TABLE III: Calculated Barrier Heights (kcal/mol) for SiH₃ + SiH₄

				MP-SAC2		MP-SAC4		
basis	HF	MP2	MP4	SiH	A2	SiH	A2	
6-31G(d)	22.0	16.4	15.2	9.6	10.6	9.6	9.4	-
6-31G(d,p)	21.5	16.0	15.2	13.6	13.5	14.0	13.2	
6-31G(2d,p)	22.5	16.1	15.2	13.5	13.7	13.9	13.4	
6-31G(d,2p)	21.2	14.6	13.6	13.0	а	13.4	а	
MC-311G(d,p)	21.2	15.0	а	13.0	12.9	а	а	

^aNot available.

polarization functions should be included on hydrogens.

Table III shows reasonably consistent barrier heights at the MP-SACn level from all basis sets with polarization functions on hydrogens. The results are not very sensitive to other details of the basis set or to which choice is made for \mathcal{F}_n . In addition there is much better agreement between the MP-SAC2 and MP-SAC4 barrier heights than between those calculated by the MP2 and MP4 methods. The predicted barrier height is in the range 13.4 \pm 0.6 kcal/mol for all these calculations. These calculations indicate good convergence both with respect to the level of perturbation theory and the number of polarization functions and also with respect to expanding the valence basis from double ζ to triple ζ . The results are very suggestive that the MP-SAC2 calculations are more reliable than MP4 calculations and equally as reliable as MP-SAC4 calculations with the same basis set, although the MP-SAC2 results are much less expensive. The barrier calculated by the MP-SAC2 method with the largest basis set and the Si-H value of \mathcal{F}_2 is 13.0 kcal/mol.

The MP-SACn option for energies, geometries, and frequencies⁶ has been added to the GAUSSIAN829 program at North Dakota State University and at the Minnesota Supercomputer Center, and to the GAUSSIAN86¹⁰ program at San Diego Supercomputer Center,11 and it should not be very difficult to implement in other versions of the GAUSSIAN programs. We hope that the conclusions about basis sets and \mathcal{F}_n values given in the present paper will be useful for studying a wide variety of reactions.

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Registry No. H, 12385-13-6; Si, 7440-21-3; P, 7723-14-0; S, 7704-34-9; Cl, 22537-15-1; SiH₃, 13765-44-1; SiH₄, 7803-62-5.

(9) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Krishnan, R.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN82; Carnegie-Mellon University: Pittsburgh, 1983. (10) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavarchari, K.;

Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Topiol, S.; Pople, J. A. GAUSSIANS86; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA 15213.

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Ultrasonic Absorption Study of the Complex Formation of Zinc(II) Carboxylates in **Aqueous Solution**

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Ultrasonic absorption of aqueous zinc(II) formate, acetate, and propionate is measured in the metal-rich concentration regions with a pulse technique over the frequency range 3-260 MHz. The single relaxations observed in all cases are attributed to the complex formation of zinc(II) carboxylates via the Eigen-Tamm mechanism of stepwise association. The reaction parameters are determined from the concentration dependences of the relaxation frequency and amplitude. Both the association constant of outer-sphere complex and the rate constant of ligand substitution indicate ligand dependences; the former is larger while the latter is smaller with the higher carboxylate. However, the uncertainties involved in these reaction parameters prevent the elucidation of the above feature. The volume changes of the outer-sphere complexing are substantially less than those of the ligand substitution; the volume change of the latter is larger for the higher carboxylate.

Introduction

Thanks to the development of relaxation kinetics,¹ considerable information on the association behavior of labile metal ions with various ligands has now accumulated.^{2,3} The experimental results have almost been well interpreted by the stepwise complexation mechanism proposed by Eigen and Tamm.² It consists of rapid formation of an outer-sphere complex and the subsequent ligand substitution for a water molecule coordinated to the metal to form the inner-sphere complex; thus, the substitution rate is controlled by the rate of the water liberation from the metal.

