A Kinetic Study of the Formation of Some Unchelated and Chelated Beryllium(II) Complexes in Aqueous Solutions

By **Bernd Gruenewald** and **Wilhelm Knoche,*** Max Planck-Institut für biophysikalische Chemie, Postfach 968, D-3400 Göttingen, West Germany

Beryllium(II) ions form unchelated $[Be(HL)]^+$ and chelated [BeL] complexes with the dicarboxylate anions (L^{2-}) oxalate, malonate, succinate, and maleate. From kinetic experiments, rate and equilibrium constants have been obtained for the formation of both types of complex. Ring closure is the rate-determining step of the overall reactions. For beryllium and hydroxycarboxylates only the formation of unchelated complexes is observed and no evidence is found for the existence of chelated complexes. The rate constant for the formation of the unchelated complexes is independent of the anion, $k_1 = 200 \pm 50\ s^{-1}$, and agrees with the corresponding value for beryllium sulphate. The rate constant for the formation of the chelated complexes and the equilibrium constants depend on the nature of the ligand.

IN previous studies [1,2] complex formation involving sulphate and formate ions as unidentate ligands with beryllium(II) has been investigated. The reactions can be described by a two-step mechanism: in the first step the metal ion and the ligand form solvent-separated ion pairs (outer-sphere complexes), and in a further slower step contact complexes (inner-sphere complexes) are formed by the removal of the separating solvent molecules. For both systems it has been found that inner- and outer-sphere complexes are present in comparable concentrations. Correspondingly, two chemical-relaxation effects are observed; kinetic and thermodynamic parameters for the reaction can then be obtained from the relaxation times and their variation with reagent concentration.

In this paper results are reported for the formation of beryllium complexes with bidentate dicarboxylates and hydroxycarboxylates. For these reactions one further step is expected, namely chelate-forming ring closure. Thermodynamic studies involving chelating ligands and beryllium have been the topic of several recent publications [3-8] (older references are quoted in these papers), but there is considerable disagreement as to the number, stoicheiometry, and stability of the complexes formed. If several complexes are present, kinetic measurements may be used to advantage, since as the different complexes may be formed at different rates their formation can be observed separately. Therefore we have used both chemical-relaxation and stopped-flow measurements to obtain information about the stoicheiometry of the complexes and the mechanism of their formation.

EXPERIMENTAL

Experiments were performed using a pressure-jump instrument [9] ($\delta P \approx 120$ atm) † and a simple stopped-flow apparatus. In both techniques the progress of reaction was detected by the electrical conductivity (at 40 kHz) of the solutions. The dead time of the stopped-flow apparatus was *ca.* 2 ms. For the evaluation of the measurements the output signal was digitized [10] and analyzed [11] by a small computer. Signal averaging of 10 measurements was used to improve the signal-to-noise ratio.

Solutions were prepared by mixing appropriate amounts of beryllium nitrate and the dicarboxylic or hydroxycarboxylic acids (oxalic, malonic, succinic, maleic, fumaric, glycolic, lactic, and mandelic acids). The pH of the solutions was adjusted by adding sodium hydroxide or perchloric acid. The addition of salts of other cations (inert electrolyte) would reduce the signal, since the progress of reaction was observed conductimetrically. Therefore no inert electrolyte was added, and the ionic strength of the solutions was determined only by the concentrations of the species listed above.

Treatment of Data.—Beryllium ions are readily hydrolyzed at pH >3.5 forming numerous hydroxo-complexes, the stoicheiometries and stabilities of which, however, are not known unambiguously. To avoid complications due to these complexes, measurements were performed only in acidic solutions ($2 < pH < 3.4$) where their concentrations are negligibly small.[12] In this pH range the ligands exist predominantly in their mono- or di-protonated forms. In the range of applicability of the pressure-jump and stopped-flow techniques we observed two relaxation effects which can be explained by the reaction scheme (1), where H_2L is the undissociated dicarboxylic acid, $[Be(OH_2)(HL)]^+$ represents the outer-sphere complex, $[Be(HL)]^+$ the inner-sphere complex where one of the water molecules of the inner hydration sphere of the beryllium ion is replaced by a

$$Be^{2+} + [HL]^- \rightleftharpoons [Be(OH_2)(HL)]^+ \underset{k_1'}{\overset{k_1}{\rightleftharpoons}}$$

$$[Be(HL)]^+ \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} [BeL] + H^+ \quad (1a)$$

$$[HL]^- + H^+ \rightleftharpoons H_2L \quad (1b)$$

---

† Throughout this paper: 1 atm = 101 325 Pa.

