A Pressure-jump Study of the Formation of Beryllium(II) Formate in Aqueous Solution

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Chemical relaxation effects in aqueous solutions of beryllium(II) formate have been studied using the pressure-jump technique. The reaction proceeds by a stepwise mechanism, for which rate and equilibrium constants have been determined. The results are compared with those found for the formation of other beryllium complexes.

THE formation of metal complexes in solution has been studied frequently using kinetic methods. These reactions proceed through a series of steps characterized by successive release of solvent molecules bound in the solvation spheres. The slowest step is replacement of a solvent molecule of the inner solvation sphere of the cation by the ligand.[1] An electrostatic model has been developed to provide a detailed mechanism of this slowest step [2] for the Be^{2+} ion in aqueous solution. The Be^{2+} ion was chosen for this model since it is tetrahedrally co-ordinated and, therefore, the computation is considerably simplified as compared to octahedrally or higher co-ordinated metal ions. The calculations on this system have been checked experimentally by a detailed study of the formation of the complex $Be[SO_4]$ in aqueous solution for which all the kinetic and thermodynamic constants were obtained.[3]

The formation of complexes of Be^{2+} with the ligands F^-,[4] HF,[4] and $[Fe(CN)_6]^{3-}$ (ref. 5) have also been investigated and rate constants have been determined. For the evaluation of these measurements the assumption had to be made that the equilibrium between the free ions and the solvent-separated ion pair is determined by an electrostatic model as described by Fuoss.[6] Chemical relaxation effects have been observed also for a number of beryllium carboxylates in the millisecond range.[7] These, however, were not attributed to specific reactions.

In this paper the formation of beryllium formate is reported. The results obtained are compared with

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those obtained for other beryllium complexes and with the predictions made from electrostatic models.[2,6]

EXPERIMENTAL

The kinetic measurements were made by means of the pressure-jump relaxation method using electrical conductance to observe the progress of reaction.[8] The observed signal was digitized and fed to a small computer.[9] Up to 10 measurements were superimposed in order to improve the signal-to-noise ratio and the relaxation time was obtained by a least-squares fit.[10] For details of the pressure-jump method, the data capturing, and the data processing the quoted literature should be consulted.

The solutions were made by mixing solutions of beryllium nitrate (E. Merck, p.a.) and formic acid (E. Merck, p.a.). The pH values of the solutions were adjusted by adding small amounts of Na[OH], and measured at 20 °C using a Metrohm (model E 500) pH meter.

RESULTS

Beryllium forms mono- and poly-nuclear hydrolyzed species in aqueous solutions.[11] In order to avoid interference from these complexes all the measurements were made at pH <4.0. In this range, the concentration of all the hydrolyzed species is less than 2% of the concentration of the beryllium(II) ion, according to the stability constants quoted in the literature.[11] Pressure-jump experiments made with a solution of 0.3 mol dm^{-3} $Be[NO_3]_2$ at pH 4.0 did not show any relaxation effect, confirming that the small concentrations of hydrolyzed species do not interfere with the results. Also, solutions containing only formic acid did not show chemical relaxation. Therefore the effects discussed below are due to the interaction between beryllium(II) and formate ions.

The limitation to the range pH <4.0 also restricts the choice of the ligand. Beryllium(II) forms only weak complexes with unidentate carboxylates,[12] so that the acid must be significantly dissociated in order to obtain detectable complex formation. Therefore the pK of the acid has to be similar to or smaller than the pH of the solution, *i.e.* we are restricted to acids with p$K \leqslant 4.0$. The simplest acid in agreement with this requirement is formic acid (pK 3.75). The measurements were extended over the temperature range 2—30 °C, the pH range 3.0—4.0, and the concentration range $c_{Be} = c_{HCO_2} = 3 \times 10^{-3}$—0.44 mol dm^{-3}, and at constant $c_{HCO_2} = 0.01$ mol dm^{-3} and $10^{-3} \leqslant c_{Be} \leqslant 0.02$ mol dm^{-3} [c_{Be} and c_{HCO_2} are the analytical concentrations of beryllium(II) and formate].

