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Pressure Effect on the Base Hydrolysis Rate of $[Co(NH_3)_5Cl]^{2+}$ in a Carbonate Buffer

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The pressure effect on the base hydrolysis reaction rate of $[Co(NH_3)_5Cl]^{2+}$ in a 0.0133 M Na_2CO_3–0.0200 M $NaHCO_3$ buffer solution was measured up to 1500 kg cm^{-2} (M=mol dm^{-3}). The activation volume ($\Delta V^{\neq}$) was found to be 33.4 ml mol^{-1}. This value is consistent with that expected from the D_{cb} mechanism.

The base hydrolysis reaction of $[Co(NH_3)_5Cl]^{2+}$,

$$[Co(NH_3)_5Cl]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + Cl^-, \quad (1)$$

has been known for some time and has been discussed extensively from various aspects.[1–4] However, no examination from the standpoint of the activation volume has been made hitherto, because $[Co(NH_3)_5Cl]^{2+}$ lacks an appropriate UV absorption peak which would allow the reaction to be followed at high pressures, as exists for $[Co(NH_3)_5Br]^{2+}$.[5] In this experiment, it was found that, in a carbonate buffer, the product, $[Co(NH_3)_5OH]^{2+}$, reacted rapidly yielding $[Co(NH_3)_5CO_3]^+$, accompanied by an increase in the UV absorption. Thus, the course of Reaction 1 in a carbonate buffer was followed at high pressures. The reaction mechanism is discussed on the basis of the activation volume.

Experimental

Materials. $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_5H_2O]Cl_3$ were prepared and purified by the standard method.[6,7] They were characterized spectrophotometrically as illustrated in Table 1. The buffer solutions were made from reagent grade chemicals.

TABLE 1. VISIBLE SPECTRA OF THE COMPLEXES USED IN THIS STUDY

Complex	Solvent	λ_{max} (nm)	ε_{max}	Ref.
$[Co(NH_3)_5Cl]Cl_2$	H_2O	534	49.8	this work
		532	50.7	8
$[Co(NH_3)_5H_2O]Cl_3$	0.01M NaOH	504	68.1	this work
		500	66.8	1

Kinetic Run at Normal Pressure. Aliquots of the reaction mixture were pipetted out from a brown-colored flask in a thermostat controlled at 35±0.1 °C after certain time intervals. They were quenched in cold water and the UV absorption spectra were recorded.

Kinetic Run at High Pressure. The procedure has been described in a previous work.[9] The temperature of the high-pressure cylinder was controlled by circulating water from a thermostat regulated at 35±0.1 °C. The pressure of the press was measured using a Bourdon gauge. The pressure in the cylinder was determined using a manganin gauge inserted in the cylinder.[10] The manganin gauge was calibrated to another Bourdon gauge, which was further calibrated to a strain gauge in the Kobe Steel Co., Ltd. The ratios of the pressure in the cylinder to that of the press were 61.0, 59.6, 58.5, and 58.4 for pressures in the cylinder of 305, 500, 1000, and 1500 kg cm^{-2}, respectively. The piston area ratio was 61.03.

Results

Reaction Rate at Normal Pressure. Figure 1(a) illustrates the changes in the UV absorption spectrum of the reaction system. Satisfactory Guggenheim plots were obtained for optical densities at 280, 290, and 300 nm. Hence, the reaction was of first order with respect to the complex ion. The rate constants in three buffer solutions of the same ionic strength were calculated by applying Guggenheim's method for optical densities at 290 nm. The results are illustrated in Table 2. The rates are approximately proportional to $[OH^-]$, and $k_2 = k_1/[OH^-]$ was obtained. Chan *et al.* obtained k_2-values for Reaction 1 at 20 °C and at various ionic strengths.[2] Using an activation energy of 28.7 kcal mol^{-1},[1] the k_2-value at 35 °C and at an ionic strength of 61.4 mM is estimated to be 164 M^{-1} min^{-1}, which is comparable to the k_2-values given in Table 2. Figure

