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Kinetic Studies of Intermolecular Hydrogen Bonding in Carboxylic Acids by Means of Ultrasonic Absorption Measurement. II. Halogeno Carboxylic Acids

Takayuki SANO, Nobuhide TATSUMOTO, Yukio MENDE, and Tatsuya YASUNAGA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

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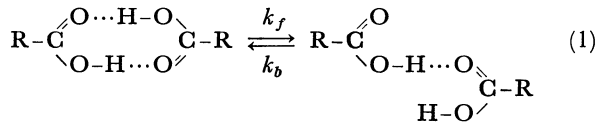
The ultrasonic absorptions in several halogeno carboxylic acids, such as monochloroacetic, dichloroacetic, trichloroacetic, trifluoroacetic, α-chloropropionic, and β-chloropropionic acids, have been measured in the frequency range from 2.5 to 95 MHz. Excess absorptions were observed in all the acids. The kinetic and the thermodynamic parameters based on the equilibrium between the open dimer and the cyclic dimer were calculated. An application of Taft's equation, $\log K=\rho^*\sigma^*+sE_s$, to the results suggests that neither the equilibrium constant nor the rate constant depends on the polarity effect of the alkyl group, but depends mainly on the steric effect, and that the reaction is controlled not only by the enthalpy change, but also by the entropy change.

In a previous paper[1] the mechanism of the ultrasonic absorption in the fatty acids has been attributed to a perturbation of the equilibrium between the cyclic dimer and the open dimer:



(1)

In view of the kinetic and thermodynamic characteristics based on the above reaction for a series of fatty acids, it has been concluded that the cyclic dimer becomes more stable because of an increase in the electron density in the carboxyl group with an increase in the inductive effect of the alkyl group. Since this conclusion has been deduced from the results for the fatty acids with only the hydrocarbon in the alkyl group, more extensive studies seemed desirable. The present study was undertaken in an attempt to confirm more completely this effect for some halogeno carboxylic acids with the help of ultrasonic absorption measurements. Because some halogeno carboxylic acids such as dichloroacetic acid[2] are occasionally used as the solvents of biopolymers, it seemed worthwhile to measure the ultrasonic absorption in halogeno carboxylic acids in order to understand the more complex biochemical and solvent interaction reactions.

Experimental

A pulse technique[3] was used to measure the ultrasonic absorptions in the liquid halogeno carboxylic acids, such as monochloroacetic, dichloroacetic, trichloroacetic, trifluoroacetic, α-chloropropionic, and β-chloropropionic acids, together with trimethylacetic acid in the frequency range from 2.5 to 95 MHz. The velocity of the sound was measured by an ultrasonic interferometer[4] operated at 3.0 MHz and

1) T. Sano, N. Tatsumoto, T. Niwa, and T. Yasunaga, This Bulletin, **45**, 2669 (1972).

2) G. Schwarz, *Ber. Bunsenges. Phys. Chem.*, **68**, 834 (1964).

3) N. Tatsumoto, *J. Chem. Phys.*, **47**, 4561 (1967).

4) T. Yasunaga, H. Oguri, and M. Miura, *ibid.*, **43**, 3512 (1965).

by the sing-around method[5] at 1.92 MHz. In order to observe the dependence of the relaxation frequency, the excess absorption, and other physical properties on the temperature, measurements were made at various temperatures over the melting point: monochloroacetic, 66.3, 70, 74, and 78°C; dichloroacetic, 20, 25, 30, 35, and 40°C; trichloroacetic, 65.4, 69.1, 73, and 77°C; trifluoroacetic, 15, 20, 25, and 30°C; α-chloropropionic, 20, 25, 30, 35, and 40°C; β-chloropropionic, 45, 50, 55, and 60°C; and trimethylacetic acids, 40 and 45°C. All the compounds are deliquescent, so the ultrasonic cell was designed to maintain a sample liquid in an inert and dry atmosphere. The densities were measured by a pycnometer, and the heat capacities, by an adiabatic-type calorimeter. The chemicals used were all of a guaranteed grade and were used without further purification.

Results

The ultrasonic absorption spectra for the monochloro-, dichloro-, trichloro-, trifluoro-, trimethylacetic, α-chloropropionic, and β-chloropropionic acids are shown in Fig. 1. In all these acids except the trimethylacetic acid, excess absorptions were observed. The relaxation spectra can all be represented by a single relaxation formula:

$$\frac{\alpha}{f^2} = \frac{A}{1+(f/f_{max})^2} + B \qquad (2)$$

where α is the ultrasonic absorption coefficient, f is the frequency of sound, f_{max} is the relaxation frequency, and A and B are the excess and classical absorptions respectively.