In previous papers,^{4,5} we have reported that the ultrasonic absorption of aqueous zinc(II) thiocyanate can well be interpreted

virtually by a single-step complexation mechanism while that of cadmium(II) thiocyanate by the two-step association mechanism. Encountering somewhat puzzling results, we have felt that further investigations are necessary on the association behavior of zinc ion with the other ligands. In earlier ultrasonic absorption studies,⁶⁻⁹ particular interest has been directed to those on zinc(II) sulfate, where one to three relaxation peaks found in the spectra were interpreted by the two- or three-step association mechanism. However, the investigations have come to substantially different conclusions as to the rate of ligand substitution on the metal ion. Unfortunately, lack of data with other techniques like rate of solvent exchange by NMR makes it difficult to properly assess the above results.

⁽¹⁾ Eigen, M.; De Maeyer, L. In *Technique of Organic Chemistry*, 2nd ed.; Friess, S. L., Lewis, E. S., Weissberger, A., Eds.; Wiley-Interscience: New York, 1963; Vol. VIII, Part 2, Chapter 18.

⁽²⁾ Eigen, M.; Wilkins, R. G. Adv. Chem. Ser. 1964, No. 49, 55.

⁽³⁾ Hewkin, D. J.; Prince, R. H. Coord. Chem. Rev. 1970, 5, 45.

⁽⁴⁾ Tamura, K. J. Chem. Phys. 1985, 83, 4539.
(5) Tamura, K. J. Phys. Chem. 1987, 91, 4596.

⁽⁶⁾ Maass, G. Z. Phys. Chem. (Frankfurt) 1968, 60, 138.

⁽⁷⁾ Hemmes, P.; Fittipaldi, F.; Petrucci, S. Acustica 1969, 21, 228. Fittipaldi, F.; Petrucci, S. J. Phys. Chem. 1967, 71, 3414.
(8) Fritsch, K.; Montrose, C. J.; Hunter, J. L.; Dill, J. F. J. Chem. Phys. 1970, 52, 2242

⁽⁹⁾ Bechtler, A.; Breitschwerdt, K. G.; Tamm, K. J. Chem. Phys. 1970, 52, 2975.



Figure 1. Ultrasonic absorption spectra of aqueous zinc(II) formate solutions, at 25 °C and I = 2 M. The number in parentheses corresponds to the sample number in Table I. The solid curves are the calculated single-relaxation curves. The arrows indicate the relaxation frequencies.

Therefore, it appears most important at present to obtain certain information on the rate of ligand substitution on zinc ion and also to examine the dependence of the rate on the nature of the ligand. For the above purpose, we studied in this work ultrasonic absorption of aqueous zinc(II) formate, acetate, and propionate. The complexation kinetics of zinc(II) acetate has already been reported by Maass⁶ in his ultrasonic absorption studies, but with limited ranges of frequency and concentration. Therefore, it may also be interesting to study the system in more detail. As has been demonstrated already,⁵ the experiments over a wide concentration range will enable us to determine the reaction parameters solely from the concentration dependences of the absorption parameters and thus will provide us with the unambiguous result.

Experimental Section

All chemicals used were of reagent grade. Sample solutions were prepared by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ and the corresponding sodium carboxylate, i.e., HCO_2Na , $CH_3CO_2Na \cdot 3H_2O$, or $C_2H_5CO_2Na$, in distilled water. The ionic strength, *I*, of the solutions was kept at 2 M by the addition of NaNO₃. The pH of the solutions was adjusted with HNO₃ and/or NaOH.

The ultrasonic absorption was measured by the pulse technique over the frequency range 3-260 MHz and the velocity of sound at 3 MHz. The methods of measurements are similar to those described previously.⁴ The frequencies of sound were calibrated with a Hewlett-Packard electronic counter, Model 5345A. The absorption coefficient at each frequency was determined by the average of at least three measurements; the experimental errors were within $\pm 2\%$.

All the measurements were carried out at 25.00 ± 0.05 °C.