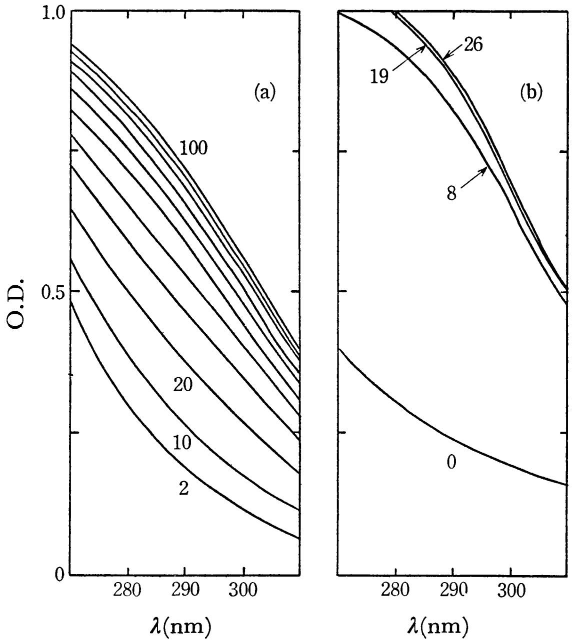

Fig. 1. Spectral change of (a) $[Co(NH_3)_5Cl]^{2+}$ and of (b) $[Co(NH_3)_5H_2O]^{3+}$ in 0.0133M Na_2CO_3–0.0200M $NaHCO_3$ solution at 35 °C.
The figures denote the reaction time in min.
(a) Concentration of $[Co(NH_3)_5Cl]^{2+}$=0.46 mM. From 20 to 100 min, the curves are drawn at 10 min intervals.
(b) Concentration of $[Co(NH_3)_5H_2O]^{3+}$=0.50 mM.

Table 2. Rate constants for the reaction of $[Co(NH_3)_5Cl]^{2+}$ in carbonate buffers at 35 °C

Run	Na_2CO_3– (M)	$NaHCO_3$ (M)	pH 35 °C	$[OH^-]$ (10^{-4} M)	k_1 (10^{-3} min^{-1})	k_2 (M^{-1} min^{-1})
(i)	0.0120—	0.0240	9.75	1.46	19.1	131
(ii)	0.0133—	0.0200	9.88	1.96	24.4	124
(iii)	0.0150—	0.0150	10.00	2.58	31.1	121

The concentration of $[Co(NH_3)_5Cl]^{2+}=0.46$ mM. The ionic strength$=61.4$ mM. The activity coefficient of OH^- ion was estimated to be 0.81.[11]

1(b) illustrates the changes in the absorption spectrum of $[Co(NH_3)_5H_2O]^{3+}$ in the 0.0133 M Na_2CO_3–0.0200 M $NaHCO_3$ buffer solution, in which complex $[Co(NH_3)_5OH]^{2+}$ exists. The spectral changes were very rapid compared to those of $[Co(NH_3)_5Cl]^{2+}$ in the same buffer solution and gave a final spectrum similar to that for the reaction with $[Co(NH_3)_5Cl]^{2+}$.

Hence, in this buffer solution, the reaction series is interpreted to be

$$[Co(NH_3)_5Cl]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + Cl^-, \quad \text{slow},$$

$$\left.\begin{aligned}
&[Co(NH_3)_5OH]^{2+} + CO_3^{2-} \longrightarrow [Co(NH_3)_5CO_3]^+ + OH^-,\\
&[Co(NH_3)_5OH]^{2+} + HCO_3^- \longrightarrow [Co(NH_3)_5HCO_3]^{2+} + OH^-,\\
&[Co(NH_3)_5HCO_3]^{2+} + OH^- \longrightarrow [Co(NH_3)_5CO_3]^+ + H_2O,
\end{aligned}\right\}\ \text{rapid}.$$

Then, the first-order reaction rates obtained in Table 2 can be regarded as the rate of Reaction 1: $k_1=k_2[OH^-]$. The relative amounts of the complex species in the final state can be estimated from the appropriate equilibrium constants at 25 °C.[12,13] The result is that the amounts of $[Co(NH_3)_5CO_3]^+$ and of $[Co(NH_3)_5OH]^{2+}$ are 97.3 and 2.7%, respectively, the amounts of the other species being negligible.

