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Pressure Effects on the Base Hydrolysis Reaction Rates of α-, β-$[Co(edda)(NH_3)_2]^+$ and α-$[Co(edda)(NO_2)_2]^-$ in a Carbonate Buffer

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The pressure effects on the base hydrolysis reaction rates of α-, β-$[Co(edda)(NH_3)_2]^+$ and α-$[Co(edda)(NO_2)_2]^-$ in a carbonate buffer were measured up to 1500 kg/cm^2 (1 kg/cm^2=98.0665 kPa). The activation volumes at normal pressure were found to be 16.6, 22.3, and 11.9 cm^3/mol respectively. These values are consistent with those expected from the S_N1 CB mechanism, where the conjugate bases dissociate *via* the I_d mechanism.

The pressure dependence of a reaction rate gives the value of the activation volume (ΔV^*). In the base hydrolysis reaction of a Co(III)-complex, the magnitude of ΔV^* is comparatively large (20±10 cm^3/mol) for the S_N1 CB mechanism, since the volume change in the pre-equilibrium to produce the conjugate base amounts to about 20 cm^3/mol.[1] In contrast, it is smaller than 9 cm^3/mol for the S_N2 mechanism.[2] Thus, the activation volume is a useful quantity for use in discriminating the mechanisms for a base hydrolysis reaction.

It has been shown by Kuroda *et al.* that, in a carbonate buffer, the base hydrolysis reactions of α-, β-$[Co(edda)(NH_3)_2]^+$ and α-$[Co(edda)(NO_2)_2]^-$,

$$\alpha\text{-}[Co(edda)(NH_3)_2]^+ + OH^- \rightarrow \alpha\text{-}[Co(edda)(NH_3)OH] + NH_3, \qquad (1)$$

$$\beta\text{-}[Co(edda)(NH_3)_2]^+ + OH^- \rightarrow \beta\text{-}[Co(edda)(NH_3)OH] + NH_3, \qquad (2)$$

$$\alpha\text{-}[Co(edda)(NO_2)_2]^- + OH^- \rightarrow \alpha\text{-}[Co(edda)(NO_2)OH]^- + NO_2^-, \qquad (3)$$

are followed by successive carbonation steps (ethylenediamine-*N,N'*-diacetic acid=H_2edda).[3–5] The rates of the carbonation step are relatively high for the reactions of α-$[Co(edda)(NH_3)_2]^+$ and α-$[Co(edda)(NO_2)_2]^-$, and relatively low for that of β-$[Co(edda)(NH_3)_2]^+$, compared to the base hydrolysis rates. By assuming a first-order reaction for the base hydrolysis, the rate constants of Reactions 1,[3] 2,[6] and 3[5] have been calculated at a normal pressure.

In this experiment, the pressure dependences of the rate constants of Reactions 1, 2, and 3 were examined up to 1500 kg/cm^2. The mechanisms are discussed from the standpoint of the activation volume.

Table 1. The preparative methods and the absorption maxima of the complexes used in this study

Complex	λ_{max}/nm(ε_{max})		Ref.	
	This work	Lit	a)	b)
α-$[Co(edda)(NH_3)_2]\cdot ClO_4\cdot H_2O$	538 (92.5) 363 (116)	538 (92.0) 363 (118)	7)	7)
β-$[Co(edda)(NH_3)_2]\cdot ClO_4\cdot 1.5H_2O$	502 (140) 359 (154)	499 (153) 358 (159)	8)	9)
α-$Cs[Co(edda)(NO_2)_2]\cdot H_2O$	520 (148)	520 (150)	10)	10)

a) Ref. for preparations. b) Ref. for spectra.

Experimental

Materials. The preparative methods and the absorption maxima of the complexes used in this study are summarized in Table 1. The buffer solutions were made from reagent-grade chemicals. The water was distilled after passing it through an ion-exchange column.