Results and Data Treatment

Table I shows the experimental conditions together with the density ρ and the velocity of sound c. Here, $\sum Zn$ and $\sum X$ denote the stoichiometric concentrations of zinc(II) and carboxylate ions, respectively. As shown in Table I, the experiments were carried out in the concentration range of $\sum Zn = 0.1-0.8$ M and $\sum X =$ 0.1–0.4 M, where the concentration ratio $\sum Zn / \sum X$ was selected as high as possible for minimizing the formation of higher complexes. The pH of the solutions lies in the range from 4 to 6, whereas most of the experiments were carried out at pH 5. The above pH range was adopted for ruling out the absorption due to the protonation reaction of carboxylate ions and also for avoiding the hydrolysis of zinc ion.¹⁰ Preliminary experiments confirmed that blank solutions of either zinc nitrate or sodium carboxylates showed no discernible relaxation effect in the observed frequency range 15-260 MHz. Thus, the relaxation absorptions, observed in all solutions containing zinc and carboxylate ions, are really attributable to zinc(II)-carboxylate interactions.



Figure 2. Ultrasonic absorption spectra of aqueous zinc(II) acetate solutions, at 25 °C and I = 2 M. The notations and remarks are the same as in Figure 1.



Figure 3. Ultrasonic absorption spectra of aqueous zinc(II) propionate solutions, at 25 °C and I = 2 M. The notations and remarks are the same as in Figure 1.

Representative sound absorption spectra are shown in Figures 1-3. All the absorption spectra can be expressed by the single-relaxation equation

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f/f_{\rm r})^2} + B \tag{1}$$

where α is the absorption coefficient and f the frequency of sound; f_r and A are the relaxation frequency and amplitude, respectively; B is the high-frequency value of α/f^2 . The absorption parameters f_r, A, and B were determined by fitting the data to eq 1 with a least-squares routine⁵ and are listed in Table I.

According to the equilibrium studies,¹¹⁻¹³ the following reaction equilibria exist in solution under the present experimental conditions

$$HX \rightleftharpoons H + X \qquad K_{\rm H} \tag{2}$$

$$MX_{n-1} + X \rightleftharpoons MX_n \qquad K_n \quad (n = 1-3)$$
 (3)

where H, M, and X denote hydrogen, zinc, and carboxylate ions, respectively; the charges of the ions are omitted for simplicity. The $K_{\rm H}$ is the dissociation constant of carboxylic acid, and K_n 's (n = 1-3) are the equilibrium constants for the successive com-

⁽¹⁰⁾ Barnum, D. W. Inorg. Chem. 1983, 22, 2297.

⁽¹¹⁾ Perrin, D. D. Stability Constants of Metal-Ion Complexes; Pergamon Press: New York, 1983; Part B.

⁽¹²⁾ Filipovic, I.; Matusinovic, T.; Mayer, B.; Piljac, I.; Bach-Dragutinovic, B.; Bujak, A. Croat. Chem. Acta 1970, 42, 541.

⁽¹³⁾ Portanova, R.; Tomat, G.; Cassol, A.; Magon, L. J. Inorg. Nucl. Chem. 1972, 34, 1685.

TABLE I: Experimental Conditions and Ultrasonic Absorption Parameters^a for Aqueous Zinc(II) Carboxylate Solutions at 25 °C and I = 2.0 M