[1] W. Knoche, C. A. Firth, and D. Hess, *Adv. Mol. Relax. Proc.*, 1974, **6**, 1.

[2] B. Gruenewald, W. Knoche, and N. H. Rees, *J.C.S. Dalton*, 1976, 2338.

[3] P. H. Tedesco and J. G. Quintana, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2628.

[4] A. Vanni and M. C. Gennaro, *Ann. Chim. (Italy)*, 1974, **64**, 397.

[5] G. Duc, F. Bertin, and G. Thomas-David, *Bull. Soc. chim. France*, 1974, 793.

[6] A. K. Sengupta and S. K. Adhikari, *Indian J. Chem.*, 1974, **12**, 1001.

[7] A. Vanni, M. C. Gennaro, and G. Ostacoli, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1443.

[8] J. Votava and M. Bartusek, *Coll. Czech. Chem. Comm.*, 1975, **40**, 2050.

[9] W. Knoche and G. Wiese, *Chem. Instr.*, 1973, **5**, 91.

[10] M. Krizan and H. Strehlow, *Chem. Instr.*, 1973, **5**, 99.

[11] H. Strehlow and J. Jen, *Chem. Instr.*, 1971, **3**, 47.

[12] C. F. Baes and R. S. Mesmer, 'Hydrolysis of Cations,' Wiley, New York, 1976.

unidentate carboxylic group of the acid, and [BeL] represents the chelate complex, formed by ring closure where two of the inner-sphere solvent molecules are replaced. The symbol $\rightleftharpoons$ is used for very fast reaction steps which are not studied here.

The equilibrium concentrations of this reaction are determined by the four stability constants in (2)—(5).

$$K_0 = \frac{[\mathrm{Be(OH_2)(HL)^+}]}{[\mathrm{Be^{2+}}][\mathrm{HL^-}]f_2} \qquad (2)$$

$$K_1 = \frac{[\mathrm{Be(HL)^+}]}{[\mathrm{Be(OH_2)(HL)^+}]} \qquad (3)$$

$$K_2 = \frac{[\mathrm{BeL}][\mathrm{H^+}]}{[\mathrm{Be(HL)^+}]} \qquad (4)$$

$$K_\mathrm{H} = \frac{[\mathrm{H_2L}]}{[\mathrm{HL^-}][\mathrm{H^+}]f_1^{\,2}} \qquad (5)$$

The activity coefficients f_1 and f_2 have been estimated by using equation (6) due to Davies,[13] where z_i is the charge of

$$\log f_i = -0.5\, z_i^2\{[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})] - 0.3\, I\} \qquad (6)$$

the ion and I the ionic strength of the solution. According to this equation the activity coefficients depend only on the valency of the ions (at a given ionic strength) and several of them cancel in equations (2)—(5). Equation (6) may be used in this study since the ionic strength never exceeds 0.2 mol dm^{-3}. The protolytic reaction (1b) and the formation of the outer-sphere complex from the free ions are much too fast to be observed by the techniques employed in this study. The rate equations for the slower steps are (7) and (8). In these equations the activity coefficients cancel

$$\mathrm{d[Be(HL)^+]/d}t = k_1[\mathrm{Be(OH_2)(HL)^+}] - (k_1' + k_2)[\mathrm{Be(HL)^+}] + k_2'[\mathrm{BeL}][\mathrm{H^+}] \qquad (7)$$

$$\mathrm{d[BeL]/d}t = k_2[\mathrm{Be(HL)^+}] - k_2'[\mathrm{BeL}][\mathrm{H^+}] \qquad (8)$$

too because of the use of equation (6). Since reactions (1) (k_1, k_1') and (2) (k_2, k_2') proceed with similar rates, the two differential equations (7) and (8) have to be solved simultaneously to calculate the two observable relaxation times τ_f and τ_s. These have a complicated dependence on the rate constants and on the equilibria (2)—(5) because there is a coupling between the reacting species on the left- and right-hand sides of equation (1a) through the protolytic reaction (1b). The relaxation times are given by equation (9). The

