November, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **55**, *3625—3629 (1982)* 3625

Volume Profile for the Aquation Reactions of *trans*- and *cis*-$[Co(en)_2NO_2Cl]^+$, *cis*-$[Co(bpy)_2NO_2Cl]^+$, *cis*-$[Co(bpy)_2NO_2Br]^+$, and *cis*-$[Co(phen)_2NO_2Br]^+$

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(Received October 21, 1981)

The activation volume at normal pressure ($\Delta V^{\ne}$) and the reaction volume (ΔV) are obtained for five aquation reactions of the Co(III) complex ion. The results are [given as the complex ion, $\Delta V^{\ne}$/cm^3 mol^{-1} (t/°C), ΔV/cm^3 mol^{-1} (t/°C)]: *trans*-$[Co(en)_2NO_2Cl]^+$, 0.1 (15), −10.4 (15); *cis*-$[Co(en)_2NO_2Cl]^+$, 0.9 (30), −9.3 (25); *cis*-$[Co(bpy)_2NO_2Cl]^+$, 2.9 (30), −9.1 (25); *cis*-$[Co(bpy)_2NO_2Br]^+$, 11.3 (30), −6.7 (25); *cis*-$[Co(phen)_2NO_2Br]^+$, 3.3 (35), −12.5 (30). These magnitudes of $\Delta V^{\ne}$ are interpreted as resulting from the counterbalance of the volume increase attributable to the dissociation of the leaving ligand and the volume decrease due to the partial incorporation of one water molecule in the activated complex.

In this decade, the reaction velocities of the complex ion have been investigated extensively under high pressure.[1–3] Activation volumes have been obtained and the magnitude of $\Delta V^{\ne}$ has been discussed in relation to the reaction mechanism. The general treatment is that $\Delta V^{\ne}$ is divided into two contributions: $\Delta V^{\ne}=\Delta V^{\ne}_{\text{int}}+\Delta V^{\ne}_{\text{solv}}$, where $\Delta V^{\ne}_{\text{int}}$ and $\Delta V^{\ne}_{\text{solv}}$ are the intrinsic and the solvational components of the activation volume respectively. Stranks has made a fundamental assumption that the intrinsic volume of a five-coordinate intermediate in the limiting dissociative mechanism is the same as that of the six-coordinate precursor.[4] Some authors have interpreted the magnitude of $\Delta V^{\ne}$ according to this postulation.[1] However, the derivation of his postulation seems to have no rational foundation.[4] The present author considers that the relation between the magnitude of $\Delta V^{\ne}$ and the mechanism should be induced from an examination of the volume profiles ($\Delta V^{\ne}$ and ΔV) for a series of related reactions.

It has been known for some time that, in a series of *trans*- and *cis*-$[Co(en)_2ACl]^{n+}$, the aquation velocity is rapid for $A=NH_2^-$, moderate for $A=N_3^-$, Cl^-, NO_2^-, and slow for $A=NH_3$.[5] Ingold *et al.* have interpreted this in relation to the electron-donating or the electron-withdrawing power of the A ligand.[5] Langford and Gray have given a slightly different interpretation of this problem and have indicated that, at least, the mechanism for $A=NH_2^-$ differs from those for $A=N_3^-$, Cl^- or NO_2^-.[6] The present author considers that the influence of the A ligand on the aquation mechanism might possibly be reflected in the volume profile.

In this work, $\Delta V^{\ne}$ and ΔV are obtained for five aquation reactions, where the complex ions have the electron-withdrawing nonlabile NO_2^- ligand in common:

$$\textit{trans}\text{-}[Co(en)_2NO_2Cl]^+ + H_2O \longrightarrow \textit{trans}\text{-}[Co(en)_2NO_2H_2O]^{2+} + Cl^- \qquad (1)^{7,8)}$$

$$\textit{cis}\text{-}[Co(en)_2NO_2Cl]^+ + H_2O \longrightarrow \textit{cis}\text{-}[Co(en)_2NO_2H_2O]^{2+} + Cl^- \qquad (2)^{7,8)}$$

$$\textit{cis}\text{-}[Co(bpy)_2NO_2Cl]^+ + H_2O \longrightarrow \textit{cis}\text{-}[Co(bpy)_2NO_2H_2O]^{2+} + Cl^- \qquad (3)^{9)}$$

$$\textit{cis}\text{-}[Co(bpy)_2NO_2Br]^+ + H_2O \longrightarrow \textit{cis}\text{-}[Co(bpy)_2NO_2H_2O]^{2+} + Br^- \qquad (4)^{9)}$$

$$\textit{cis}\text{-}[Co(phen)_2NO_2Br]^+ + H_2O \longrightarrow \textit{cis}\text{-}[Co(phen)_2NO_2H_2O]^{2+} + Br^- . \qquad (5)^{10)}$$