sample					<u> </u>		10 ¹⁷ A.	10 ¹⁷ B.
no.	$\sum Zn, M$	ΣX, M	pН	ρ , g cm ⁻³	<i>c</i> , m s ^{−1}	$f_{\rm r}$, MHz	$cm^{-1} s^2$	$cm^{-1}s^2$
				Forma	te			
1	0.100	0.100	5.02	1.1058	1576	7.9 ± 1.0	75 ± 13	22.2 ± 0.4
2	0.200	0.100	5.01	1.1076	1578	7.8 ± 0.6	120 ± 11	22.5 ± 0.4
3	0.200	0.200	5.00	1.1098	1579	9.2 ± 0.5	191 ± 12	23.4 ± 0.4
4	0.300	0.200	5.00	1.1124	1569	10.4 ± 0.4	185 ± 8	24.1 ± 0.3
5	0.400	0.200	4.00	1.1118	1559	10.1 ± 0.5	185 ± 10	24.5 ± 0.4
6	0.400	0.200	5.00	1.1121	1560	11.0 ± 0.6	180 ± 10	24.5 ± 0.5
7	0.400	0.200	5.80	1.1112	1558	10.9 ± 0.5	183 ± 9	24.5 ± 0.5
8	0.500	0.200	5.00	1.1122	1557	11.2 ± 0.4	172 ± 7	25.9 ± 0.4
9	0.600	0.150	5.00	1.1093	1546	11.1 ± 0.8	130 ± 10	25.6 ± 0.4
10	0.600	0.200	5.00	1.1111	1545	11.3 ± 0.5	178 ± 8	25.8 ± 0.5
11	0.700	0.200	4.99	1.1126	1541	12.4 ± 0.5	160 ± 7	26.0 ± 0.4
12 ^b	0.800	0.200	5.00	1.1263	1546	14.2 ± 0.8	135 ± 7	26.2 ± 0.5
13°	0.800	0.400	5.01	1.1350	1549	13.3 ± 0.6	319 ± 13	30.0 ± 0.8
				Aceta	te			
14	0.100	0 100	5.00	1.1052	1578	4.6 ± 0.2	592 ± 35	22.7 ± 0.3
15	0.200	0.100	5.00	1,1060	1568	5.9 ± 0.2	563 ± 24	22.6 ± 0.3
16	0.200	0.200	5.00	1.1077	1572	6.3 ± 0.3	1070 ± 60	24.2 ± 0.6
17	0.300	0.100	5.00	1.1059	1563	6.4 ± 0.2	563 ± 22	23.4 ± 0.3
18	0.400	0.100	4.00	1.1040	1557	7.6 ± 0.4	237 ± 18	23.4 ± 0.3
19	0.400	0.100	5.00	1.1053	1554	7.5 ± 0.2	479 ± 19	23.7 ± 0.4
20	0.400	0.100	5.69	1.1078	1559	7.5 ± 0.2	494 ± 20	24.5 ± 0.4
21	0.400	0.200	4.08	1.1042	1553	7.7 ± 0.3	524 ± 23	24.1 ± 0.4
22	0.400	0.200	5.00	1.1092	1560	7.9 ± 0.3	932 ± 50	25.5 ± 0.7
23	0.500	0.100	5.00	1.1051	1547	7.8 ± 0.3	459 ± 19	24.5 ± 0.4
24	0.600	0.100	5.00	1.1046	1539	8.4 ± 0.2	422 ± 11	24.9 ± 0.3
25	0.600	0.200	5.00	1.1084	1543	8.9 ± 0.3	804 ± 28	27.3 ± 0.5
26 ^b	0.800	0.100	5.00	1.1217	1541	9.7 ± 0.3	336 ± 11	25.7 ± 0.4
27 ^b	0.800	0.200	5.00	1.1247	1546	10.0 ± 0.2	657 ± 17	28.3 ± 0.5
				Propior	nate			
28	0.100	0.100	5.00	1.1069	1580	4.3 ± 0.1	724 ± 28	22.8 ± 0.2
29	0.200	0.100	5.00	1.1081	1579	4.7 ± 0.2	926 ± 48	24.3 ± 0.3
30	0.300	0.100	5.00	1.1072	1568	5.7 ± 0.1	770 ± 23	23.9 ± 0.2
31	0.400	0.100	4.00	1.1053	1562	6.6 ± 0.3	322 ± 18	23.5 ± 0.3
32	0.400	0.100	5.00	1.1078	1560	6.1 ± 0.2	762 ± 29	24.8 ± 0.3
33	0.400	0.100	5.88	1.1070	1559	6.7 ± 0.2	753 ± 26	24.7 ± 0.3
34	0.400	0.200	5.00	1.1122	1563	6.8 ± 0.2	1350 ± 56	26.5 ± 0.5
35	0.600	0.100	5.00	1.1065	1543	7.4 ± 0.2	596 ± 20	25.7 ± 0.3
36	0.600	0.200	5.00	1.1109	1554	7.9 ± 0.1	1140 ± 24	27.6 ± 0.3
375	0.800	0.100	5.00	1.1227	1543	7.9 ± 0.2	538 ± 15	26.5 ± 0.3
38*	0.800	0.200	5.00	1.1250	1549	8.6 ± 0.2	993 ± 27	28.7 ± 0.4

^a The error interval denotes the 99.7% confidence area. ${}^{b}I = 2.3$ M. ${}^{c}I = 2.2$ M.