Reaction Rate at High Pressures. k_1 was determined from the first-order rate law,

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

where D_∞, $D_{t'}$ and D_t represent the optical densities at 290 nm at equilibrium, at the moment the high pressure is reached, and at the moment the pressure is released, respectively. D_∞ and D_0 (OD at the moment of dissolution of the complex) were calculated from the k_1-value and the OD at each reaction time for run (ii) at normal pressure. $D_{t'}$ was estimated from D_0 and t' (the time interval from dissolution to the attainment of a high pressure, *ca.* 3 min). Similarly for the estimation of D_t, the evolution of the reaction during the time from the pressure release to quenching was taken into account. The results are summarized in Table 3. The rate constants have been corrected for small contributions from the simultaneous aquation reaction:[14]

$$[Co(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} + Cl^-. \qquad (2)$$

Table 3. $k_1\times 10^3$ (min^{-1}) for the reaction of $[Co(NH_3)_5Cl]^{2+}$ in 0.0133M Na_2CO_3–0.0200 M $NaHCO_3$ at 35 °C

P(kg cm^{-2})	1	500	1000	1500
	22.6(40.4)	10.5(40)	6.7(40)	4.8(60)
	23.8(50.5)	11.6(60)	7.2(60)	4.5(80)
	21.6(60.3)	13.4(80)	7.4(80)	4.3(100)
average	22.7	11.8	7.1	4.5
a)	22.4	11.4	6.6	4.0
b)	22.4	11.1	6.2	3.7

The numbers in parenthesis denote the reaction time in min. a) After correction for aquation. b) After correction for variations of the dielectric constants and the densities.

The aquation rate at each pressure was estimated from those obtained by Jones *et al.* at 25 °C,[15] using an activation energy of 22.9 kcal mol^{-1}.[1] The velocity of Reaction 1 depends on the dielectric constant and on the density of the solution (the Brönsted-Bjerrum equation). The rate constants were further corrected for variations of the dielectric constants and densities at high pressures.[16,17] The k_1-values thus corrected are well represented by the formula

$$\ln(k_1/k_{1\circ}) = -1.478\times 10^{-3}P + 1.857\times 10^{-7}P^2,$$

where $k_{1\circ}$ is the rate constant at 1 atm and P is expressed in kg cm^{-2}. The activation volume at normal pressure is obtained as[9]

$$\begin{aligned}
\Delta V^{*} &= -RT\frac{d\ln k_2}{dP} = -RT\frac{d\ln k_1}{dP} + RT\frac{d\ln[OH^-]}{dP}\\
&= -RT\frac{d\ln k_1}{dP} + RT\frac{d\ln K_w}{dP} - RT\frac{d\ln K_2}{dP}\\
&= 33.4\ \text{ml mol}^{-1},
\end{aligned}$$

where K_W and K_2 represent the ionic product for water and the 2nd dissociation constant of carbonic acid, respectively. The differentiations were carried out for normal pressure.

Discussion

Two reaction mechanisms, *i.e.*, S_N2 and S_N1 CB, have been proposed for this reaction, and evidence in favor of the latter was recently reported.[3,4] For the S_N2 mechanism, ΔV^* is estimated to be smaller than 9 ml mol^{-1}.[9] The large positive value of ΔV^* obtained in this experiment can then be considered as further evidence for the S_N1 CB mechanism. In this case, the reaction series is

$$[Co(NH_3)_5Cl]^{2+} + OH^- \rightleftarrows [Co(NH_3)_4(NH_2)Cl]^+ + H_2O, \quad \text{rapid},$$

$$[Co(NH_3)_4(NH_2)Cl]^+ \longrightarrow [Co(NH_3)_4(NH_2)]^{2+} + Cl^-, \quad \text{slow},$$

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \longrightarrow [Co(NH_3)_5OH]^{2+}, \quad \text{rapid}.$$