Kinetic Measurement. The procedures were the same as those in a previous work.[11]

Results

The first-order rate constant, k_1, of the base hydrolysis was determined by

$$\ln[(D_\infty - D_{t'})/(D_\infty - D_t)] = k_1(t-t'),$$

where $D_{t'}$ and D_t represent the optical densities at the moment when the high pressure is reached, and at the moment when the high pressure is released, respectively. For the reaction of α-$[Co(edda)(NH_3)_2]^+$, D_∞ represents the optical density (OD) at equilibrium. For the reactions of β-$[Co(edda)(NH_3)_2]^+$ and α-$[Co(edda)(NO_2)_2]^-$, D_∞ represents the estimated OD values of the base hydrolysis products: β-$[Co(edda)(NH_3)OH]$ and α-$[Co(edda)(NO_2)OH]^-$ respectively. Kuroda's D_∞/D_0 values are used, where D_0 represents the OD at the moment of the dissolution of the initial complex. The D_∞/D_0 values (λ(nm) used to follow the reaction) are 1.9 (540) for Reaction 1,[3] 0.7 (500) for Reaction 2,[6] and 4.86 (590) for Reaction 3.[5] $(t-t')$ is the reaction time. The k_1 values at each pressure are summarized in Table 2. An increase in pressure by 1000 kg/cm^2 reduces the k_1 values below half, from which large positive magnitudes (*ca.* 20 cm^3/mol) of the activation volumes can be expected for these reactions. They were fitted to the formula, $\ln(k_1/k_{10}) = aP + bP^2$, where k_{10} is the rate constant at a normal pressure and where P is expressed in kg/cm^2 (Fig. 1).

At a normal pressure, the k_1 values are proportional to $[OH^-]$ *i.e.*, $k_1 = k_2[OH^-]$.[3,5,6] Then, the activation volume and its pressure dependence are given by[2]

$$\Delta V^* = -RT\frac{\mathrm{d}\ln k_2}{\mathrm{d}P} = -RT\frac{\mathrm{d}\ln k_1}{\mathrm{d}P} + RT\frac{\mathrm{d}\ln[OH^-]}{\mathrm{d}P}$$

$$= -RT(a+2bP) + RT\frac{\mathrm{d}\ln K_w}{\mathrm{d}P} - RT\frac{\mathrm{d}\ln K_2}{\mathrm{d}P}$$

$$\frac{\mathrm{d}\Delta V^*}{\mathrm{d}P} = -2bRT + RT\frac{\mathrm{d}^2\ln K_w}{\mathrm{d}P^2} - RT\frac{\mathrm{d}^2\ln K_2}{\mathrm{d}P^2},$$

where K_w and K_2 represent the ionic product of water and the second dissociation constant of carbonic acid respectively. By using the known pressure dependences of the K_w and K_2, the values of ΔV^* and $d\Delta V^*/dP$ at the normal pressure are calculated.[2] El'yanov and Hamann have proposed a formula for the pressure dependence of the volume change of an acid-base equilibrium:

$$d\Delta V/dP = (-1.80\times10^{-4}\,\mathrm{cm^2/kg})\Delta V,$$

where ΔV is the volume change at a normal pressure.[11] The second derivatives of K_w and K_2 are estimated following their method. The results are summarized in Table 3.

Discussion

From the proportionality of the k_1 values to [OH$^-$], the S_N2 and S_N1 CB mechanisms are possible for these reactions. In the case of the S_N2 mechanism, ΔV^* is estimated to be smaller than 9 cm^3/mol.[2] The large positive values of ΔV^* obtained for Reactions 1 and 2 can then be considered as evidence for the S_N1 CB mechanism. For Reaction 3, the obtained magnitude of ΔV^* is not large enough. However, this complex ion has a negative charge, and so the formation of a seven-coordinated intermediate or an ion pair with an OH$^-$ ion would be improbable. Therefore, Reaction 3 should also proceed *via* the S_N1 CB mechanism.

Table 2. $k_1\times10^3$ (min^{-1}) for the base hydrolysis reactions in a carbonate buffer

α-[Co(edda)(NH$_3$)$_2$]$^+$

in 0.2 M Na$_2$CO$_3$-0.2 M NaHCO$_3$, pH$_{65\,°C}$=9.38, $t^{a)}$=65.6 °C.