TABLE II: Reaction Parameters^a for the Formation of Zinc(II) Carboxylates at 25 °C and I = 2.0 M^b

ligand	K ₁₂	K ₂₃	$10^{-7}k_{23}, s^{-1}$	$10^{-7}k_{32}$, s ⁻¹	ΔV_{12} , cm ³ mol ⁻¹	ΔV_{23} , cm ³ mol ⁻¹
HCO ₂ -	1.1 ± 0.6	3.6 ± 2.8	11.8 ± 7.0	3.3 ± 0.6	0.2 ± 2.4	4.7 ± 1.7
$C_{1}C_{2}C_{2}C_{2}^{-}$	1.2 ± 0.3 1.8 ± 0.8	4.7 ± 2.3 4.5 ± 2.5	9.1 ± 3.3 6.7 ± 2.5	1.9 ± 0.3 1.5 ± 0.3	-0.2 ± 2.9	10.5 ± 2.1

^aThe error intervals denote 99.7% confidence area. ^bThe equilibrium constants used are the following: $pK_H = 3.56$ (ref 13), $K_1 = 5.0 \pm 0.3$, $K_2 = 2.4 \pm 0.6$, and $K_3 = 1.3 \pm 0.5$ (ref 12), for the zinc(II) formate system; $pK_H = 4.59$ (ref 13), $K_1 = 7.0 \pm 0.6$, and $K_2 = 3.3 \pm 0.4$ (ref 12), for the zinc(II) acetate system; $pK_H = 4.73$ (ref 13), $K_1 = 9.9 \pm 0.7$, $K_2 = 0.93 \pm 0.55$, and $K_3 = 15 \pm 9$ (ref 12), for the zinc(II) propionate system; the error intervals denote the standard errors. The pK_H values are those at 20 °C and I = 1 M.

plexation equilibria. The values of K_n 's used in this study are those by Filipovic et al.¹² obtained from the potentiometric studies and are given, together with the pK_H values,¹³ in the footnote of Table II. The results of the equilibrium analysis¹⁴ confirm that the concentrations of only species M, X, and MX are of reasonable order of magnitude over all concentration ranges studied. Therefore, the relaxation absorptions under study can be ascribed mainly to the complexation equilibria of n = 1 in eq 3. If one adopts the Eigen-Tamm mechanism of stepwise association,² the complexation reactions are described as

$$M + X \frac{k_{12}}{k_{21}} M(OH_2) \cdot X \frac{k_{23}}{k_{32}} MX$$
(4)

where $M(OH_2)$ ·X and MX denote the outer-sphere and innersphere complexes, respectively. In the above mechanism, the first step represents the diffusion-controlled formation of an ion pair with the metal ion and ligand still separated by one water molecule. The second step represents the substitution of one of the water molecules in the inner coordination sphere of the metal by the ligand and corresponds to the rate-determining step of the complexation.

The relaxation frequency f_r for the above scheme is given by

$$2\pi f_{\rm r} = k_{23} \left\{ \frac{K_{12}([{\rm M}] + [{\rm X}])}{1 + K_{12}([{\rm M}] + [{\rm X}])} + \frac{1}{K_{23}} \right\}$$
(5)

where the square brackets indicate molar concentrations at equilibrium. The quantities K_{12} (= k_{12}/k_{21}) and K_{23} (= k_{23}/k_{32}) are the equilibrium constants of the first- and second-step reactions, respectively, of eq 4 and are related to the complex formation

⁽¹⁴⁾ The hydrogen ion concentration was calculated by the equation [H] = $10^{\text{pH}}/0.86$, where the denominator is the mean activity coefficient of 2 M HNO₃ solution at 25 °C [Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1959; p 491].