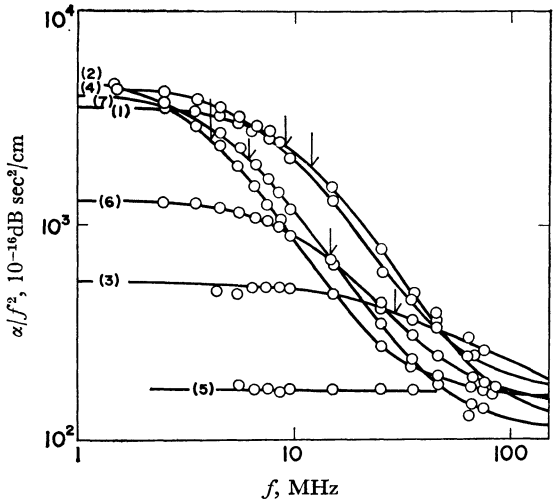


Fig. 1. Ultrasonic absorption spectra in some carboxylic acids: (1): monochloroacetic, 66.3°C; (2): dichloroacetic, 25°C; (3): trichloroacetic, 65°C; (4): trifluoroacetic, 30°C; (5): trimethylacetic, 40°C; (6): α-chloropropionic 25°C; and (7): β-chloropropionic acids, 50°C.

A least-squares computer program is routinely used to evaluate the three parameters, A, B, and f_{max}. The uncertainties in A, B, and f_{max} are approximately ±10, ±5, and ±5% respectively. These values are

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

TABLE 1. THE ACOUSTICAL CHARACTERISTICS OF HALOGENO CARBOXYLIC ACIDS AT THE VARIOUS TEMPERATURES

T (°K)	f_{max} (MHz)	A (10^{-16} dB·sec^2 cm^{-1})	B	$(\alpha'\lambda)_{max}$ (10^{-1} dB)
		Monochloroacetic acid		
339	12	3550	110	2.58
343	14	3301	100	2.77
347	16	2907	110	2.76
351	18	2618	100	2.77
		Dichloroacetic acid		
293	3.3	5300	165	1.10
298	4.1	4800	155	1.23
303	5.0	4400	140	1.36
308	6.1	3900	123	1.46
313	7.5	3500	120	1.60
		Trifluoroacetic acid		
288	6.5	4980	240	1.14
293	7.3	4571	220	1.15
298	8.1	4240	220	1.16
303	9.0	4293	164	1.27
		α-Chloropropionic acid		
293	12	1250	162	0.915
298	14.5	1150	145	1.00
303	17	1050	130	1.06
308	20	960	115	1.13
313	23	890	95	1.19
		β-Chloropropionic acid		
318	5.5	4400	130	1.51
323	6.0	4100	110	1.52
328	6.7	3950	110	1.61
333	7.3	3670	110	1.62

TABLE 2. THE THERMODYNAMIC PARAMETERS FOR THE HALOGENO CARBOXYLIC ACIDS

T (°K)	u (10^5 cm sec^{-1})	ρ (g cm^{-3})	l (10^{-4} deg^{-1})	C_p^0 (cal g^{-1}· deg^{-1})
		Monochloroacetic acid		
339	1.2117	1.4043	9.670	0.479
343	1.2009	1.3982	9.670	0.479
347	1.1901	1.3921	9.670	0.479
351	1.1793	1.3860	9.670	0.479
		Dichloroacetic acid		
293	1.2682	1.2963	9.780	0.382
298	1.2556	1.2902	9.780	0.382
303	1.2433	1.2841	9.780	0.382
308	1.2321	1.2780	9.780	0.382
313	1.2213	1.2720	9.780	0.382
		Trifluoroacetic acid		
288	0.7074	1.5031	7.219	0.464
293	0.6918	1.4905	7.219	0.464
298	0.6762	1.4788	7.219	0.464
303	0.6606	1.4670	7.219	0.464
		α-Chloropropionic acid		
293	1.2201	1.5633	6.469	0.350
298	1.2076	1.5583	6.469	0.350
303	1.1941	1.5535	6.469	0.350
308	1.1793	1.5486	6.469	0.350
313	1.1654	1.5436	6.469	0.350
		β-Chloropropionic acid		
318	1.2482	1.1822	10.25	0.555
323	1.2343	1.1776	10.25	0.555
328	1.2201	1.1730	10.25	0.555
333	1.2061	1.1684	10.25	0.555