P/kg cm^{-2}	1	500	1000	1500
	11.3(41.2)	7.5(50)	4.0(50)	2.4(50)
	11.8(50.6)	7.9(60)	4.6(60)	2.2(60)
	11.8(60.6)	7.7(70)	4.0(70)	2.3(70)
Average	11.6	7.8	4.2	2.3

β-[Co(edda)(NH$_3$)$_2$]$^+$

in 0.2 M Na$_2$CO$_3$-0.2 M NaHCO$_3$, pH$_{45\,°C}$=9.54, t=42.8 °C.

P/kg cm^{-2}	1	500	1000	1500
	7.4(40.7)	4.4(50)	2.4(60)	1.3(70)
	7.2(50.5)	4.3(60)	2.7(70)	1.6(80)
	7.2(60.6)	4.3(70)	2.5(80)	1.4(90)
Average	7.3	4.3	2.5	1.4

α-[Co(edda)(NO$_2$)$_2$]$^-$

in 0.3 M Na$_2$CO$_3$-0.1 M NaHCO$_3$, pH$_{65\,°C}$=9.86, t=65.6 °C.

P/kg cm^{-2}	1	500	1000	1500
	10.3(30.8)	8.0(40)	5.3(40)	3.4(50)
	10.1(40.9)	7.5(50)	5.7(50)	3.3(60)
	11.5(50.9)	7.4(60)	4.7(60)	3.2(70)
Average	10.6	7.6	5.2	3.3

a) Reaction temperature. The numbers in parentheses denote the reaction time in min. M=mol/dm^3.

In this mechanism, the reaction series for Reactions 1 and 2 are

$$\alpha\text{-, }\beta\text{-[Co(edda)(NH}_3)_2]^+ + \mathrm{OH}^-$$
$$= \alpha\text{-, }\beta\text{-[Co(edda)(NH}_2)(\mathrm{NH}_3)] + \mathrm{H_2O}$$
$$\alpha\text{-, }\beta\text{-[Co(edda)(NH}_2)(\mathrm{NH}_3)] \rightarrow$$
$$\alpha\text{-, }\beta\text{-[Co(edda)(NH}_2)] + \mathrm{NH_3}$$
$$\alpha\text{-, }\beta\text{-[Co(edda)(NH}_2)] + \mathrm{H_2O} \rightarrow$$
$$\alpha\text{-, }\beta\text{-[Co(edda)(NH}_3)\mathrm{OH}],$$

where the first and the third steps are rapid and where

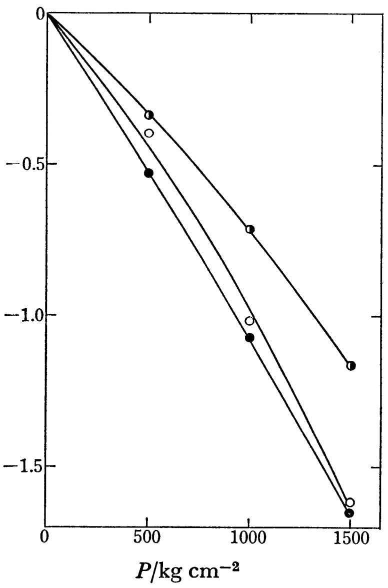

Fig. 1. The pressure dependence of the k_1-value.
○: α-[Co(edda)(NH$_3$)$_2$]$^+$
$\ln(k_1/k_{10}) = -7.60\times10^{-4}P - 2.18\times10^{-7}P^2$,
●: β-[Co(edda)(NH$_3$)$_2$]$^+$
$\ln(k_1/k_{10}) = -10.3\times10^{-4}P - 0.497\times10^{-7}P^2$,
◑: α-[Co(edda)(NO$_2$)$_2$]$^-$
$\ln(k_1/k_{10}) = -5.96\times10^{-4}P - 1.21\times10^{-7}P^2$.