Figure 4. Concentration dependence of f_r for aqueous zinc(II) carboxylate solutions, at 25 °C and I = 2 M: (**①**) formate; (**O**) acetate; (**●**) propionate.

constant K_1 as $K_1 = K_{12}(1 + K_{23})$. The protolytic reaction of the carboxylate ions reaches equilibrium much faster than the metal-complex reaction,^{15,16} and it can be assumed to be in equilibrium at all times. However, the contribution of this equilibrium to the relaxation effect can be ruled out under the experimental conditions studied,¹⁷ and thus this effect has been ignored in eq 5. The inner-sphere formation constant K_{23} in eq 5 can be determined from the relation $K_{23} = K_1/K_{12} - 1$, with the known value of the complexation constant K_1 and an assumed value of the outersphere association constant K_{12} . Thus, the observed f_r was fitted to eq 5 by using K_{12} and k_{23} as adjustable parameters. The results for the three reaction systems are shown in Figure 4. Each of the straight lines in the figure expresses the calculated f_r , which agrees well with the observed f_r in the entire concentration range studied; the rms percentage deviations between the calculated and observed values of f_r are 5.9, 4.6, and 5.2 for the formate, acetate, and propionate systems, respectively. The reaction parameters determined are shown in Table II.

The maximum excess absorption per wavelength, $\mu_{\rm m}$ (=cAf_r/2), for the reaction scheme is expressed by⁵

$$\mu_{\rm m} = \frac{\pi\Gamma}{2RT\beta_{\rm s}} \left\{ \frac{\Delta V_{12}}{1 + K_{12}([{\rm M}] + [{\rm X}])} + \Delta V_{23} \right\}^2 \qquad (6)$$

where R is the gas constant, T the absolute temperature, and β_s the adiabatic compressibility of the solution; ΔV_{12} and ΔV_{23} are the reaction volume changes of the first and second steps, respectively, of eq 4. The Γ term represents the following quantity:

$$\Gamma = K_{12}[M][X] \left\{ \frac{K_{12}([M] + [X])}{1 + K_{12}([M] + [X])} + \frac{1}{K_{23}} \right\}^{-1}$$
(7)

The observed $\mu_{\rm m}$ was fitted to eq 6 by using ΔV_{12} and ΔV_{23} as adjustable parameters. The results are shown in Figures 5 and 6 with the plots of $(2RT\beta_s\mu_m/\pi\Gamma)^{1/2}$ vs $\{1 + K_{12}([M] + [X])\}^{-1}$. The straight lines express the calculated μ_m 's. The rms percentage deviations between the calculated and observed values of μ_m are



Figure 5. $(2RT\beta_{s}\mu_{m}/\pi\Gamma)^{1/2}$ vs $\{1 + K_{12}([M] + [X])\}^{-1}$ plot for aqueous zinc(II) formate and acetate solutions, at 25 °C and I = 2 M: (**0**) formate; (O) acetate.



Figure 6. $(2RT\beta_{s}\mu_{m}/\pi\Gamma)^{1/2}$ vs $\{1 + K_{12}([M] + [X])\}^{-1}$ plot for aqueous zinc(II) propionate solution, at 25 °C and I = 2 M.

8.3, 6.9, and 3.9 for the formate, acetate, and propionate systems, respectively. The determined values of ΔV_{12} and ΔV_{23} are shown in Table II; the error intervals include the effects of the uncertainties involved in K_{12} .

Discussion

In the above data treatment, a reaction pathway via the neutral ligand HX has been omitted. If the pathway was included in the mechanism, k_{23} in eq 5 would involve an additional term proportional to hydrogen ion concentration. Nevertheless, as shown in Figure 4, the calculated f_r agrees uniformly well with the observed f_r in the pH range 4-6, for all three reaction systems, without including an additional hydrogen ion dependent term. We may therefore conclude that, within experimental error, the major contribution to the relaxation expression involves only the term arising from the scheme of eq 4.