$$\frac{1}{\tau_{\mathrm{f,s}}} = \tfrac{1}{2}(C_{00} - BC_{10} + C_{11}) \pm \tfrac{1}{2}[(C_{00} - BC_{10} + C_{11})^2 - 4(C_{00}C_{11} + C_{01}C_{10})]^{\frac{1}{2}} \qquad (9)$$

plus and minus sign in front of the square bracket refers to the shorter and to the longer relaxation time, respectively. In equation (9) the following abbreviations have been used:

$$B = \frac{K_0 f_2[\mathrm{Be^{2+}}]}{\alpha + K_0 f_2(\beta[\mathrm{Be^{2+}}] + \alpha[\mathrm{HL^-}])}$$

$$C_{00} = k_1' + \frac{k_1 K_0 f_2(\beta[\mathrm{Be^{2+}}] + \alpha[\mathrm{HL^-}])}{\alpha + K_0 f_2(\beta[\mathrm{Be^{2+}}] + \alpha[\mathrm{HL^-}])}$$

$$C_{01} = \frac{k'_1 K_0 f_2\{[\mathrm{Be^{2+}}](1 + \beta) + \alpha[\mathrm{HL^-}]\}}{\alpha + K_0 f_2(\beta[\mathrm{Be^{2+}}] + \alpha[\mathrm{HL^-}])}$$

$$C_{10} = \frac{k_2\{\alpha + K_0 f_2(\beta[\mathrm{Be^{2+}}] + \alpha[\mathrm{HL^-}])\}}{K_0 f_2(\beta[\mathrm{Be^{2+}}] + \alpha[\mathrm{HL^-}])} + \frac{k_2'[\mathrm{BeL}]}{K_0 f_2\{[\mathrm{Be^{2+}}] - ([\mathrm{Be^{2+}}] + [\mathrm{HL^-}])\gamma\}}$$

$$C_{11} = k_2\left(\frac{[\mathrm{Be^{2+}}]}{1 + \beta[\mathrm{Be^{2+}}] + \alpha[\mathrm{HL^-}]}\right) + \frac{k_2'([\mathrm{H^+}] + [\mathrm{BeL}])\{[\mathrm{Be^{2+}}] - ([\mathrm{Be^{2+}}] + [\mathrm{HL^-}])\delta\}}{[\mathrm{Be^{2+}}] - ([\mathrm{Be^{2+}}] + [\mathrm{HL^-}])\gamma}$$

$$\alpha = 1 + \frac{[\mathrm{H^+}]}{[\mathrm{H_2L}]} + \frac{[\mathrm{H^+}]}{[\mathrm{HL^-}]}$$

$$\beta = 1 + \frac{[\mathrm{H^+}]}{[\mathrm{H_2L}]}$$

$$\gamma = 1 + \frac{[\mathrm{HL^-}]}{[\mathrm{H^+}]} + \frac{[\mathrm{HL^-}]}{[\mathrm{H_2L}]}$$

$$\delta = 1 + \frac{[\mathrm{HL^-}]}{[\mathrm{H_2L}]}$$

In the derivation of equation (9) any change of activity coefficients during the reaction has been neglected. This approximation is justified since the ionic strength of the solution is determined to a large extent by non-reacting ions ($[\mathrm{NO_3}]^-$, $[\mathrm{ClO_4}]^-$, and $\mathrm{Na^+}$) and changes only slightly as the reaction proceeds. Details of the derivation are in the Appendix.

The amplitudes of the relaxation effects are observed as a change of electrical conductivity after the pressure jump. They cannot be evaluated quantitatively since scheme (1) is too complicated. As an example let us consider the overall reaction (10) coupled to the fast protolytic reaction (1b). At

$$\mathrm{Be^{2+}} + [\mathrm{HL}]^- \longrightarrow [\mathrm{BeL}] + \mathrm{H^+} \qquad (10)$$