Table 3. Activation parameters for reactions 1—5

a)	Complex	ΔV^*	ΔV_{pre}	$\Delta V^{*\prime}$	$\dfrac{d\Delta V^*}{dP}$	$\dfrac{d\Delta V^{*\prime}}{dP}$	E_a	ΔS^*	b)
1	α-[Co(edda)(NH$_3$)$_2$]$^+$	16.6	16.9	−0.3	13.4	16.4	157	145	3)
2	β-[Co(edda)(NH$_3$)$_2$]$^+$	22.3	16.9	5.4	3.6	6.6	172	213	6)
3	α-[Co(edda)(NO$_2$)$_2$]$^-$	11.9	13.9	−2.0	7.9	10.4	161	143	5)
4	β-[Co(edda)(tn)]$^+$	14.7	16.9	−2.2	0.2	3.2	151	124	17)
5	β-[Co(edda)(en)]$^+$	20.0	16.9	3.1	−1.4	1.6	176	195	4)

a) Reaction number. b) Ref. for E_a and ΔS^*. The units are: ΔV^*, ΔV_{pre}, $\Delta V^{*\prime}$ (cm^3/mol); $\dfrac{d\Delta V^*}{dP}$, $\dfrac{d\Delta V^{*\prime}}{dP}$ (10^{-3} cm^6 mol^{-1} kg^{-1}); E_a (kJ/mol); and ΔS^* (J K^{-1} mol^{-1}).

the second is the rate-determining process. Analogously, the series for Reaction 3 is

$$\alpha\text{-}[\mathrm{Co(edda)(NO_2)_2}]^- + \mathrm{OH}^- = \alpha\text{-}[\mathrm{Co(edda^*)(NO_2)_2}]^{2-} + \mathrm{H_2O}$$

$$\alpha\text{-}[\mathrm{Co(edda^*)(NO_2)_2}]^{2-} \rightarrow \alpha\text{-}[\mathrm{Co(edda^*)(NO_2)}]^- + \mathrm{NO_2}^-$$

$$\alpha\text{-}[\mathrm{Co(edda^*)(NO_2)}]^- + \mathrm{H_2O} \rightarrow \alpha\text{-}[\mathrm{Co(edda)(NO_2)OH}]^-,$$

where edda* represents the conjugate base of the edda ligand. Thus, the activation volume is given by $\Delta V^{*}=\Delta V_{\mathrm{pre}}+\Delta V^{*\prime}$, where ΔV_{pre} is the volume change in the pre-equilibrium and $\Delta V^{*\prime}$ is the activation volume of the second step.

The isomerization reactions in a carbonate buffer,

$$\beta\text{-}[\mathrm{Co(edda)(tn)}]^+ \rightarrow \alpha\text{-}[\mathrm{Co(edda)(tn)}]^+, \quad (4)$$

$$\beta\text{-}[\mathrm{Co(edda)(en)}]^+ \rightarrow \alpha\text{-}[\mathrm{Co(edda)(en)}]^+, \quad (5)$$

also proceed *via* the $S_{\mathrm{N}}1$ CB mechanism. In a previous report, the ΔV_{pre} value for Reactions 4 and 5 was estimated as 18.8 $\mathrm{cm^3/mol}$.[2] Later, for the equilibrium,

$$\alpha\text{-}[\mathrm{Co(edda)(H_2NCH_2CH_2OH)}]^+ + \mathrm{OH}^- = \alpha\text{-}[\mathrm{Co(edda)(H_2NCH_2CH_2O)}]^0 + \mathrm{H_2O}, \quad (6)$$

the volume change ($\Delta V=16.9\pm0.7\ \mathrm{cm^3/mol}$) was obtained at 25 °C and a low ionic strength.[1] This equilibrium is analogous to the pre-equilibria of Reactions 1, 2, 4, and 5, and the ΔV_{pre} values for these reactions may be taken approximately as 16.9 $\mathrm{cm^3/mol}$. In Equilibrium 6, $\Delta Z^2=-1$, where Z is the charge of the complex ion; the contribution (ΔV_{el}) of the electrostrictive volume change of the complex ion is positive. In contrast, in the pre-equilibrium for Reaction 3 ($\Delta Z^2=3$), ΔV_{el} would be negative and ΔV_{pre} would be smaller than 16.9 $\mathrm{cm^3/mol}$. Values of $\Delta V=19.9\pm1\ \mathrm{cm^3/mol}$ are known for the neutralization equilibria of trivalent complex ions ($\Delta Z^2=-5$) such as $[\mathrm{Fe(H_2O)_6}]^{3+}$, $[\mathrm{Co(NH_3)_5(H_2O)}]^{3+}$, and $[\mathrm{Cr(H_2O)_6}]^{3+}$.[1] Since ΔV_{el} is proportional to ΔZ^2, the ΔV_{pre} value for Reaction 3 must be approximately 13.9 $\mathrm{cm^3/mol}$.[1] The magnitudes of $\Delta V^{*\prime}$ thus obtained for Reactions 1, 2, and 3 are comparable to those for Reactions 4 and 5. In the activated states of Reactions 4 and 5, the $-\mathrm{NH_2}$ group liberated from the conjugate base must remain in the vicinity of the five-coordinated intermediate, since it is linked to the intermediate through the molecular chain of tn or en. Therefore, the conjugate bases in Reactions 1, 2, and 3 may dissociate *via* the $\mathrm{I_d}$ mechanism; *i.e.*, in the activated state the leaving group remains in the second coordination sphere.