The values of the outer-sphere association constant K_{12} in Table II are of the same order of magnitude as that found previously for cadmium(II) thiocyanate, i.e., $K_{12} = 1.05$ (at 25 °C and I =3 M),⁵ which has been shown to be in reasonable agreement with the value estimated from the Fuoss equation.¹⁸ The rate constants k_{23} of ligand substitution in Table II lie in the range (7-12) × $10^7 \, \text{s}^{-1}$. These values can be compared in magnitude with the value $3.2 \times 10^7 \text{ s}^{-1}$ (at 20 °C and I = 0) reported by Maass⁶ for the complex formation of zinc(II) acetate and also with the value 7 × 10⁷ s⁻¹ (at 25 °C and I = 0) obtained by Miceli and Stuehr¹⁹

⁽¹⁵⁾ Sano, T.; Miyazaki, T.; Tatsumoto, N.; Yasunaga, T. Bull. Chem. Soc. Jpn. 1973, 46, 43.
(16) Jackopin, L. G.; Yeager, E. Technical Report No. 35, ONR Contract No. 1439(04), Project No. 384-305, Western Reserve University, 1969.

⁽¹⁷⁾ By including the rapid protolytic reaction of the carboxylate ions, the relaxation frequency is expressed by $2\pi f_r = k_{23}[K_{12}\phi/(1+K_{12}\phi)+1/K_{23}]$, where $\phi = [M]/(1+\gamma) + [X]$ and $\gamma = [H]/([X] + K_H)$. However, the quantity γ is less than 0.013 under the experimental conditions in Table I and can be ignored compared with unity in the second expression.

⁽¹⁸⁾ Fuoss, R. M. J. Am. Chem. Soc. 1958, 80, 5059.

⁽¹⁹⁾ Miceli, J. A.; Stuehr, J. E. Inorg. Chem. 1972, 11, 2763.

for the complexing of zinc(II) glycinate with the temperature-jump technique.

A noticeable feature of the present results is that the K_{12} and k_{23} values indicate ligand dependences; i.e., the association constant K_{12} is larger while the rate constant k_{23} is smaller with the higher carboxylate. For the confirmation of the above result, in the first place the experimental data were examined by a method of analysis analogous to that given by Brintzinger and Hammes.²⁰ Rearranging eq 5, we obtain

$$\tau = \frac{K_{12}K_{23}}{k_{23}K_1} \left\{ 1 + \frac{K_{23}}{1 + K_1([\mathbf{M}] + [\mathbf{X}])} \right\}$$
(8)

where τ is the relaxation time with $\tau^{-1} = 2\pi f_r$. The τ vs {1 + $K_1([M] + [X])^{-1}$ plot gave a straight line for each reaction system. The reaction parameters evaluated from the slopes and intercepts of these lines agree with those of Table II. In the second place, the effects of the medium on the reaction parameters should be examined; the high ionic strength adopted in this study might affect the activity coefficients of the systems studied in different ways for the different carboxylate ions to result in the ligand dependences observed. According to the potentiometric studies by Gerding,²¹ the K_1 value of cadmium(II) acetate decreases only 7% by the variation of the ionic strength from 0.25 to 2 M. Thus, the medium effect on the activity coefficient factor of K_{12} 's would be, even if it differed from system to system, of this order of magnitude. As for the rate constant k_{23} , the medium effect should be much less, since the rate constant involves the ratio of the activity coefficients of the outer-sphere and activated complexes which is expected to be approximately unity for the analogous structures of these complexes.

Thus, as far as the above investigations are concerned, the ligand dependences of K_{12} and k_{23} seem to be realistic. However, in view of the small differences in the reaction parameters compared with the statistical uncertainties involved, together with the errors originating from the uncertainties of the complexation constants used,²² it is difficult at present to elucidate the above feature. A

- (20) Brintzinger, H.; Hammes, G. G. Inorg. Chem. 1966, 5, 1286. (21) Gerding, P. Acta Chem. Scand. 1968, 22, 1283.

(22) The variations of K_1 , K_2 , and K_3 within the reported error intervals (the standard errors) yielded the changes of the reaction parameters in the range ± 10 , ± 12 , and $\pm 8\%$ for the K_{12} 's and ± 6 , ± 5 , and $\pm 3\%$ for the k_{23} 's of the formate, acetate, and propionate systems, respectively.

full interpretation must await further accumulation of the experimental data.

