Contribution from the Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University,
Chikusa, Nagoya 464-01, Japan, and Institut de Chimie Minérale et Analytique,
Faculté des Sciences, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland

Variable-Pressure Kinetic and Equilibrium Study of the Complexation of the Beryllium(II) Ion with 4-Isopropyltropolone in Acidic Aqueous Solution

Masahiko Inamo,[1a] Koji Ishihara,[1b,c] Shigenobu Funahashi,*[1b] Yves Ducommun,[1a] André E. Merbach,*[1a]
and Motoharu Tanaka[1b]

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Kinetics and equilibria for the formation and dissociation of the 1:1 complex of the beryllium(II) ion with 4-isopropyltropolone (Hipt) in acidic aqueous solution have been studied spectrophotometrically at various temperatures and pressures at an ionic strength of 0.100 M ((Na,H)ClO$_4$). Equilibrium measurements gave the following results: $K = [\mathrm{Be(ipt)^+}][\mathrm{H^+}][\mathrm{Be^{2+}}]^{-1}[\mathrm{Hipt}]^{-1} = 1.17 \pm 0.06$ (25.0 °C), $\Delta H^\circ = 2.4 \pm 0.3$ kJ mol^{-1}, $\Delta S^\circ = 9.2 \pm 1.1$ J K^{-1} mol^{-1}, $\Delta V^\circ = +5.3 \pm 0.2$ cm^3 mol^{-1} (25.0 °C). The reaction volumes for the proton dissociation of Hipt and for the complexation of Be^{2+} with ipt$^-$ are -8.2 ± 0.5 and $+13.5 \pm 0.6$ cm^3 mol^{-1}, respectively, at 25.0 °C. The rate constants and activation parameters for formation and dissociation of the complex are as follows: $k_f = 58.1 \pm 0.5$ M^{-1} s^{-1} (25.0 °C), $k_r = 49.8 \pm 0.5$ M^{-1} s^{-1} (25.0 °C), $\Delta H_f^\ddagger = 38.1 \pm 0.4$ kJ mol^{-1}, $\Delta H_r^\ddagger = 35.7 \pm 0.4$ kJ mol^{-1}, $\Delta S_f^\ddagger = -83.5 \pm 1.3$ J K^{-1} mol^{-1}, $\Delta S_r^\ddagger = -92.7 \pm 1.2$ J K^{-1} mol^{-1}, $\Delta V_f^\ddagger = -7.1 \pm 0.2$ cm^3 mol^{-1} (25.0 °C), $\Delta V_r^\ddagger = -12.4 \pm 0.2$ cm^3 mol^{-1} (25.0 °C). The negative values of entropy and volume of activation indicate that the reaction proceeds with an associative mode of activation.

Introduction

Kinetic data for substitution reactions of tetrahedral complexes are scarce. To our knowledge, there are only three kinetic studies on the substitution of tetrahedral complexes at high pressure.[2] The substitution of Ni(CO)$_4$ with P(OEt)$_3$ in heptane is characterized by an activation volume of +8 cm^3 mol^{-1}, suggesting a dissociative mechanism.[3a] This is consistent with previous results at ambient pressure, which showed the rate independent of the concentration and nature of the entering ligands.[3b–d] Another report is a high-pressure NMR study on the triphenylphosphine (PPh$_3$) exchange of the CoBr$_2$(PPh$_3$)$_2$ complex.[4] The negative volume of activation of −12.1 cm^3 mol^{-1} supports an associative activation mode (I$_a$). Recently, a variable-pressure study of solvent exchange at the beryllium(II) ion has been attempted for various solvents. The most negative activation volume ($\Delta V_{ex}^\ddagger = -13.6$ cm^3 mol^{-1}) ever obtained for water exchange at metal ions in aqueous solution clearly indicates the associative character of this reaction.[5]

In this work, we report a variable-temperature and -pressure study of the reaction of the tetrahedral beryllium(II) ion with 4-isopropyltropolone (Hipt) as a bidentate ligand. Hipt, sometimes named hinokitiol or β-thujaplicin, is a naturally occurring nonbenzenoid aromatic compound with a spectroscopic absorption maximum in the UV region.[6] Tropolone and its derivatives form very stable chelate complexes with many metal ions and are thus useful ligands.[7] This is the first high-pressure study of the complex formation reaction of the beryllium(II) ion. On the basis of the pressure effect, we depict the volume profile and discuss the reaction mechanism for the complexation of the beryllium(II) ion in aqueous solution.