pH $\gg$ pK_H, where the concentration of the undissociated acid, $\mathrm{H_2L}$, can be neglected, this reaction is accompanied by an increase in conductance due to the release of a proton having a very high mobility. At a pH $\approx$ pK_H the concentrations of $\mathrm{H_2L}$ and $[\mathrm{HL}]^-$ are similar and the solution is buffered. The proton formed reacts with another $[\mathrm{HL}]^-$ to form $\mathrm{H_2L}$ and the reaction is accompanied by a decrease in electrical conductance due to the neutralization of a positive and a negative charge. At pH $\ll$ pK_H the concentration of $[\mathrm{HL}]^-$ can be neglected and the reaction proceeds as in (11) with again a strong increase in conductivity. At

$$\mathrm{Be^{2+}} + \mathrm{H_2L} \rightleftharpoons [\mathrm{BeL}] + 2\,\mathrm{H^+} \qquad (11)$$

intermediate pH the reaction will proceed with no measurable change in conductance at all. The calculation of the relaxation amplitudes is even more complicated because the formation of the outer- and inner-sphere complexes containing the unidentate ligand also has to be considered in reaction (1). The amplitudes of the relaxation effects could be estimated only if all the equilibrium constants, rate constants, reaction volumes, and mobilities of the ions were known precisely.

Analogous arguments hold for the relaxation amplitudes due to the formation of the complex $[\mathrm{Be(HL)}]^+$. Consequently, both relaxations can be observed simultaneously only in certain pH ranges; in others only a single relaxation is obtained, with the advantage that its relaxation time can be evaluated with higher precision.

In chemical-relaxation experiments the signal change s (proportional to the changes in concentration of the reacting species) is a superimposition of exponentially decaying

---

[13] C. W. J. Davies, ' Ion Association,' Butterworths, London, 1962.

curves which are independent of the order of the reactions studied, *i.e.* as in (12). This is due to the fact that the

$$s = \Sigma s_i \exp(-t/\tau_i) \qquad (12)$$

system investigated is close to its equilibrium state and squared terms may be neglected in the rate equations. In stopped-flow experiments this simplification is not allowed, and exponentially decaying signals are observed only for first- or pseudo-first-order reactions. However, for all the stopped-flow experiments reported in this study the signal fits well either a single exponentially decaying curve or the superimposition of two such curves with opposite signs, *i.e.* $s_1/s_2 < 0$, and we used equation (9) for an approximate evaluation of the measurements.

RESULTS

The interaction of Be^{2+} with dicarboxylic acid ligands was studied using oxalic, malonic, succinic, and maleic acids. Measurements were also performed using fumaric acid (the *trans* form of maleic acid) where the fumarate ion cannot form chelate complexes for steric reasons. The acids tend to ionize over the pH range of the measurements, and pK_a values are given in Table 5.

With oxalic, malonic, succinic, and maleic acids two relaxation effects are observed both in pressure-jump and stopped-flow experiments. In order to identify the reaction steps causing these relaxations we carried out stopped-flow experiments by mixing solutions of beryllium nitrate with solutions of the dicarboxylic acids. Perchloric acid was added to $Be[NO_3]_2$ or sodium hydroxide to the ligand solution in order to adjust the pH of the mixture to a value where the acid exists predominantly in its monoprotonated form. In this case the faster relaxation is connected with a decrease and the slower one with an increase of electrical conductivity. This behaviour fits scheme (1a): within the mixing time the equilibrium free ions $\rightleftharpoons$ outer-sphere complex is established. In the fast observed relaxation the unchelated inner-sphere complex $[Be(HL)]^+$ is formed partly from the outer-sphere complex and partly from the free ions. This causes a decrease of conductivity since charges are neutralized. In the following slower step the chelated complex [BeL] is formed which is associated with an increase in conductivity due to the release of a proton.

In addition experiments the concentrations of the reactants and the pH of the solutions were adjusted to values where single relaxation times could be obtained with the highest precision. To achieve this, concentrations were chosen such that the amplitude of one relaxation was large compared to that of the other, and the relaxation time was evaluated only for the former. The error in the relaxation times was *ca.* ±10%. For solutions where the relaxation times could be measured both by the stopped-flow and pressure-jump techniques the results obtained with the two techniques agreed within this error. Therefore, for the different measurements we always used the technique showing the best signal-to-noise ratio.