listed in Table 1. On the other hand, in the trimethylacetic acid the value of α/f^2 remains constant at 165×10^{-16} dB sec^2/cm in the frequency range from 3.5 to 85 MHz, and the temperature dependence of the excess absorption in the trichloroacetic acid can not be measured because of the high relaxation frequency. The other values required for the calculation of the kinetic and thermodynamic parameters (*e.g.*, the sound velocity, u; the density, ρ; the thermal expansion coefficient, l, and the heat capacity at a constant pressure, C_p) are listed in Table 2. The experimental errors in u, ρ, l, and C_p are approximately ±0.01, ±0.05, ±0.5, and $\pm10\%$ respectively.

If the same type of reaction, which does not accompany any volume change, as that reported previously in the case of the fatty acids is considered to be the origin of the excess absorptions in the acid studied in this report, the reaction type can be given by:

$$A \underset{k_b}{\overset{k_f}{\rightleftarrows}} B \tag{3}$$

and the kinetic and thermodynamic parameters can be given by equations:

$$K = \frac{k_f}{k_b} \tag{4}$$

$$2\pi f_{max} = k_f + k_b \tag{5}$$

$$C_v^r = C_p^r = \frac{(\Delta H)^2}{RT^2}\cdot\frac{K}{(1+K)^2} \tag{6}$$

$$K = \exp(-\Delta G/RT) \tag{7}$$

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

$$\frac{\partial \ln (k_i/T)}{\partial(1/T)} = -\frac{\Delta H_i^*}{R} \tag{9}$$

where K is the equilibrium constant, and where k_f and k_b are the forward and backward rate constants respectively. C_v^r and C_p^r are the relaxation heat capacities at a constant volume and a constant pressure respectively. ΔH is the heat of reaction; ΔG, the free energy, and ΔS, the entropy of reaction. k_i represents k_f or k_b, and ΔH_i^* is the heat of activation. The kinetic and thermodynamic parameters were calculated from Eqs. (4)—(9). However, the kinetic values, such as K, k_f, and k_b, cannot be compared directly with those of other cmpounds because the measurements had to be done at various temperatures over the melting point. Consequently, the kinetic parameters at 30°C are estimated by extrapolations of K, k_f, and k_b respectively *vs.* the temperature; they are listed in Table 3. The errors are approximately $\pm20\%$ in K, ΔG, ΔH, and ΔS, ±5 and $\pm10\%$ in k_b and ΔH_b^*, and ±10 and $\pm20\%$ in k_f and ΔH_f^*.

Discussion

As can be seen in Fig. 1, the halogeno carboxylic acids studied in the present paper show an ultrasonic absorption similar with regard to the position of the relaxation frequency and the magnitude of B to that in the fatty acids reported in the previous paper. This suggests that the ultrasonic absorptions in the halogeno carboxylic acids are associated with the same type of reaction as in the fatty acids.

In order to confirm the polarity effect of the alkyl group on Reaction (1), the following Taft's equation was used:

$$\log K_i = \rho_i^*\sigma^* + s_iE_s \tag{10}$$

where K_i is the rate constant or equilibrium constant, where σ^* and E_s are the polarity and steric parameters respectively, where ρ_i^* and s_i are the proportionality constants and depend only on the type of reaction, and where the subscript i represents K or k_b. The plots of $\log K$ against σ^* and E_s are represented in Figs. 2 and