Experimental Section

Reagents. Hydrated beryllium(II) perchlorate [Be(OH$_2$)$_4$](ClO$_4$)$_2$ was prepared by dissolving beryllium(II) oxide (Fluka, purum) in perchloric acid solution, followed by recrystallization.[8] Hipt (Takasago Perfumery Co., Tokyo) was purified by vacuum sublimation. 3-Morpholinopropanesulfonic acid (MOPS; Dojindo Laboratories, Kumamoto, Japan) was recrystallized twice from aqueous ethanol. Doubly distilled water was used for preparation of all solutions. The ionic strength was maintained at 0.100 M by using purified sodium perchlorate and perchloric acid.

Measurements. The hydrogen ion concentration in aqueous solutions was measured by using a pH meter. A glass electrode was calibrated by the titration of a perchloric acid solution ([HClO$_4$] = 1.00 × 10^{-2} M, I = 0.100 M) with a 1 M sodium hydroxide solution over the pH range between 2 and 10. The 1.00 × 10^{-2} M perchloric acid solution was used as a standard solution of the hydrogen ion concentration. The temperature of solutions was controlled to within ±0.1 °C. Concentrations are always given in molarities at ambient pressure.[9]

The acid dissociation constant of Hipt and equilibrium constant of the 1:1 complex of Be^{2+} with Hipt were determined by spectrophotometry. UV–visible absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer and a Shimazu UV-265FW spectrophotometer. Spectra at various pressures up to 200 MPa were obtained by using an optical pressure device with a cell of the le Noble type. In order to avoid hydrolysis and polymerization of the Be^{2+} ion, its total concentration C_{Be} was kept less than 1 × 10^{-3} M and −log [H$^+$] was varied between 1.9 and 3.3.[10] The total concentration of Hipt (C_{Hipt}) was set to about 5 × 10^{-5} M.

The reaction was followed by using a stopped-flow spectrophotometer (RA-401, Union Giken, Osaka) at ambient pressure and a high-pressure stopped-flow apparatus (Type FIT-3)[11] at elevated pressures. Beryllium(II) perchlorate was used in large excess over C_{Hipt} in order to maintain pseudo-first-order conditions. C_{Hipt} was much smaller than [H$^+$] to keep a constant hydrogen ion concentration during the reaction: $4 \times 10^{-4} < C_{Be}/\mathrm{M} < 1 \times 10^{-3}$, $2 \times 10^{-5} < C_{Hipt}/\mathrm{M} < 5 \times 10^{-5}$, and $2 \times 10^{-3} < [\mathrm{H^+}]/\mathrm{M} < 6 \times 10^{-3}$. Reaction rates were measured by monitoring the increase in absorbance at 360 nm after mixing solutions of the Be^{2+} ion and Hipt. Under the present experimental conditions, the reaction is pseudo-first-order with respect to Hipt; observed first-order rate constants k_0 were determined by analyzing at least the first 3 half-lives of the reaction curve. Reproducibility of the k_0 values were better than ±5%.

Results

Reaction Volume for Proton Dissociation of Hipt. The equilibrium constant of the proton dissociation reaction of Hipt (eq 1) was determined spectrophotometrically. MOPS was used as a pH buffer reagent. Over the pH range 5–9, the observed spectra of Hipt solutions at various hydrogen ion concentrations at constant

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(1) (a) Université de Lausanne. (b) Nagoya University. (c) Present address: Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku, Tokyo 169, Japan.

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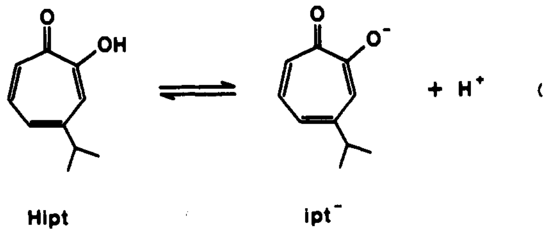