For the evaluation of the measurements the outer-sphere equilibrium constant [equation (2)] has to be known. It may be estimated by the Fuoss formula [14] which gives as a result K_0 *ca.* 5 $dm^3\ mol^{-1}$ for a distance of closest approach of 4—6 Å. However, it has been shown that this value is too small by a factor of about two for beryllium formate [2] and nickel acetate.[15] Therefore $K_0 = 10\ dm^3\ mol^{-1}$ has been estimated for the beryllium carboxylates in this study. The equilibrium constants K_1 and K_2 [equations (3) and (4)] and the rate constants k_1 and k_2 [equation (1a)] were calculated by a least-squares fit to the relaxation times in equation (9). The results of the measurements together with the calculated relaxation times are summarized in Tables 1—4. The following symbols are used in the Tables: $[Be]_T$ is the total concentration of beryllium, $[L]_T$ the total concentration of the ligand L, τ_s and τ_f are the slow and the fast relaxation times respectively, and $(\tau_s)_{calc.}$ and $(\tau_f)_{calc.}$ are the corresponding calculated relaxation times. For solutions where the total concentrations of beryllium and ligand are equal, the symbol $c_T = [Be]_T = [L]_T$ is used. The values of the rate and equilibrium constants obtained by this calculation are summarized in Table 5.

TABLE 1

Relaxation times of solutions of beryllium oxalate at 25 °C

$[Be]_T$ / mol dm^{-3}	$[L]_T$ / mol dm^{-3}	pH	τ_f / ms	$(\tau_f)_{calc.}$ / ms	τ_s / ms	$(\tau_s)_{calc.}$ / ms
0.002 5 [a]	0.01	3.1	20	17		
0.005 [a]	0.01	3.1	13.5	13.5		
0.01 [a]	0.01	3.1	9.0	10.0		
0.02 [a]	0.01	3.1	7.2	7.9		
0.04 [a]	0.01	3.1	6.5	6.5		
0.001 [b]	0.001	2.35			102	92
0.005 [b]	0.005	2.35			54	54
0.01 [b]	0.01	2.35			38	40
0.016 [b]	0.016	2.35			30	32
0.03 [b]	0.03	2.35			26	24

[a] Stopped-flow experiments. [b] Pressure-jump experiments.

TABLE 2

Relaxation times of solutions of beryllium malonate at 25 °C; stopped-flow experiments

c_T / mol dm^{-3}	pH	τ_f / ms	$(\tau_s)_{calc.}$ / ms	τ_f / ms	$(\tau_s)_{calc.}$ / ms
0.001	3.4	16	13		
0.003	3.4	14	12.5		
0.01	3.4	9.6	11.3		
0.03	3.4	8.0	9.0		
0.1	3.4	5.9	5.8		
0.001	2.0			245	250
0.002 5	2.0			205	210
0.005	2.0			160	160
0.01	2.0			115	108
0.025	2.0			60	57
0.05	2.0			38	36
0.07	2.0			27	30
0.09	2.0			26	27
0.10	2.0			23.5	25

TABLE 3

Relaxation times of solutions of beryllium maleate at 25 °C; pressure-jump experiments

c_T / mol dm^{-3}	pH	τ_s / ms	$(\tau_s)_{calc.}$ / ms
0.002 5	3.10	8.1	9.1
0.002 5	3.39	7.6	9.3
0.005	2.80	6.1	6.0
0.005	3.11	6.0	6.6
0.005	3.39	4.5	5.2
0.01	3.10	3.7	4.0
0.01	3.39	2.84	2.61
0.017	2.81	3.3	3.4
0.017	3.10	2.60	2.56
0.017	3.20	1.98	2.45
0.017	3.27	2.18	1.92
0.017	3.39	1.54	1.51

In the cases of beryllium oxalate and malonate both

---

[14] R. M. Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059.

[15] A. Bonsen, F. Eggers, and W. Knoche, *Inorg. Chem.*, 1976, **15**, 1212.

relaxation times could be obtained. With maleate and succinate as ligands both relaxation effects were observed but only the slower one could be evaluated since the faster was too small in amplitude. In solutions of beryllium fumarate only one relaxation effect was observed with relaxation times of *ca.* 5 ms at 25 °C. Again the effects were too small for an accurate evaluation of the measurements.