The aquo-exchange reaction,

$$[\mathrm{Co(NH_3)_5H_2O}]^{3+} + \mathrm{H_2O^*} \rightarrow [\mathrm{Co(NH_3)_5H_2O^*}]^{3+} + \mathrm{H_2O}, \quad (7)$$

also proceeds *via* the $\mathrm{I_d}$ mechanism and $\Delta V^{*}=1.2\ \mathrm{cm^3/mol}$ is known at 25 °C.[13] In the activation step of Reaction 7, the electrostrictive volume change is not involved. In the dissociative activation steps for Reactions 1 and 2, a neutral $\mathrm{NH_3}$ departs from the neutral conjugate base, and the electrostrictive volume change is also ignored. In that of Reaction 3, only a separation of charge occurs, and the electrostrictive volume change may be insignificant. Therefore, the $\Delta V^{*\prime}$ values for the $\mathrm{I_d}$ dissociation in Reactions 1, 2, and 3 may be expected to be comparable to the ΔV^{*} for Reaction 7. The experimentally obtained magnitudes of $\Delta V^{*\prime}$ are consistent with this expectation.

If the conjugate bases completely dissociate in the activated state (D mechanism), $\Delta V^{*\prime}$ can be estimated from the partial molar volumes ($\bar{V}$) by

$$\Delta V^{*\prime} = \bar{V}(\alpha\text{-},\beta\text{-}[\mathrm{Co(edda)(NH_2)}]) - \bar{V}(\alpha\text{-},\beta\text{-}[\mathrm{Co(edda)(NH_2)(NH_3)}]) + \bar{V}(\mathrm{NH_3}),$$

and

$$\Delta V^{*\prime} = \bar{V}(\alpha\text{-}[\mathrm{Co(edda^*)(NO_2)}]^-) - \bar{V}(\alpha\text{-}[\mathrm{Co(edda^*)(NO_2)_2}]^{2-}) + \bar{V}(\mathrm{NO_2}^-).$$

Stranks assumes that the intrinsic volume difference between the five-coordinated intermediate and its six-coordinated precursor is zero.[14] This volume difference may be estimated from the volume difference between a square pyramid or a trigonal bipyramid and an octahedron, with each center-apex length 3 Å. This leads to the intrinsic volume difference of −10.8 and −7.6 $\mathrm{cm^3/mol}$. $\bar{V}(\mathrm{NH_3})$ is *ca.* 24.9 $\mathrm{cm^3/mol}$.[15] Then, in the D mechanism, the $\Delta V^{*\prime}$ values for Reactions 1 and 2 would be 14.1 $\mathrm{cm^3/mol}$ or larger. $\bar{V}(\mathrm{NO_2}^-)$ is *ca.* 31.6 $\mathrm{cm^3/mol}$.[16] Taking account of the electrostrictive volume expansion (*ca.* 2.3 $\mathrm{cm^3/mol}$) of the complex, the $\Delta V^{*\prime}$ value for Reaction 3 would be 23.1 $\mathrm{cm^3/mol}$ or larger in the D mechanism. Thus, the values of $\Delta V^{*\prime}$ to be expected from the D mechanism are considerably larger than those obtained from the experimental results.