(1)

temperature and pressure have clear isosbestic points at 276, 316, 344, and 362 nm. The apparent molar absorption coefficient $\bar{\epsilon}$ is expressed as $\bar{\epsilon} = (\epsilon_1 + \epsilon_2 K_a[H^+]^{-1})(1 + K_a[H^+]^{-1})^{-1}$, where ϵ_1 and ϵ_2 are molar absorption coefficients of Hipt and ipt$^-$, respectively, and K_a is the acid dissociation constant of Hipt. The $\bar{\epsilon}$ value of the solution at 387 nm as a function of hydrogen ion concentration was analyzed by a nonlinear least-squares-fitting method. Furthermore, absorption spectra of Hipt solutions were measured under various pressures up to 200 MPa at several hydrogen ion concentrations ($6.2 < -\log [H^+] < 7.5$) at 25.0 °C. Hydrogen ion concentrations of the solution at high pressures were calculated by using the value (−7.1 ± 0.2 cm^3 mol^{-1}) of the reaction volume for proton dissociation of MOPS.[12] pK_a values obtained are 7.01 at 0.1 MPa, 6.94 at 39.2 MPa, 6.87 at 78.5 MPa, 6.82 at 117.7 MPa, 6.77 at 156.9 MPa, and 6.73 at 196.1 MPa. The reaction volume for the proton dissociation of Hipt was then calculated to be $\Delta V^\circ = -8.2 \pm 0.5$ cm^3 mol^{-1} (25.0 °C, I = 0.100 M).

Equilibrium of the Beryllium(II) Ion with Hipt. Under the present experimental conditions, the beryllium(II) ion exists as the aqua ion, judging from the equilibrium constants for hydrolysis of Be^{2+}.[10] 4-Isopropyltropolone is present in its neutral form, Hipt, judging from the protonation constant of Hipt ($K_H = [H_2ipt^+][Hipt]^{-1}[H^+]^{-1} = 1.78$ M^{-1})[13] and its pK_a value. Beryllium(II) forms the 1:1 complex with Hipt under conditions where it is present in large excess over the ligand. Figure 1 shows, as an example, the absorption spectra of the solutions containing Be^{2+} and Hipt at various pH's. Changes in the spectra were attributed to the formation of Be(ipt)$^+$ as expressed by eq 2.

$$Be^{2+} + Hipt \rightleftharpoons Be(ipt)^+ + H^+ \qquad (2)$$

The equilibrium constant of reaction 2 at a given condition ($K = [Be(ipt)^+][H^+][Be^{2+}]^{-1}[Hipt]^{-1}$) was determined by analyzing the absorbance data taken every 10 nm between 270 and 400 nm by use of a nonlinear least-squares fitting program (SPECFIT).[14] The equilibrium constants obtained at temperatures from 5.0 to 45.0 °C under ambient pressure and at several pressures up to 200 MPa at 25.0 °C are summarized in Table I. Thermodynamic parameters were determined by using both the equilibrium constants and rate constants for reaction 2, as described in the kinetic section (vide infra).

Kinetics of the Reaction of the Beryllium(II) Ion with Hipt. The dependence of the observed first-order rate constant k_0 on the concentrations of beryllium(II) and hydrogen ions is shown in Figures 2 and 3, respectively. These plots clearly indicate that the reverse reaction of eq 2 contributes to k_0. The absorbance change accompanying the complex formation depends on the concentrations of both beryllium(II) and hydrogen ions and decreases with increasing [H$^+$], as expected from reaction 2. The slope and intercept in Figure 2 correspond to the second-order rate constant for formation (k_f) and $k_r[H^+]$, respectively, where k_r is the second-order rate constant for dissociation of the Be(ipt)$^+$ complex. In Figure 3 the slope and intercept are k_r and $k_f[Be^{2+}]$, respectively. k_0 is thus expressed by eq 3. Pressure dependences of k_0 are shown in Figures 4 and 5.