The volume profiles are compared with those of other Co(III) aquation reactions, and the magnitudes of $\Delta V^{\ne}$ are discussed on this basis. The acid dissociation constant (K_a) is obtained for the *cis*-$[Co(en)_2NH_3H_2O]^{3+}$ at four temperatures. The ΔH° and ΔS° are calculated for this equilibrium:

$$\text{cis-}[Co(en)_2NH_3H_2O]^{3+} + OH^- = [Co(en)_2NH_3OH]^{2+} + H_2O. \qquad \text{(i)}$$

This equilibrium is treated as a model for the preequilibrium of the base-hydrolysis of the Co(III) complex ion.

Experimental

Material. The following complexes were obtained by the published methods: *trans*-$[Co(en)_2NO_2Cl]NO_3$ (**1**),[11] *cis*-$[Co(en)_2NO_2Cl]Cl$ (**2**),[11] *cis*-$[Co(bpy)_2NO_2Cl]Cl\cdot 2H_2O$ (**3**),[12] *cis*-$[Co(bpy)_2NO_2Br]Br$ (**4**),[12] *cis*-$[Co(phen)_2NO_2Br]Br\cdot 2H_2O$ (**5**),[10] and *cis*-$[Co(en)_2NH_3H_2O]Br_3\cdot H_2O$ (**6**).[13] The Co(III) complex with the *bis* bpy or the *bis* phen ligands has the *cis*-configuration.[14] The *cis*-configuration of **6** was identified spectrophotometrically.[15] The results of the elemental analysis (C, H, N) for Complexes **1**—**6** were in good agreement with the theoretically expected values.[16]

Kinetic Measurement. The aquation velocity was followed *in situ* in a thermostatted (±0.1 °C) Hawley and Chase-type high-pressure optical cell with a pair of sapphire windows.[17] This cell was fitted to a Nihon Bunko, model UVIDEC 505, double-beam spectrophotometer. The path length of the sample solution was 1.3 cm. The reference was air. The pressure of the sample solution was measured by means of a Nagano Keiki Bourdon gauge calibrated to a Nagano Keiki-type IP3-178 dead-weight-pressure gauge tester. Each reaction was followed at a certain wavelength to *ca.* 90% completion. The first-order rate constants were obtained from Guggenheim plots of the optical densities.

Dilatometry. A globular glass vessel (39.2 cm^3) fitted with an upright capillary tube (15 cm long) was used as a dilatometer. A capillary tube with an internal diameter of 0.0404 cm was used for the runs of Reactions 2 and 3. Another capillary tube with an internal diameter of 0.0202 cm was used for the runs of Reactions 1, 4, and 5. Distilled water was boiled for several minutes. It was then degassed overnight and was used to dissolve the complex. A weighed quantity of the complex was dissolved in water (45 cm^3) at the reaction temperature. The solution was poured into the dilatometer, which had been immersed beforehand in a thermostat controlled at the reaction temperature. The capillary tube was then joined, and the overflowing solution was wiped off at the top of the capillary tube. The height (h_t) of the meniscus was followed by the use of a cathetometer. The dilatometer was covered by a piece of aluminium foil to avoid the influence of light. The thermostat temperature was observed by a Beckmann thermometer graduated to 0.001 °C. The maximum variation in the temperature during the dilatometric run was within 0.001 °C in the runs of Reactions 1—4, while it was undetectably small (*ca.* within 0.0002 °C) in the runs of Reaction 5.