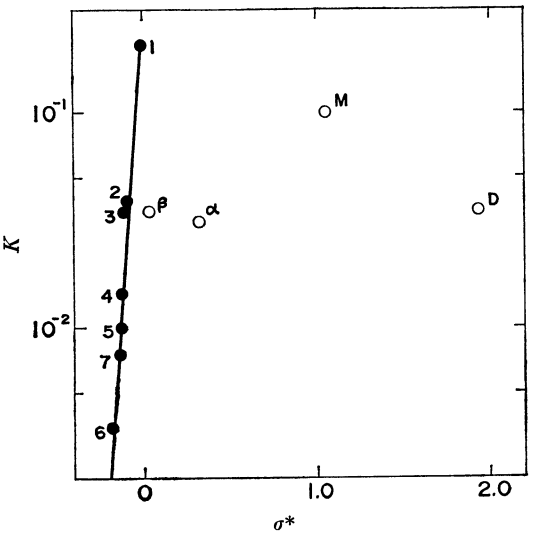


Fig. 2. The plot of ln K against σ^* for a series of carboxylic acids along with the aliphatic acids. Symbols identify the compounds corresponding to individual point as follows: (1): acetic; (2): propionic; (3): butyric; (4): valeric; (M): monochloroacetic; (D): dichloroacetic; (T), trifluoroacetic; (α): α-chloropropionic; and (β): β-chloropropionic acids. These symbols are used in the same way hereafter.

Table 3. The kinetic parameters for a series of carboxylic acids at 30°C

	K (10^{-2})	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/deg)	k_b (10^7/sec)	ΔH_b^* (kcal/mol)	k_f (10^5/sec)	ΔH_f^* (kcal/mol)
Acetic acid[a)]	21.9	0.95	2.7	5.9	0.47	8.9	10.3	~12
Monochloroacetic acid	9.8	1.4	2.9	4.9	1.4	7.1	11.5	~10
Dichloroacetic acid	0.75	1.5	3.6	6.7	10	5.5	7.45	~ 9
Trifluoroacetic acid	1.7	1.0	2.9	6.0	4.8	3.4	8.2	~ 7
Propionic acid[b)]	3.3	2.0	4.3	7.3	1.7	6.8	5.9	~11
α-Chloropropionic acid	3.2	3.4	4.4	7.7	3.1	7.7	10	~12
β-Chloropropionic acid	3.5	2.0	3.9	6.3	2.6	3.9	9.1	~11

a), b) The values calculated from data in leteratures.

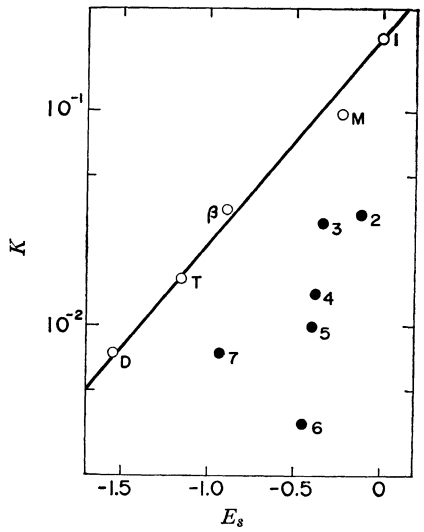


Fig. 3. The plot of ln K against E_s.

3 respectively, along with that of the fatty acids obtained in the previous report. The values of σ^* and E_s are found in the literature.[6] In Fig. 2, it can be seen that the relationship between log K and σ^* is linear in the case of the fatty acids, but is not linear in that of the halogeno carboxylic acids. With respect to the relationship between log K and E_s in Fig. 3, the halogeno carboxylic acids give a better straight line than the fatty acids. The value of s_K for the equilibrium constant calculated from the plot is 0.954. As to the relationships between log k_b and σ^* and E_s, similar explanations can also be given from Figs. 4 and 5. The value of s_{k_b} for the rate constant is calculated to be −0.869. Therefore, it can be deduced that both K and k_b depend mainly on the steric effect of the alkyl group in halogeno carboxylic acids; this is in contrast with the case of fatty acids.

Moreover, it can be seen in Table 3 that the relationship between log K and ΔH and that between log k_b and $\Delta H_b^{\neq}$ are not linear. Though the results are unfortunately, inconsistent with our expectations with regard to the behavior of the kinetic values, the difference may be ascribed to the large size of the halogen atom; that is, the substitution of the large halogen atoms for the hydrogen atom in the alkyl group of the acids may lead to an intermolecular steric interaction rather than to an intramolecular electrostatic effect. Because the relationship between log K and ΔS is also not linear, as can be seen in Table 3, it can be deduced that the reaction in the halogeno carboxylic acids is controlled not only by the enthalpy change, but also by the entropy change.