$$k_0 = k_f[Be^{2+}] + k_r[H^+] \qquad (3)$$

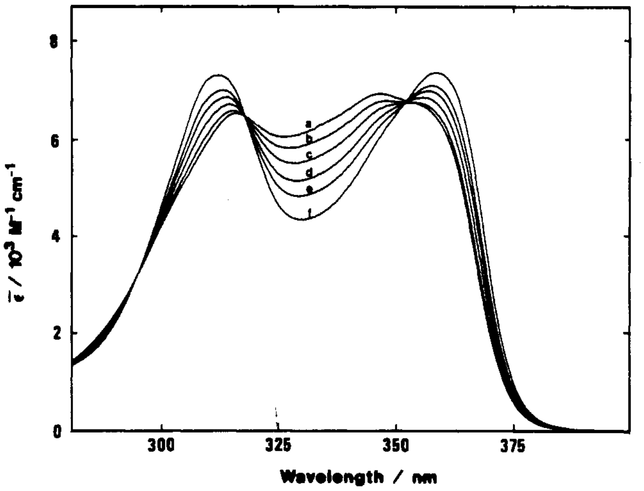

Figure 1. Example of the UV–visible absorption spectra of the solution containing Be(II) and Hipt. $C_{Be} = 6.60 \times 10^{-4}$ M. $C_{Hipt} = 5.06 \times 10^{-5}$ M. $-\log ([H^+]/M) = 2.193$ (a), 2.438 (b), 2.683 (c), 2.892 (d), 3.046 (e), 3.285 (f). T = 25.0 °C.

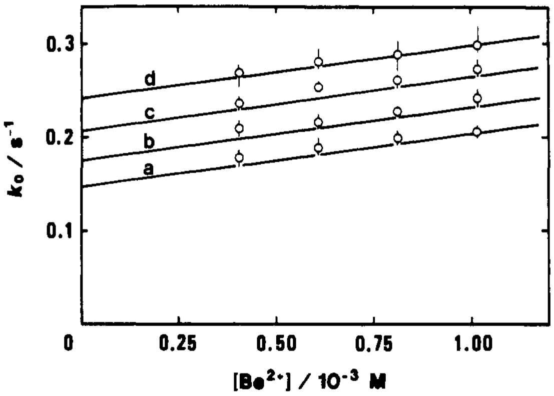

Figure 2. Dependence of k_0 on the concentration of Be(II) at ambient pressure. $C_{Hipt} = 2.04 \times 10^{-5}$ M. $[H^+]/M = 2.94 \times 10^{-3}$ (a), 3.51×10^{-3} (b), 4.13×10^{-3} (c), 4.83×10^{-3} (d). T = 25.0 °C. In Figures 2–5 each point is the average of several determinations and a vertical bar indicates the range of values of rate constant obtained.

Table I. Values of the Equilibrium Constant K for the Reaction of the Beryllium(II) Ion with Hipt under Various Conditions

T/°C	P/MPa	K[a]	T/°C	P/MPa	K[a]
5.0	0.1	1.09	25.0	25.0	1.11
10.0	0.1	1.11	25.0	50.0	1.06
15.0	0.1	1.13	25.0	75.0	0.99
20.0	0.1	1.14	25.0	100.0	0.94
25.0	0.1	1.17	25.0	125.0	0.89
30.0	0.1	1.18	25.0	150.0	0.85
35.0	0.1	1.20	25.0	175.0	0.82
40.0	0.1	1.22	25.0	200.0	0.79
45.0	0.1	1.24			

[a] Errors in K are less than 5%.

Table II. Thermodynamic and Kinetic Parameters for Formation and Dissociation of the [Be(ipt)(OH$_2$)$_2$]$^+$ Complex

K	1.17 ± 0.06[a]	ΔS°/J K^{-1} mol^{-1}	9.2 ± 1.1
k_f/M^{-1} s^{-1}	58.1 ± 0.5[a]	$\Delta S_f^\ddagger$/J K^{-1} mol^{-1}	−83.5 ± 1.3
k_r/M^{-1} s^{-1}	49.8 ± 0.5[a]	$\Delta S_r^\ddagger$/J K^{-1} mol^{-1}	−92.7 ± 1.2
ΔH°/kJ mol^{-1}	2.4 ± 0.3	ΔV°/cm^3 mol^{-1}	+5.3 ± 0.2
$\Delta H_f^\ddagger$/kJ mol^{-1}	38.1 ± 0.4	$\Delta V_f^\ddagger$/cm^3 mol^{-1}	−7.1 ± 0.2
$\Delta H_r^\ddagger$/kJ mol^{-1}	35.7 ± 0.4	$\Delta V_r^\ddagger$/cm^3 mol^{-1}	−12.4 ± 0.2

[a] At 25.0 °C and 0.1 MPa.