Results

Kinetic Results. The rate constants in Table 1 were obtained for the respective complex ion in an aqueous solution without added electrolyte and acid. For the reaction of *trans*-$[Co(en)_2NO_2Cl]^+$, the contribution of the base-hydrolysis can be estimated to be $k_b[OH^-]=8\times10^{-8}\ s^{-1}$ at 15 °C and $[OH^-]=10^{-7}$ M (1 M=1 mol dm^{-3}), where k_b is the 2nd-order rate constant of the base-hydrolysis.[7,18] For the reaction of *cis*-$[Co(en)_2NO_2Cl]^+$, $k_b[OH^-]$ can be estimated to be $2\times10^{-7}\ s^{-1}$ at 30 °C and $[OH^-]=10^{-7}$ M.[7,18] These magnitudes of $k_b[OH^-]$ are small enough compared to the corresponding aquation velocities, and the contribution of the base-hydrolysis can be neglected. The contribution of the base-hydrolysis is also neglected for the reactions of *cis*-$[Co(bpy)_2NO_2Cl]^+$, *cis*-$[Co(bpy)_2NO_2Br]^+$, and *cis*-$[Co(phen)_2NO_2Br]^+$, since these complexes have no acidic proton. It can be noticed that the rate constants of Reactions 1—5 remain unchanged or decrease slightly under high pressures. The average k values at each pressure are fitted by the least-squares method to the quadratic formula: $\ln(k/k_0)=aP+bP^2$, where k_0 is the rate constant at normal pressure. The activation volumes at normal pressure are calculated by means of $\Delta V^{\neq}=-RT(\mathrm{d}\ln k/\mathrm{d}P)=-RTa$ (Table 2).

TABLE 1. RATE CONSTANTS ($k/10^{-5}\ s^{-1}$) OF THE AQUATION REACTION AT EACH PRESSURE (P/kg cm^{-2})[a]

1[b], *trans*-$[Co(en)_2NO_2Cl]^+$, 1 mM[c], 10 °C[d], 380 nm[e] $\ln(k/k_0)=0.11\times10^{-4}P-1.45\times10^{-8}P^2$ [f]							
P		1	400	800	1200	1600	2000
k	16.5	15.8	16.5	16.3	15.7	17.2	16.2
	16.3		16.2	16.7	15.0	15.3	14.8
1, *trans*-$[Co(en)_2NO_2Cl]^+$, 1 mM, 15 °C, 380 nm $\ln(k/k_0)=-0.06\times10^{-4}P-0.76\times10^{-8}P^2$							
P		1	400	800	1200	1600	2000
k		32.0	32.2	31.5	31.5	30.5	30.0
		32.0	32.0	31.2	31.0	32.3	30.8
1, *trans*-$[Co(en)_2NO_2Cl]^+$, 1 mM, 20°C, 380 nm $\ln(k/k_0)=-0.14\times10^{-4}P-0.52\times10^{-8}P^2$							
P		1	400	800	1200	1600	2000
k		61.2	61.5	61.0	60.8	59.5	59.2
		62.5	59.7	62.7	58.2	61.2	58.2
2, *cis*-$[Co(en)_2NO_2Cl]^+$, 5 mM, 30 °C, 393 nm $\ln(k/k_0)=-0.33\times10^{-4}P-2.47\times10^{-8}P^2$							
P		1	400	800	1200	1600	2000
k	22.8	22.3	22.3	21.5	21.2	20.2	18.8
	22.5	22.7	21.8	21.5	21.5	20.0	19.3
3, *cis*-$[Co(bpy)_2NO_2Cl]^+$, 1 mM, 30 °C, 398 nm $\ln(k/k_0)=-1.13\times10^{-4}P-0.90\times10^{-8}P^2$							
P		1	400	800	1200	1600	2000
k	37.5	36.7	39.8	31.7	32.7	31.7	29.7
	38.2	38.5	38.3	32.7	32.7	29.7	28.5
4, *cis*-$[Co(bpy)_2NO_2Br]^+$, 1 mM, 30 °C, 404 nm $\ln(k/k_0)=-4.40\times10^{-4}P+13.1\times10^{-8}P^2$							
P		1	320	720	1140	1540	
k	36.8	38.8	32.5	30.0	27.3	25.2	
	36.8	37.8	32.3	29.2	26.8	26.7	
5, *cis*-$[Co(phen)_2NO_2Br]^+$, 1 mM, 35 °C, 416 nm $\ln(k/k_0)=-1.27\times10^{-4}P+1.73\times10^{-8}P^2$							
P		1	320	720	1140	1540	1960
k	34.2	32.0	32.8	29.7	27.5	27.0	25.5
	34.0	30.3	32.3	28.7	30.3	29.2	28.8

a) 1 kg cm^{-2}=98.0665 kPa. b) Reaction number. c) Concentration of the complex. d) Reaction temperature. e) The reaction was followed at this wavelength. f) See text.