The signs of the volume changes are not determined from the absorption data alone since the square of the linear combination of the volume changes is involved in μ_m ; hence, the signs of the ΔV_{23} 's were taken to be positive on the basis of the electrostriction effect of the metal ion. As shown in Table II, the ΔV_{12} values lie in the narrow range of -0.2 to 2.5 cm³ mol⁻¹, being substantially less than the ΔV_{23} values. They are also much less than the volume change 7–9 cm³ mol⁻¹ reported for the outer-sphere complexing of magnesium and manganese sulfates.^{23,24} However, considering the weak electrostatic interaction for the 2–1 valent ion pairs,^{23,25} together with the effect of the high ionic concentration of the medium,²⁶ the ΔV_{12} 's in Table II are of reasonable magnitude. Table II also shows that the ΔV_{23} value increases almost linearly with the number of hydrocarbon chains of the carboxylate ions. Here, it is interesting to note that the same tendency has also been observed for the volume changes on protonation of the carboxylate ions.²⁷

Through the above investigation, kinetic behaviors of the complexation of zinc(II) formate, acetate, and propionate all proved to be similar; the concentration dependences of the relaxation parameters together with the obtained values of the reaction parameters are wholly consistent with the Eigen-Tamm mechanism. Although the result reveals a feature that the rate of ligand substitution depends on the nature of the ligand, the uncertainties inolved preclude definite conclusion at present. Recently, we studied the complex formation of zinc ion with thiourea, a highly nucleophilic ligand, and noticed that the rate constant of ligand substitution on the metal is 2×10^8 s⁻¹, which is much larger than those of Table II. The detailed result will be reported in due course.

Registry No. Zn, 7440-66-6; formic acid, 64-18-6; acetic acid, 64-19-7; propionic acid, 79-09-4.

- (26) Spiro, T. G.; Revesz, A.; Lee, J. J. Am. Chem. Soc. 1968, 90, 4000.
 (27) Kauzmann, W.; Bodanszky, A.; Rasper, J. J. Am. Chem. Soc. 1962,
- 84, 1777.

Stabilities of Substituted Benzyl Radicals: Dissociation Rates of Amino-, Hydroxy-, and Cyanoethylbenzenes

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Rates of the thermal unimolecular decomposition of amino-, hydroxy-, and cyanoethylbenzenes have been determined by the very low pressure pyrolysis technique. Assuming equal A factors, these rates, relative to the rate of dissociation of ethylbenzene, yield the following ortho, meta, and para, respectively, substituent effects on benzylic C-C bond strengths (kcal/mol): NH₂, -2.7, -0.3, -1.7; OH, -1.7, -0.7, -1.1; and CN, -0.3, 0.4, -1.5. These effects are generally smaller than those for substituted anisoles and follow different trends. Along with the results of ESR studies of Nicholas and Arnold (Can. J. Chem. 1986, 64, 270), the present substituent effects indicate that a 1-G change in the benzylic hyperfine coupling constant corresponds to a 1.8 kcal mol⁻¹ change in bond strength.

Introduction

The effect of a substituent on reaction thermodynamics is perhaps the most fundamental of "substituent effects". In freeradical reactions, other factors, most notably "polar effects", are typically deduced from deviations in thermodynamic/rate correlations. A detailed understanding of radical substituent effects therefore requires thermodynamic information.

These thermodynamic effects can be expressed as differences in bond dissociation energies in substituted and unsubstituted molecules, ΔBDE , as illustrated below for benzyl radicals:

 $\Delta BDE = BDE(XC_6H_4CH_2-R) - BDE(C_6H_5CH_2-R) \quad (1)$

In the present work, we report $\triangle BDE$ (R = methyl) values for hydroxy, amino, and cyano substituents. These values are derived

⁽²³⁾ Hemmes, P. J. Phys. Chem. 1972, 76, 895.

 ⁽²⁴⁾ Jackopin, L. G.; Yeager, E. J. Phys. Chem. 1970, 74, 3766.
 (25) Grant, M. W. J. Chem. Soc., Faraday Trans. 1 1973, 69, 560.