Eyring plots of both k_f and k_r showed little deviation from linearity. Plots of ln k_f and ln k_r against pressure were also linear. The refined kinetic and thermodynamic parameters summarized in Table II were computed by a simultaneous fit of the varia-

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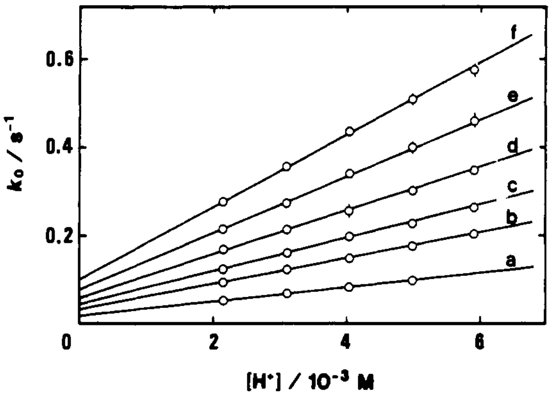


Figure 3. Dependence of k_0 on the concentration of the hydrogen ion at ambient pressure. C_{Be} = 1.02 × 10^{-3} M. C_{Hipt} = 4.52 × 10^{-5} M. T/°C = 5.0 (a), 15.0 (b), 20.0 (c), 25.0 (d), 30.0 (e), 35.0 (f).

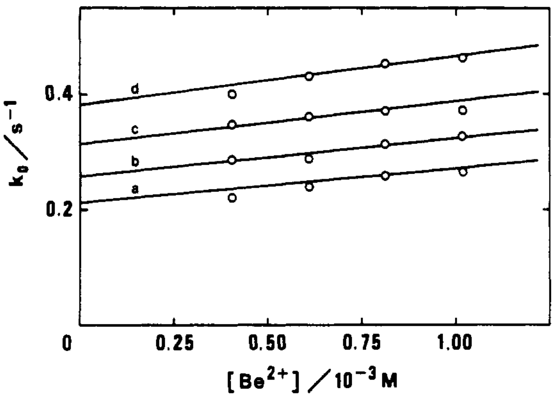


Figure 4. Pressure dependence of k_0 at various concentrations of Be(II). C_{Hipt} = 2.15 × 10^{-5} M. [H$^+$] = 4.13 × 10^{-3} M. P/MPa = 0.1 (a), 39.2 (b), 78.5 (c), 117.7 (d). T = 25.0 °C.

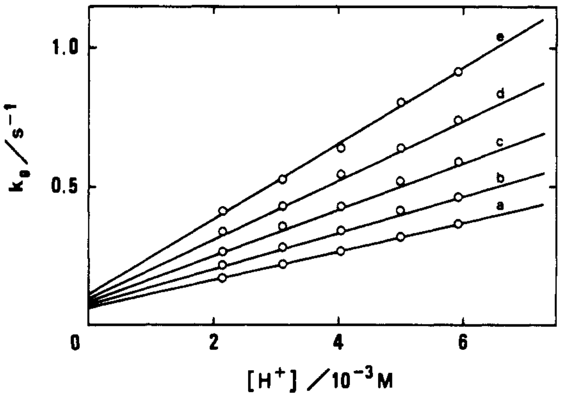


Figure 5. Pressure dependence of k_0 at various concentrations of the hydrogen ion. C_{Be} = 1.02 × 10^{-3} M. C_{Hipt} = 4.56 × 10^{-5} M. P/MPa = 0.1 (a), 49.0 (b), 98.1 (c), 147.1 (d), 196.1 (e). T = 25.0 °C.

ble-temperature data for K and k_0 to eq 3 and the Eyring equation for $\Delta H_f^\ddagger$, $\Delta S_f^\ddagger$, $\Delta H_r^\ddagger$ (or $\Delta H°$), and $\Delta S_r^\ddagger$ (or $\Delta S°$) and of the variable-pressure data to eqs 3–6 for $\Delta V_f^\ddagger$ and $\Delta V_r^\ddagger$ (or $\Delta V°$).