Thus, ΔV^* originates from two contributions,

$$\Delta V^* = \Delta V_{pre} + \Delta V^{*\prime},$$

where ΔV_{pre} is the volume change accompanying the first step, and $\Delta V^{*\prime}$ is the activation volume of the second step. ΔV_{pre} should then be about 20 ml mol^{-1}, since a volume change of 20.6 ml mol^{-1} at 25 °C has been reported for an analogous equilibrium case:[18]

$$[Co(NH_3)_5H_2O]^{3+} + OH^- \rightleftarrows [Co(NH_3)_5OH]^{2+} + H_2O. \qquad (3)$$

The absolute partial molar volume ($\bar{V}(OH^-)$) of OH^- ions is estimated to be 1.5 ml mol^{-1}.[19] The difference between the partial molar volume of $[Co(NH_3)_4(NH_2)Cl]^+$ and that of $[Co(NH_3)_5Cl]^{2+}$ is estimated from the equation of Born[9] to be 5.4 ml mol^{-1}, assuming both crystal radii to be equal to that of $[Co(NH_3)_6]^{3+}$ (2.55 Å).[20] Thus, $\Delta V_{pre}=\bar{V}(H_2O)-\bar{V}(OH^-)+\bar{V}([Co(NH_3)_4(NH_2)Cl]^+)-\bar{V}([Co(NH_3)_5Cl]^{2+})=18.1-1.5+5.4=22.0$ ml mol^{-1}. From this, $\Delta V^{\neq\prime}$ is found to be 11.4 ml mol^{-1}.

For aquation Reaction 2, which is considered to proceed *via* the I_d mechanism, an activation volume ($\Delta V^{\neq}{}_{aq}$) of -10.6 ml mol^{-1} has been obtained at 25 °C.[15] This magnitude is interpreted as $\Delta V^{\neq}{}_{aq}=1.3-11.9$ ml mol^{-1}, where the 1.3 ml mol^{-1} is due to the Co–Cl bond elongation and the -11.9 ml mol^{-1} is due to solvation enhancement from the initial to the activated state. If the conjugate base $[Co(NH_3)_4(NH_2)Cl]^+$ dissociates also *via* the I_d mechanism, the value of $\Delta V^{\neq\prime}$ should not differ too much from that of $\Delta V^{\neq}{}_{aq}$. The distinct positive value of $\Delta V^{\neq\prime}$ obtained in this experiment must then be interpreted using some other mechanism, for which a larger value of $\Delta V^{\neq\prime}$ is expected.

In the D mechanism,[21] where $[Co(NH_3)_4(NH_2)Cl]^+$ dissociates into $[Co(NH_3)_4(NH_2)]^{2+}$ and Cl^-, a comparatively large positive value of $\Delta V^{\neq\prime}$ is expected due to the large value of $\bar{V}(Cl^-)$ (=23.5 ml mol^{-1}).[19] In this case, $\Delta V^{\neq\prime}$ is given by

$$\Delta V^{\neq\prime} = \bar{V}(Cl^-) + \bar{V}([Co(NH_3)_4(NH_2)]^{2+}) - \bar{V}([Co(NH_3)_4(NH_2)Cl]^+).$$

$\bar{V}([Co(NH_3)_4(NH_2)]^{2+})$ must be smaller than $\bar{V}([Co(NH_3)_4(NH_2)Cl]^+)$, because $[Co(NH_3)_4(NH_2)]^{2+}$ should be more solvated than $[Co(NH_3)_4(NH_2)Cl]^+$ (by 5.4 ml mol^{-1} according to the Born equation[9]) and because the intrinsic volume of the former should be smaller than that of the latter. Hence, $\Delta V^{\neq\prime}$ should be around 18.1 ml mol^{-1} or smaller, which agrees qualitatively with the experimental results. The total volume change (ΔV) for Reaction 1 is also known.[18] The remarkable decrease in volume (-24.4 ml mol^{-1}) during the change from the activated state to the final state should originate mainly from the incorporation of one water molecule into the complex ion, *i.e.*, the reverse of Reaction 3. Thus, the interpretation that $[Co(NH_3)_4(NH_2)Cl]^+$ dissociates *via* the D mechanism appears to be reasonable. For this mechanism, using the experimental value of $\Delta V^{\neq\prime}$ to calculate the magnitude of $\bar{V}([Co(NH_3)_4(NH_2)]^{2+})-\bar{V}([Co(NH_3)_4(NH_2)Cl]^+)$, the result would be -12.1 ml mol^{-1}. This is close to the magnitude of the electrostrictive part of $\Delta V^{\neq}{}_{aq}$, the electrostrictive volume contraction resulting from the separation of $[Co(NH_3)_5Cl]^{2+}$ to $\{[Co(NH_3)_5]^{3-\delta}\cdots Cl^{-1+\delta}\}$. This coincidence may be more than accidental, since an analogous coincidence is found for the base hydrolysis of $[Co(NH_3)_5SO_4]^+$.