Dilatometric Result. Reaction 1 was followed at 15 °C in a 3.4 mM solution of **1** from 26 to 99% completion; Reaction 2, at 25 °C in a 10.9 mM solution of **2** from 14 to 98% completion; Reaction 3, at 25 °C in an 8.5 mM solution of **3** from 31 to 82% completion, and Reaction 4, at 25 °C in a 5.0 mM solution of **4** from 36 to 71% completion. For Reactions 1—4, ΔV is obtained from the intercept at $t=0$ of the $\ln(h_t-h_\infty)$ *vs.* t plot, where the h_∞ value is calculated from the h_t's (Table 2). The solubility of **5** in water is limited (*ca.* 1.8 mM at 30 °C). Three independent runs were performed where Reaction 5 was followed at 30 °C in a 1.2 mM solution of **5** from 43 to 61%, from 47 to 68%, and from 39 to 61% completion. For Reaction 5, ΔV is calculated from the ratios of Δh_t to $\Delta\xi$, where ξ is the degree of reaction (Table 2). The values of ξ are estimated from the rate constant ($2.08\times10^{-4}\ s^{-1}$ at 30 °C) obtained spectrophotometrically at 404 nm. The average error in ΔV for Reaction 5 is ±1.3 cm^3 mol^{-1}. In Reactions 1—4, the rate constants obtained dilatometrically are in good agreement with those in the literature.[7—9]

pK_a *of* cis-$[Co(en)_2NH_3H_2O]^{3+}$. Complex **6** was dissolved in boiled water; no other electrolyte was added. The solution (5 mM, 25 cm^3) was titrated with a 0.1 M KOH, while nitrogen gas free from oxygen or carbon dioxide was slowly bubbled into the solution.[19] The values of pK_a were [given as t/°C, pK_a]: 2, 6.30±0.07; 10, 6.10±0.07; 20, 5.83±0.07; 40, 5.39±0.07. This temperature dependence can be described by: $\ln K_a=-4800/T+2.91$, from which $\Delta H°=39.9$ kJ mol^{-1} and $\Delta S°=24.2$ J K^{-1} mol^{-1} are calculated for the equilibrium: *cis*-$[Co(en)_2NH_3H_2O]^{3+}=[Co(en)_2NH_3OH]^{2+}+H^+$. Thus, $\Delta H°=-15.9$ kJ mol^{-1} and $\Delta S°=104.9$ J K^{-1} mol^{-1} are obtained for Equilibrium i.[20]

Discussion

In Table 2, the volume profiles obtained in this work are summarized, along with those for other aquation reactions of the Co(III) complexes, where the leaving

TABLE 2. VOLUME PROFILE AND ACTIVATION ENTROPY FOR AQUATION REACTIONS OF Co(III) COMPLEXES

Reaction number	Complex	$\Delta V^{\ddagger}$/cm^3 mol^{-1} (t/°C)	ΔV/cm^3 mol^{-1} (t/°C)	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1	*trans*-$[Co(en)_2NO_2Cl]^+$	−0.3(10)[a)] 0.1(15)[a)] 0.3(20)[a)]	−10.4(15)[a)]	−10[b)]
2	*cis*-$[Co(en)_2NO_2Cl]^+$	0.9(30)[a)]	−9.3(25)[a)]	−28[b)]
3	*cis*-$[Co(bpy)_2NO_2Cl]^+$	2.9(30)[a)]	−9.1(25)[a)]	−104[c)]
4	*cis*-$[Co(bpy)_2NO_2Br]^+$	11.3(30)[a)]	−6.7(25)[a)]	−117[c)]
5	*cis*-$[Co(phen)_2NO_2Br]^+$	3.3(35)[a)]	−12.5(30)[a)]	−49[c)]
6	*trans*-$[Co(dtcd)N_3Cl]^+$	8.3(25)[d)]		−51[d)]
7	*trans*-$[Co(dtcd)N_3Br]^+$	5.3(21)[d)]		−34[d)]
8	*cis*-$[Co(en)_2Cl_2]^+$	−0.3(30)[e)]		−18[e)]
9	*trans*-$[Co(en)_2Cl_2]^+$	−1.1(30)[e)]		44[e)]
10	$[Co(NH_3)_5Cl]^{2+}$	−10.6(25)[f)]	−11.6(30)[g)]	−39[h)]
11	$[Co(NH_3)_5Br]^{2+}$	−9.2(25)[f)]	−10.8(30)[g)]	−20[h)]
12	$[Co(NH_3)_5NO_3]^{2+}$	−6.3(25)[f)]	−7.2(30)[g)]	3[h)]
13	$[Co(NH_3)_4(NH_2)Cl]^+$	15.0(35)[i)]	−9.4(30)[i)]	35[i)]
14	$[Co(NH_3)_4(NH_2)Br]^+$	13.6(25)[i)]	−8.6(30)[i)]	82[i)]