$$\ln K = \ln K^0 - \Delta V^0 P/RT \qquad (4)$$

$$\ln k_f = \ln k_f^0 - \Delta V_f^\ddagger P/RT \qquad (5)$$

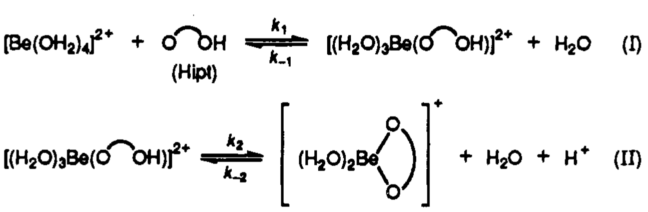
$$\ln k_r = \ln k_r^0 - \Delta V_r^\ddagger P/RT \qquad (6)$$

K^0 and k^0 are the equilibrium constant and the rate constant, respectively, at zero pressure. Solid lines in Figures 2–5 were calculated from the parameters listed in Table II.

Discussion

The hydration number of beryllium(II) in aqueous solution has been determined to be 4 in its inner-coordination sphere by NMR spectroscopy.[5,15] An X-ray diffraction study of an aqueous solution of $BeCl_2$ indicated that four water molecules are tetrahedrally coordinated to Be^{2+}.[16] The structure in aqueous solution is consistent with the crystal structure determined by X-ray diffraction,[17] neutron diffraction,[18] and infrared and Raman scattering spectroscopy.[19] Furthermore, an ab initio molecular orbital study also confirms a tetrahedral environment.[20]

Scheme I



Tropolonate and its derivatives have been shown to act as bidentate ligands to form chelate complexes with many di- and trivalent metal ions.[21] The stability constant of the monocomplex of Be^{2+} with tropolonate is K = 2.5 × 10^7 M^{-1} (25.0 °C, I = 0.100 M),[21] which is comparable to the value (K = [Be(ipt)$^+$][Be^{2+}]$^{-1}$[ipt$^-$]$^{-1}$ = 1.0 × 10^7 M^{-1}) for the Be(ipt)$^+$ complex obtained in the present study.

The reaction is outlined in Scheme I. The first step (step I) is the substitution of a coordinated water molecule by the ligand to form an intermediate [$(H_2O)_3$Be(O⌒OH)]$^{2+}$ where Hipt (O⌒OH) acts as a unidentate ligand. The second step (step II) is chelate-forming ring closure. Ring closure is usually much faster than the preceding replacement of a coordinated solvent molecule by the entering ligand. In some cases, as in the reactions of Co(II) with β-alanine[22] and β-aminobutyrate[23] in water, and of [Al(Me_2SO)$_6$]$^{3+}$ with 2,2′-bipyridine in nitromethane,[24] the ring closure has been claimed to be sterically less favored, and then chelate formation is thus considerably slower than complexation with unidentate ligands.

The rate constant for complexation of Be^{2+} with a noncharged and unidentate ligand such as hydrogen fluoride is available.[25] The second-order rate constant of the reaction of Be^{2+} with HF is 73 M^{-1} s^{-1} at 25.0 °C, which is comparable to the value for the Hipt reaction. This similarity indicates that the rate-determining step of the present system is not the chelate formation of step II, but the substitution of step I. The molecule of Hipt has two oxygen atoms that bind to the Be^{2+} ion in the Be(ipt)$^+$ complex. Since the basicity of the oxygen atom of the keto type is stronger than that of the –OH group, the former should attack the Be^{2+} ion first to form the intermediate.

The reaction volume of reaction 2 is +5.3 cm^3 mol^{-1} (see Table II). With the knowledge of the reaction volume of proton dissociation of Hipt of −8.2 cm^3 mol^{-1}, the volume of the reaction of Be^{2+} with ipt$^-$ to form Be(ipt)$^+$ is estimated to be +13.5 ± 0.6 cm^3 mol^{-1}. In this case, charge neutralization should cause the

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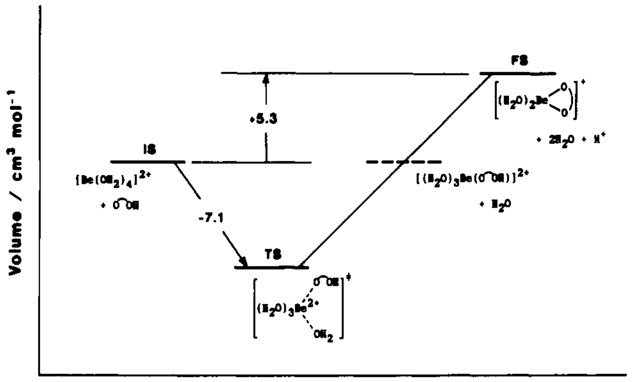