For $[Co(NH_3)_5SO_4]^+$ and $[Co(NH_3)_5Br]^{2+}$, the values of $\Delta V^{\neq}$ and ΔV for base hydrolysis and that of $\Delta V^{\neq}{}_{aq}$ for aquation are also known, as listed in Table 4. In the base hydrolysis of $[Co(NH_3)_5SO_4]^+$, an analogous deduction leading to the assumption of the D_{cb} mechanism is also consistent. Estimating that $\Delta V_{pre}=18.0$ ml mol^{-1}, $\Delta V^{\neq\prime}$ is 1.5 ml mol^{-1}, whereas $\bar{V}(SO_4{}^{2-})+$(elecrostrictive part of $\Delta V^{\neq}{}_{aq}$)$=23.4-19.8=3.6$ ml mol^{-1}. This is close to the value of $\Delta V^{\neq\prime}$.[15] A large volume decrease (-18.1 ml mol^{-1}) during the change from the activated state to the final state can also be understood by assuming the incorporation of one water molecule into the complex ion. In contrast, in the base hydrolysis of $[Co(NH_3)_5Br]^{2+}$, the magnitude of $\Delta V^{\neq\prime}$ should be $8.5-22.0=-13.5$ ml mol^{-1}. This is close to the value of $\Delta V^{\neq}{}_{aq}$ for $[Co(NH_3)_5Br]^{2+}$. Hence, $[Co(NH_3)_4(NH_2)Br]^+$ may dissociate *via* the I_d mechanism as for aquation or the reaction may proceed through the S_N2 mechanism as has been interpreted by Burris and Laidler.[5]

TABLE 4. VOLUME CHANGES (ml mol^{-1}) FOR THE REACTIONS OF $[Co(NH_3)_5X]^{3-n}$

Complex	Base hydrolysis				Aquation
	$\Delta V^{\neq}$	t °C	Ref.	ΔV[a]	$\Delta V^{\neq}_{aq}$[b]
$[Co(NH_3)_5Cl]^{2+}$	33.4	35	this work	9.0	-10.6
$[Co(NH_3)_5SO_4]^+$	19.5	15	22	1.4	-18.5
$[Co(NH_3)_5Br]^{2+}$	8.5	30	5	9.8	-9.2

a) At 30 °C, Ref. 18. b) At 25 °C, Ref. 15.

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14) The small contributions to the k_1-value from simultaneous pseudo first-order reactions other than aquation, which might possibly exist, were neglected. If any do exist and we denote the contribution by k_1', then

$$k_1 = k_2[OH^-] + k_1'$$

$$\frac{d\ln k_1}{dP} = \frac{d\ln k_2[OH^-]}{dP} + \frac{d}{dP}\ln\left\{1+\frac{k_1'}{k_2[OH^-]}\right\}.$$

The ratio $k_1'/k_2[OH^-]$ is small at normal pressure, since k_1 is

approximately proportional to [OH⁻]. This ratio may increase with an increase in pressure, since no activation volume for a reaction in water exceeds *ca.* 30 ml mol^{-1}. However, the increase would be insignificant because k_1 decreases monotonically with the pressure and does not converge to a limiting value. Hence, neglect of this effect may lead to a slightly smaller value of $\Delta V^{\neq}$ for base hydrolysis.

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