The relative change in conductance (κ) due to the chemical relaxation effect was smaller than $\delta\kappa/\kappa = 0.8 \times 10^{-3}$ for a pressure jump of $\delta P = 180$ atm.* Since the adiabatic pressure jump is related to a temperature change, thermal equilibration occurs after the pressure jump. This also changes the electrical conductance and thus interferes with the observation of the chemical relaxation. In dilute aqueous solutions the adiabatic temperature change decreases with decreasing temperature and disappears at *ca.* 4 °C. Therefore the most precise measurements could be made at this temperature and the experimental results shown below refer to those at 5 °C. Table 1 shows the relaxation times and their dependence on temperature determined for solutions at pH 3.95. The results were obtained by a linear interpolation of ln $1/\tau$ against $1/T$ for measurements between 5 and 15 °C. At low concentrations the error width is determined by the very small amplitude of the relaxation effect. At higher concentrations ($c \geqslant 0.03$ mol dm^{-3}) a second faster relaxation effect (τ *ca.* 5 ms) with a smaller amplitude interfered with the main relaxation and thus increased the error. It was not possible to evaluate the faster relaxation time, which is probably caused by the formation of $Be[O_2CH]_2$.

TABLE 1

Relaxation times and their dependence on temperature for solutions containing beryllium nitrate and formic acid at 5 °C and pH 3.95

c_{Be} / mol dm^{-3}	c_{HCO_2} / mol dm^{-3}	$10^3\ \tau$ / s	$10^{-3}(d\ln \tau^{-1}/dT^{-1})$ / K	$10^3\tau$(calc.) / s
0.003	0.003	45.7 ± 3.2	5.9	49.3
0.005	0.005	45.5 ± 2.3	5.8	46.0
0.01	0.01	41.5 ± 1.2	6.0	41.3
0.03	0.03	36.5 ± 2.6	5.7	34.1
0.05	0.05	28.2 ± 2.8	5.1	31.1
0.07	0.07	25.8 ± 2.6	6.0	29.2
0.1	0.1	26.4 ± 1.9	5.8	27.3
0.24	0.24	22.4 ± 1.6	5.0	23.0
0.44	0.44	21.5 ± 1.6	5.2	20.3
0.001	0.01	43.2 ± 3.0	5.1	45.1
0.005	0.01	45.3 ± 3.1	5.9	43.7
0.021	0.012	38.9 ± 2.9	5.5	36.9
0.05	0.01	31.2 ± 2.2	5.1	30.6

τ(calc.) was calculated assuming reaction scheme (1) and the constants $k' = 168\ s^{-1}$, $K_i = 3.1$, and $K_a = 100\ dm^3\ mol^{-1}$.

In order to check whether the reaction is acid or base catalyzed the dependence of the relaxation time on pH was studied for a solution where $c_{Be} = c_{HCO_2} = 0.01$ mol dm^{-3}. The relaxation times decreased only by *ca.* 4% when going from pH 4.0 to 3.0. This small change can be explained by the change in concentration as discussed later. (At lower pH the concentration of HCO_2^- decreases at the expense of HCO_2H.)

Besides beryllium formate we also investigated other beryllium complexes of unidentate carboxylates. For solutions containing beryllium fumarate relaxation times between 10 and 20 ms were observed at 5 °C depending on the concentration of the solute. (For steric reasons the fumarate ion behaves only as a unidentate ligand.) Similarly, the relaxation times and their dependence on concentration for solutions of beryllium chloroacetate resembled those found for the formation of beryllium formate. However, a detailed discussion of the formation of these two complexes is not possible since the amplitudes of the observed relaxation effects were even smaller than those of beryllium formate and, therefore, the accuracy of the measurements was lower. A relaxation time in the 10 ms region was also observed in solutions of Be^{2+} with bidentate carboxylic ligands. In this case, however, a second relaxation time was superimposed on the first and is caused by a ring-closure process; the evaluation of the measurements is thus much more complicated. The investigation of beryllium complex formation with bidentate ligands is continuing.

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* 1 atm = 101 325 Pa.