TABLE 4

Relaxation times of solutions of beryllium succinate at 25 °C and pH 3.0; pressure-jump experiments

$\frac{c_T}{\text{mol dm}^{-3}}$	$\frac{\tau_s}{\text{ms}}$	$\frac{(\tau_s)_{\text{calc.}}}{\text{ms}}$
0.001	320	250
0.003	170	140
0.004	70	88
0.007	44	63
0.01	42	45
0.02	34	31
0.03	24	27
0.04	22	25

Chelate complexes are also formed between metal ions and hydroxycarboxylate ions. For instance, the formation of the chelate complexes nickel(II) glycolate[16] and nickel(II) lactate[17,18] has been reported. We used the pressure-jump technique in order to study the complex formation of beryllium with the hydroxycarboxylates glycolate, lactate, and phenylglycolate. With all these ligands only one relaxation effect was observed in the ranges $2.0 < \text{pH} < 4.0$ and $10^{-3} < c_T < 0.1$ mol dm^{-3}. The relaxation times varied between 4 and 8 ms at 25 °C.

TABLE 5

Equilibrium and rate for the formation of beryllium carboxylates at 25 °C and $I = 0$

Ligand	pK_a[a]	K_1	$\frac{K_2}{\text{dm}^3\ \text{mol}^{-1}}$	$\frac{k_1}{\text{s}^{-1}}$	$\frac{k_2}{\text{s}^{-1}}$
Formate[b]	3.75	3.1 ± 4		200 ± 50	
Oxalate	1.23	17 ± 2	$(1 \pm 0.3) \times 10^{-3}$	170 ± 20	20 ± 2
Malonate	2.83	18 ± 2	$(2.2 \pm 0.2) \times 10^{-2}$	215 ± 20	62 ± 5
Succinate	4.16	30 ± 10	$(2 \pm 0.5) \times 10^{-3}$		20 ± 10
Maleate	1.83	30 ± 10	$(3 \pm 1) \times 10^{-4}$		2 ± 0.5
Phenylglycolate	3.85	1.4 ± 0.5		170 ± 50	

[a] For dicarboxylic acids the first pK_a only is listed, since this is used in the calculations. [b] Ref. 2.

A systematic study of beryllium phenylglycolate showed that the relaxation time is independent of hydrogen-ion concentration in the range $2.9 < \text{pH} < 4.0$ and that it increases nearly linearly with c_T for $10^{-3} < c_T < 0.1$ mol dm^{-3}. We evaluated the measurements according to scheme (1) with the estimation $K_0 = 10$ dm^3 mol^{-1} and neglecting the formation of the chelate complex and obtained $k_1 = 170 \pm 50$ s^{-1} and $k_1' = 120 \pm 30$ s^{-1}.

DISCUSSION

Solutions of beryllium salts of dicarboxylic acids show two relaxation effects both in stopped-flow and pressure-jump experiments. For the following reasons the faster effect is attributed to the formation of the inner-sphere unchelated complex $[\text{Be(HL)}]^+$ and the slower one to the formation of the chelate complex [BeL]. (*i*) In stopped-flow experiments solutions of $\text{Be[NO}_3]_2$ and dicarboxylic acid are mixed and the signal observed is a superimposition of two exponentially decaying curves with opposite signs. Such a signal is obtained only if the faster reaction precedes the slower, since in the opposite case one always observes a monotonically changing signal. (*ii*) In stopped-flow experiments the faster effect causes a decrease and the slower an increase in conductivity. This fits scheme (1a) only if chelate formation is the slower reaction. (*iii*) Chelate formation is not possible with fumarate as ligand, and solutions of beryllium fumarate show only the faster relaxation. (*iv*) The evaluation of the measurements according to equation (1) yields rate constants for the formation of the inner-sphere unchelated complexes which coincide with the corresponding value for beryllium formate. This agrees with the general rule[19] that this rate constant is determined mainly by the metal ion and depends only weakly on the nature of the ligand.

Thus ring closure is the slowest step in the formation of beryllium dicarboxylates. Pearson and Moore[20] studied the dissociation of the chelate beryllium pentane-2,4-dionate. They also observed that the ring opening is the slowest step of the reaction. For other metal chelate complexes it is not unambiguously known which step is rate determining. For instance, in the case of nickel(II) malonate different workers have suggested that either ring closure[21] or unchelated complex formation[22,23] is rate determining in the reaction.

