (\bigcirc , data from ref. 21–23)

might be much slower than (ii) \rightleftharpoons (iii). If this is the case, the K_a dependences of the overall rate constants are expected to be the same as those in the aqueous solution, and the index K_a will be 0 and 1 in eqn. (14) and (15), respectively. Detailed discussion on this problem has been developed in our previous paper.^{3,4}

As seen in Table 2, ΔV is larger in the micellar solution and dependent on K_a as shown in Fig. 6. Similar tendencies have been observed for BAD in DAC and DPC solutions. With increase of pK_{a} , localization of charge density of the carboxylate anion increases and hydration is promoted. While the molar volume might not be greatly affected in the non-ionic form, then ΔV increases with pK_a . Hepler studied the protolysis of acids and amines in aqueous solution and observed a linear relationship between ΔV and ΔS^{24} If this is the case, a linear relationship is expected between ΔV and pK_a and the volume change is mainly attributed to the change of the arrangement of water molecules around the reaction species. The slope of the linear relationship between ΔV and pK_a in TTAB solution is larger than that in aqueous solution; this indicates that the compactness of water molecules around the non-ionic form in the micellar solution decreases compared to it in the aqueous solution.

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