Figure 6. Volume diagram for formation and dissociation of the $[Be(ipt)(OH_2)_2]^+$ complex. $\mathrm{O{\frown}OH}$ stands for Hipt. IS, TS, and FS refer to initial, transition, and final states, respectively.

release of the electrostriction of the surrounding water molecules and may be one of the main factors contributing to the reaction volume. The following four factors have been taken into consideration in order to better understand reaction volumes for the complex formation reaction[26]

$$[MS_x]^{m+} + L^{n-} \rightleftharpoons [MLS_{x-y}]^{(m-n)+} + yS \qquad (7)$$

where M^{m+} denotes a metal ion, S a solvent molecule, and L^{n-} a ligand: (1) change of electrostriction around charged species; (2) elongation of the M–S bond by electron donation from the bound ligand L^{n-}; (3) different contractions of coordinated donor atoms in $[MS_x]^{m+}$ and $[MLS_{x-y}]^{(m-n)+}$; (4) volume chelate effects resulting from different packings of the multidentate ligand on the metal ion and in the bulk solvent.

Since Be^{2+} is small (ionic radius is 27 pm)[27] and the coordination number is 4 as described above, the electrostriction on Be^{2+} should be large. The partial molar volume of Be^{2+} is reported to be −22.8 $cm^3\ mol^{-1}$, relative to that of H^+ of −5.4 $cm^3\ mol^{-1}$.[28] The charge on the Be(II) complex decreases from +2 to +1 for the complexation with ipt^-. The contribution of the charge decrease to the reaction volume can be estimated by the modified Drude–Nernst equation.[26,29] Values of −7.9 $cm^3\ mol^{-1}$ for the Be^{2+} ion and −2.0 $cm^3\ mol^{-1}$ for an ion of geometry similar to Be^{2+} with unipositive charge were obtained as the electrostriction around the ions. From the reaction volume of the deprotonation of Hipt (−8.2 $cm^3\ mol^{-1}$) and the partial molar volume of H^+, the electrostriction around the ipt^- ion was estimated to be −2.8 $cm^3\ mol^{-1}$. Thus the effect of the charge neutralization due to the complex formation of the Be^{2+} ion with ipt^- is calculated to be +8.7 $cm^3\ mol^{-1}$. The difference of +4.8 $cm^3\ mol^{-1}$ between the observed reaction volume of +13.5 $cm^3\ mol^{-1}$ for the complexation of Be^{2+} with ipt^- and the estimated value of +8.7 $cm^3\ mol^{-1}$ for the charge neutralization consists of small contributions from elongation, contraction, and chelation. Unfortunately, there are no available structural data on Be(II) complexes to allow each contribution to be estimated as performed in the case of Ni(II) complexation.[26]

In Figure 6 is shown the volume profile for the formation and dissociation of the $Be(ipt)^+$ complex. The negative value of activation volume of −7.1 $cm^3\ mol^{-1}$ for the forward reaction (k_1 path) clearly indicates that the mechanism of this process is associative in character, since the solvational part should be close to 0 $cm^3\ mol^{-1}$ for the complex formation of Hipt having no formal charge.[30] On the other hand, in the reverse reaction there is the preequilibrium of protonation to the $Be(ipt)^+$ complex to form the intermediate $[(H_2O)_3Be(\mathrm{O{\frown}OH})]^{2+}$, followed by the release of $\mathrm{O{\frown}OH}$ ligand. Because of the absence of formal charge on $\mathrm{O{\frown}OH}$, the reaction volume of the following reaction should be close to zero: $[Be(OH_2)_4]^{2+} + \mathrm{O{\frown}OH} \rightleftharpoons [(H_2O)_3Be(\mathrm{O{\frown}OH})]^{2+} + H_2O$ (step I in Scheme I). Therefore, $[(H_2O)_3Be(\mathrm{O{\frown}OH})]^{2+}$ is at about the same level as the initial state in the volume profile (see Figure 6). Thus, the activation volume for the dissociation of $\mathrm{O{\frown}OH}$ from the intermediate by the attack of a water molecule (k_{-1} path) is also negative, indicating an associative mode of activation.

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