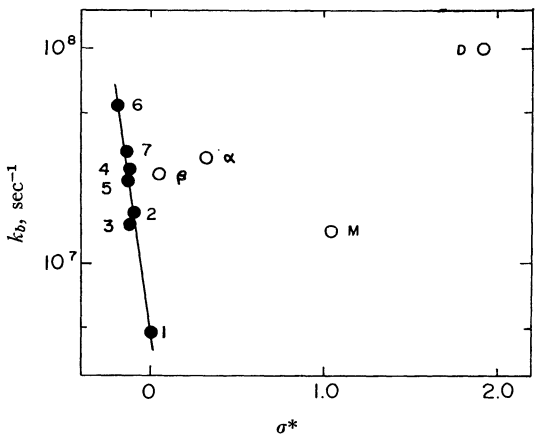


Fig. 4. The plot of ln k_b against σ^*.

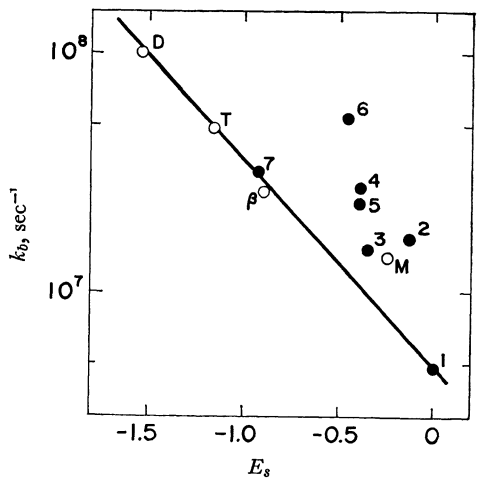


Fig. 5. The plot of ln k_b against E_s.

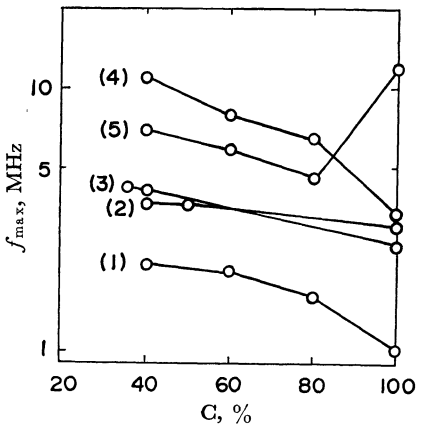


Fig. 6. The plot of the relaxation frequency against volume percent of the some carboxylic acids in dioxane solutions: (1): acetic; (2): propionic; (3): butyric; (4): dichloroacetic; and (5): α-chloropropionic acids.

In order to observe only the abnormal behavior of the relaxation frequency in solutions, ultrasonic absorption measurements were carried out in dioxane solutions of some carboxylic acids, such as acetic, propionic, butyric, dichloroacetic, and α-chloropropionic acids. The results are shown in Fig. 6. In all the acids, the relaxation frequencies shift to the higher-frequency side with a decrease in the concentration; they do this in spite of the existence of a concave point in the case of the α-chloropropionic acid. This fact may support the suggestion that the ultrasonic absorption mechanism in the halogeno carboxylic acids is the same reaction as in the fatty acids. From the above discussion and the quite recent investigations by

6) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 2729 (1952); R. W. Taft, Jr., *ibid.*, **75**, 4538 (1953).

Corsaro and Atkinson,[7,8] it is reasonable to conclude that the excess absorptions in the series of carboxylic acids studied in this and previous papers are to be attributed to the perturbation of the equilibrium between the cyclic dimer and the open dimer, and also that the reaction in the case of the halogeno carboxylic acids depends mainly on the steric effect rather than on the polarity effect of the alkyl group, and that it is controlled by both the enthalpy and the entropy changes. While it might be interesting to study the cause of the concave point in the α-chloropropionic acid, visible in Fig. 6, the investigation of such a solvent effect is beyond the scope of this discussion.

Finally, the presence of other excess absorptions is to be expected in the higher-frequency ranges over 100 MHz, because the carboxylic acids studied in this and previous papers all have similar values greater than about 100×10^{-16} dB·sec²/cm of the classical absorption; B. Thus, the ultrasonic absorption measurements over a wider frequency range, and the interpretation of the overall absorptions, will lead to a final solution of the problem of the ultrasonic absorption in the carboxylic acids.

7) R. D. Corsaro and G. Atkinson, *J. Chem. Phys.*, **54**, 4090 (1971).
8) R. D. Corsaro and G. Atkinson, *ibid.*, **55**, 1971 (1971).