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DISCUSSION

The relaxation observed is attributed to the formation of the complex $[Be(O_2CH)]^+$ according to the mechanism (1). The undissociated HCO_2H has to be taken into

$$HCO_2H + Be^{2+} \underset{\pm H^+}{\rightleftharpoons} HCO_2^- + Be^{2+} \rightleftharpoons$$
$$[Be(OH_2)(O_2CH)]^+ \underset{k'}{\overset{k}{\rightleftharpoons}} [Be(O_2CH)]^+ \quad (1)$$

account, since formic acid is only partly dissociated in the pH range studied. The rate-determining step is the formation of the inner-sphere complex $[Be(O_2CH)]^+$ from the solvent-separated outer-sphere complex $[Be(OH_2)(O_2CH)]^+$. For this process the relaxation time is given by equation (2) where c_+ and c_- are the

$$\frac{1}{\tau} = k'\left[1 + \frac{K_iK_0f_+(c_+ + c_-\gamma_+)}{1 + K_0f_+(c_+ + c_-\gamma_+)}\right] \quad (2)$$

concentrations of Be^{2+} and HCO_2^-, respectively, c_0 is the concentration of $[Be(OH_2)(O_2CH)]^+$, and c_i is that of $[Be(O_2CH)]^+$. The other constants in equation (2) are defined as in (3)—(5), where f_+ is the activity

$$K_i = c_i/c_0 \quad (3)$$

$$K_0 = c_0/c_+c_-f_+ \quad (4)$$

$$\gamma_+ = 1 + \frac{\partial \ln f_+}{\partial \ln c_+} \quad (5)$$

coefficient of the Be^{2+} ion. In the derivation of equation (2) the assumption was made that the activity coefficients only depend on the valency of the ions; in particular that the activity coefficients are the same for the formate and the beryllium formate ions. For the calculation of the activity coefficients we used Davies' formula [13] (6) where I is the ionic strength of the solution.

$$\log f = -0.5z^2\left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.3I\right) \quad (6)$$

Equation (2) is valid only if the concentration of the acid is large compared to that of the proton in solution. However, if this is not so the concentration of the undissociated acid HCO_2H appears explicitly in equation (2). The overall association constant, K_a, is related to K_i and K_0 by equation (7).

$$K_a = \frac{c_0 + c_i}{c_+c_-f_+} = K_0(1 + K_i) \quad (7)$$

In a fast reaction the outer-sphere complex $[Be(OH_2)(O_2CH)]^+$ is formed from the free solvated ions. This reaction proceeds in *ca.* 10^{-9} s and can be studied by ultrasonic absorption. For 2 : 1 valent ion pairs the relaxation effect is very small (see, for example, ref. 14) and it cannot be decided experimentally whether the formation of the outer-sphere complex is a single step or a multiple-step reaction. Therefore the most simple mechanism [equation (1)] is used for the evaluation of the experiments. On the other hand, the introduction of a further step (the formation of an outer-sphere complex) does not influence the evaluation of the slow step significantly.

The three unknown quantities k', K_i, and K_0 were obtained by a least-squares fit of the experimental data to equation (2). This calculation was performed on a small computer and taking into account equations (2)—(6), the dissociation constant of formic acid, and the proton concentration as given in (8). The results at

$$c_H = 10^{-pH}/f_H^{-1} \quad (8)$$

5 °C were $k' = 168 \pm 3\ s^{-1}$, $K_i = 3.1 \pm 0.4$, and $\log K_0 = 1.4 \pm 0.3$. The logarithmic form is preferred for K_0 because of its large error. Table 1 shows the good agreement between the experimentally determined relaxation times and the values calculated from these constants. The rate constant $k = 52 \pm 6\ s^{-1}$ and the overall association constant K_a can be calculated from the values of k', K_i, and K_0. The small error in k results from a partial compensation of the errors in k' and K_i.