The values of $\mathrm{d}\Delta V^{*\prime}/\mathrm{d}P$ are calculated from $\mathrm{d}\Delta V^{*}/\mathrm{d}P$ (Table 3):

$$(\mathrm{d}\Delta V^{*\prime}/\mathrm{d}P) = (\mathrm{d}\Delta V^{*}/\mathrm{d}P) - (\mathrm{d}\Delta V_{\mathrm{pre}}/\mathrm{d}P),$$

where $\mathrm{d}\Delta V_{\mathrm{pre}}/\mathrm{d}P$ is -3×10^{-3} and $-2.5\times10^{-3}\ \mathrm{cm^5\,mol^{-1}\,kg^{-1}}$ for $\Delta V_{\mathrm{pre}}=16.9$ and 13.9 $\mathrm{cm^3/mol}$ respectively (estimated after El'yanov and Hamann).[12] The values of $\mathrm{d}\Delta V^{*\prime}/\mathrm{d}P$ are comparatively small for Reactions 4 and 5, where the liberated $-\mathrm{NH_2}$ group is linked to the five-coordinated intermediate. In contrast, they are comparatively large for Reactions 1, 2, and 3, where the leaving group is not linked to the intermediate. Hence, the increases in the $\Delta V^{*\prime}$ with the increase in the pressure are caused by the enhancement of the separation of the leaving group from the five-coordinated intermediate at high pressures. In other words, the mechanism of the dissociation of the conjugate base changes from the $\mathrm{I_d}$ mechanism at a normal pressure to the D mechanism at higher pressures. A possible factor promoting the separation at high pressures may be the increasing stability of the hydrogen bonds between the leaving group and the water molecules, which decreases the interaction between the leaving group and the intermediate.

The activation energies (E_{a}) obtained by Kuroda are listed in Table 3. In the $S_{\mathrm{N}}1$ CB mechanism, $E_{\mathrm{a}}\simeq\Delta H_{\mathrm{pre}}+E_{\mathrm{a}}'$, where ΔH_{pre} is the enthalpy change for the pre-equilibrium and where E_{a}' is the activation energy for the dissociation of the conjugate base. ΔH_{pre} would be negative, since an evolution of heat was noticed in the analogous neutralization Equilibrium 6.[1] The abnormally large magnitudes of E_{a}'

can be understood only by considering the Co–N bond rupture to be the activation step.3) There can be found an qualitative correspondence relation between the magnitude of E_a and the position of the first absorption band.9,17) This indicates that the ligand-field strength is one factor which influences the activation energy. The activation entropies calculated from the first-order rate constants are listed in Table 3. An ordinary compensation relation is found between the magnitudes of E_a and ΔS^*. This relation is often found for a series of related reactions and is interpreted as indicating that the essential reaction mechanism is the same for all of a given series.18) Another linear correlation is found between ΔS^* and ΔV^* except for Reaction 3. Thus, the values of $\Delta V^{*\prime}$, E_a, and ΔS^* for Reactions 2 and 5 are comparatively larger than those for Reactions 1 and 4. One possible interpretation of this may be that, in the activated states for Reactions 2 and 5, the leaving group is more separated from the five-coordinated intermediate than in those for Reactions 1 and 4. Then, the smaller magnitude of $\mathrm{d}\Delta V^{*\prime}/\mathrm{d}P$ for Reaction 2 than that for Reaction 1 may be interpreted as showing that, for Reaction 2, the separation increases rather moderately with the pressure, since it is already considerable at the normal pressure.

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6) The first-order rate constants ($k_1 \times 10^3$ min^{-1}) obtained by K. Kuroda for the base hydrolysis of β-[Co(edda)$(NH_3)_2$]$^+$ in carbonate buffers are as follows at a normal pressure:

Condition	(pH at 60 °C)	40 °C	45 °C	50 °C
0.1 M Na_2CO_3–0.3 M $NaHCO_3$	(9.48)	3.3	10	25
0.2 M Na_2CO_3–0.2 M $NaHCO_3$	(9.81)		15	
0.3 M Na_2CO_3–0.1 M $NaHCO_3$	(10.18)		30	

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