The equilibrium and rate constants obtained in this investigation are summarized in Table 5. All the data refer to ionic strength $I = 0$. The stability constants K_1 of the unchelated complexes are larger for the dicarboxylates than for the monocarboxylates. This may be due to a hydrogen bridge which exists in the unchelated complex between the free carboxyl group of the dicarboxylates and one of the water molecules bound in the inner hydration sphere of the cation. The stability constant K_2 is largest for beryllium malonate. This indicates that for beryllium chelate complexes a six-membered ring is more stable than five- (oxalate) or seven-membered (succinate and maleate) rings. As

---

[16] S. Harada, Y. Okuue, H. Kan, and T. Yasanuga, *Bull. Chem. Soc. Japan*, 1973, **47**, 769.

[17] H. Hoffmann and U. Nickel, *Z. Naturforsch.*, 1971, **266**, 299.

[18] S. Harada, H. Tanabe, and T. Yasunaga, *Bull. Chem. Soc. Japan*, 1973, **46**, 3125.

[19] H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass, and R. Winkler, *Pure Appl. Chem.*, 1969, **20**, 93.

[20] R. G. Pearson and J. W. Moore, *Inorg. Chem.*, 1966, **5**, 1528.

[21] U. Nickel, H. Hoffmann, and W. Jaenicke, *Ber. Bunsengesellschaft. Phys. Chem.*, 1968, **72**, 526.

[22] F. P. Cavasino, *J. Phys. Chem.*, 1965, **69**, 4380.

[23] J. L. Bear and C.-T. Lin, *J. Phys. Chem.*, 1968, **72**, 2026.

mentioned above, the rate constant k_1 for the formation of the inner-sphere complexes is approximately the same for all the beryllium carboxylates. It also agrees with the value $k_1 = 185 \pm 25\ \mathrm{s^{-1}}$ reported for beryllium sulphate.[1] A mechanistic model for the inner-sphere complex formation of the tetrahedrally co-ordinated beryllium(II) cation has been discussed,[24] according to which k_1 depends only weakly on the nature of the ligand.

In this study we found no evidence for other complexes between beryllium and dicarboxylates quoted in the literature[3,8] such as $[\mathrm{Be(HL)_2}]$ or $[\mathrm{BeL_2}]^{2-}$. For beryllium malonate the complex $[\mathrm{Be(HL)}]^+$ has also been observed by Tedesco and Quintana.[3] For the association constant in (13) they obtained $K_a = 450 \pm 50$

$$K_a = \frac{[\mathrm{Be(HO_2)(HL)^+}] + [\mathrm{Be(HL)^+}]}{[\mathrm{Be^{2+}}][\mathrm{HL^-}]} = K_0(1 + K_1) \qquad (13)$$

$\mathrm{dm^3\ mol^{-1}}$ at $I = 1.0\ \mathrm{mol\ dm^{-3}}$ compared to our value of $K_a = 300\ \mathrm{dm^3\ mol^{-1}}$ for $I = 0$. For beryllium succinate, values of $K_a = 300 \pm 40$ and $200\ \mathrm{dm^3\ mol^{-1}}$ are quoted at $I = 1.0\ \mathrm{mol\ dm^{-3}}$ by Tedesco and Quintana[3] and Vanni *et al.*[7] respectively, compared to our value of $330\ \mathrm{dm^3\ mol^{-1}}$ at $I = 0$. A detailed comparison of these values is not possible since they are obtained at different ionic strengths and since our value is based on an estimation for K_0.

Solutions of beryllium hydroxycarboxylates showed only the fast relaxation effect attributed to the formation of unchelated complexes, and we found no indication for chelate formation of these complexes.

APPENDIX

Equations needed for the Derivation of Equation (9).—With the definition (A1) where $x\{\mathrm{A}\}$ is the deviation of the actual

$$x\{\mathrm{A}\} = [\mathrm{A}] - [\mathrm{A}]_\mathrm{E} \qquad (\mathrm{A}1)$$

$$x\{\mathrm{A}\} \ll [\mathrm{A}] \qquad (\mathrm{A}2)$$

concentration [A] from the equilibrium concentration $[\mathrm{A}]_\mathrm{E}$ of species A, and with the relation (A2) (since the deviations from equilibrium are small in chemical-relaxation experiments), we obtain from equations (7) and (8) those of (A3) and (A4). The mass balances of beryllium, ligand, and