The activation energy of the inner-sphere complex formation was obtained from the temperature dependence of the relaxation times. At low concentrations the second term on the right-hand side of equation (2) is small compared to the first one, and equation (9) is

$$\frac{\partial \ln \tau^{-1}}{\partial T^{-1}} \approx \frac{\partial \ln k'}{\partial T^{-1}} = -\frac{E'}{R} \quad (9)$$

applicable. At high concentrations the fraction in equation (2) is close to unity and we obtain (10),

$$\frac{\partial \ln \tau^{-1}}{\partial T^{-1}} \approx \frac{\partial \ln k'(1 + K_i)}{\partial T^{-1}} = -\frac{E'}{R} - \frac{K_i}{(1 + K_i)} \cdot \frac{\Delta H_i}{R} \quad (10)$$

$\Delta H_i = E' - E$ being the enthalpy of reaction. As shown in Table 1, $d \ln \tau^{-1}/dT^{-1} = -(5.5 \pm 0.5) \times 10^3\ K$ was independent of concentration. Therefore, the second term on the right-hand side of equation (10) is small compared to the first, and we obtain $E = 46 \pm 6$ kJ mol^{-1}. The uncertainty in $d \ln \tau^{-1}/dT^{-1}$ permits only an estimation of the enthalpy of reaction of $\Delta H_i = 0 \pm 8$ kJ mol^{-1}.

With these values, the rate and equilibrium constants were calculated at 25 °C. In order to compare them with results obtained for other beryllium complexes, they are summarized in Table 2. For beryllium formate the outer-sphere association constant is larger than that obtained from the Fuoss equation,[6] which yields $\log K_0$ 0.75. The difference may be due to the fact that Fuoss assumed an ion with spherical charge distribution, whereas in the case of the formate ion the charge is localized at one side of the molecule. Nevertheless, the Fuoss value yields a good first approximation despite its difference from the experimentally determined value. The inner-sphere association constant K_i of beryllium

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formate is large compared with that of beryllium sulphate and hexacyanoferrate. This may be due to the stronger contribution of covalent bonding in the formation of beryllium formate, whereas the bonding in the sulphate and hexacyanoferrate is almost purely electrostatic. The covalent contribution is even stronger for $[BeF]^+$ and $[Be(HF)]^{2+}$.[4] We obtained a value of log K_a 1.9 ± 0.3 for the overall association constant. This constant has not been determined by any other technique. We can only compare it with the association constant of beryllium acetate for which log K_a 1.62.[12] The two values are in good agreement as expected since the beryllium ion should form similarly strong complexes with both ligands.

TABLE 2

Rate and equilibrium constants for the formation of beryllium complexes at 25 °C

	log K_0	K_i	k / s^{-1}	E / kJ mol^{-1}	Ref.
$[Be(O_2CH)]^+$	1.4 ± 0.3	3.1 ± 0.4	200 ± 50	46 ± 6	
$Be[SO_4]$	2.0 ± 0.1	0.65 ± 0.1	185 ± 25	51 ± 2	3
$[BeFe(CN)_6]^-$	2.85 [a]	0.1 ± 0.05	300 ± 200	38 ± 4	5
$[BeF]^+$	0.75 [a]	6.9×10^4	473	37 ± 3	4
$[Be(HF)]^{2+}$ [b]	−0.45 [a]	3.7×10^2	203	37 ± 3	4

[a] Calculated from the Fuoss equation.[6] [b] Refers to the reaction $Be^{2+} + HF \rightleftharpoons [Be(OH_2)(HF)]^{2+} \rightleftharpoons [BeF]^+ + H^+$.

For all the investigated beryllium complexes the rate constants, *k*, of formation of the inner-sphere complex and the corresponding activation energies are approximately independent of the ligand. This fits an S_N1 mechanism. For this process, however, the activation energy should be given by the energy needed for the removal of the water molecule which is *ca.* 400 kJ mol^{-1}. Since the observed activation energy is only *ca.* 40 kJ mol^{-1} a concerted mechanism has to be assumed for the formation of beryllium complexes.[2] Even though the amplitudes of the relaxation effects for the other beryllium complexes with unidentate carboxylates were too small for an accurate determination of the relaxation times, it can be assumed that these are also formed by the same mechanism since they have similar rate and equilibrium constants as beryllium formate.

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