$$\mathrm{d}x\{\mathrm{Be(HL)^+}\}/\mathrm{d}t = k_1 x\{\mathrm{Be(OH_2)(HL)^+}\} - (k_1' + k_2)x\{\mathrm{Be(HL)^+}\} + k_2'([\mathrm{BeL}]_\mathrm{E}x\{\mathrm{H^+}\} + [\mathrm{H^+}]_\mathrm{E}x\{\mathrm{BeL}\}) \qquad (\mathrm{A}3)$$

$$\mathrm{d}x\{\mathrm{BeL}\}/\mathrm{d}t = k_2 x\{\mathrm{Be(HL)^+}\} - k_2'([\mathrm{BeL}]_\mathrm{E}\,x\,\{\mathrm{H^+}\} + [\mathrm{H^+}]x\{\mathrm{BeL}\}) \qquad (\mathrm{A}4)$$

$$x\{\mathrm{Be^{2+}}\} + x\{\mathrm{Be(OH_2)(HL)^+}\} + x\{\mathrm{Be(HL)^+}\} + x\{\mathrm{BeL}\} = 0 \qquad (\mathrm{A}5)$$

$$x\{\mathrm{HL^-}\} + x\{\mathrm{Be(OH_2)(HL)^+}\} + x\{\mathrm{Be(HL)^+}\} + x\{\mathrm{BeL}\} + x\{\mathrm{H_2L}\} = 0 \qquad (\mathrm{A}6)$$

$$x\{\mathrm{H^+}\} + x\{\mathrm{H_2L}\} - x\{\mathrm{BeL}\} = 0 \qquad (\mathrm{A}7)$$

hydrogen yield equations (A5), (A6), and (A7), respectively.

The reaction step free ions $\rightleftharpoons$ outer-sphere complex and the protonation reaction (1b) are fast compared to the reaction steps studied here. Therefore these reactions may be assumed to be in equilibrium giving (A8) and (A9). In the derivation of equations (A8) and (A9) any change of

$$\frac{x\{\mathrm{Be^{2+}}\}}{[\mathrm{Be^{2+}}]} + \frac{x\{\mathrm{HL^-}\}}{[\mathrm{HL^-}]} = \frac{x\{\mathrm{Be(OH_2)(HL)^+}\}}{[\mathrm{Be(OH_2)(HL)^+}]} \qquad (\mathrm{A}8)$$

$$\frac{x\{\mathrm{HL^-}\}}{[\mathrm{HL^-}]} + \frac{x\{\mathrm{H^+}\}}{[\mathrm{H^+}]} = \frac{x\{\mathrm{H_2L}\}}{[\mathrm{H_2L}]} \qquad (\mathrm{A}9)$$

activity coefficients during the reaction has been neglected. This approximation is justified, since the ionic strength of the solution is determined to a large extent by non-reacting ions ($[\mathrm{NO_3}]^-$, $[\mathrm{ClO_4}]^-$, and $\mathrm{Na^+}$) and changes only slightly as the reaction proceeds.

In equations (A3)—(A9) there are seven unknowns: $x\{\mathrm{Be(HL)^+}\}$, $x\{\mathrm{Be(OH_2)(HL)^+}\}$, $x\{\mathrm{BeL}\}$, $x\{\mathrm{Be^{2+}}\}$, $x\{\mathrm{H_2L}\}$, $x\{\mathrm{HL^-}\}$, and $x\{\mathrm{H^+}\}$. Five of them may be eliminated in equations (A3) and (A4) with the help of (A5)—(A9). Thus we are left with two linear independent differential equations with two unknowns. The solution of these equations yields equation (9). For details of the mathematical procedure books on chemical relaxation[25,26] should be consulted.

We thank Dr. J. Jen for help with the Fortran program, Dr. N. H. Rees, University of Wales at Cardiff, for valuable discussion, and Mrs. M. Gudlin for assistance with the measurements.

[7/1447 *Received, 8th August,* 1977]

---

[24] H. Strehlow and W. Knoche, *Ber. Bunsengesellschaft. Phys. Chem.*, 1969, **73**, 427.

[25] C. F. Bernasconi, 'Relaxation Kinetics,' Academic Press, New York, 1976.

[26] H. Strehlow and W. Knoche, 'Fundamentals of Chemical Relaxation,' Verlag Chemie, Weinheim, 1977.