a) This work. b) Ref. 8. c) Ref. 9. d) In 0.1 M HNO_3. Ref. 21. e) In 0.01 M HNO_3 (I=0.1 M). Ref. 3. f) In 0.1 M $LiClO_4$–5×10^{-5} M $HClO_4$. Ref. 22. g) Refs. 22 and 23. h) Ref. 24. i) See text.

ligand is a univalent anion:

$$trans\text{-}[Co(dtcd)N_3Cl]^+ + H_2O \longrightarrow [Co(dtcd)N_3H_2O]^{2+} + Cl^- \quad (6)\,^{21)}$$

$$trans\text{-}[Co(dtcd)N_3Br]^+ + H_2O \longrightarrow [Co(dtcd)N_3H_2O]^{2+} + Br^- \quad (7)\,^{21)}$$

$$cis\text{-}[Co(en)_2Cl_2]^+ + H_2O \longrightarrow [Co(en)_2ClH_2O]^{2+} + Cl^- \quad (8)\,^{3)}$$

$$trans\text{-}[Co(en)_2Cl_2]^+ + H_2O \longrightarrow [Co(en)_2ClH_2O]^{2+} + Cl^- \quad (9)\,^{3)}$$

$$[Co(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} + Cl^- \quad (10)\,^{22,23)}$$

$$[Co(NH_3)_5Br]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} + Br^- \quad (11)\,^{22,23)}$$

$$[Co(NH_3)_5NO_3]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} + NO_3^- \quad (12)\,^{22,23)}$$

$$[Co(NH_3)_4(NH_2)Cl]^+ + H_2O \longrightarrow [Co(NH_3)_5OH]^{2+} + Cl^- \quad (13)\,^{23,25)}$$

$$[Co(NH_3)_4(NH_2)Br]^+ + H_2O \longrightarrow [Co(NH_3)_5OH]^{2+} + Br^-. \quad (14)\,^{23,26)}$$

The volume profiles of Reactions 13 and 14 are calculated from those of the corresponding base-hydrolysis reactions. The S_N1 CB mechanism is now widely established for the base-hydrolysis reaction of $[Co(NH_3)_5X]^{2+}$ ($X^-=Cl^-$, Br^-).[27–30] In this mechanism, the reaction proceeds in two steps:

$$[Co(NH_3)_5X]^{2+} + OH^- = [Co(NH_3)_4(NH_2)X]^+ + H_2O \quad \text{(ii)}$$

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

The volume profile ($\Delta V^{\ddagger}_{b}$ and ΔV_b) of the base-hydrolysis is then, written as; $\Delta V^{\ddagger}_{b}=\Delta V_{pre}+\Delta V^{\ddagger}_{cb}$, and $\Delta V_b=\Delta V_{pre}+\Delta V_{cb}$, where ΔV_{pre} is the volume change of the preequilibrium ii and where $\Delta V^{\ddagger}_{cb}$ and ΔV_{cb} are the activation volume and the reaction volume respectively of the succeeding aquation Reaction iii of the conjugate-base complex ion $[Co(NH_3)_4(NH_2)X]^+$.[25] The magnitude of ΔV_{pre} is not known. Volume changes are known for four analogous neutralization equilibria of a metal complex ion:[31]

$[Co(NH_3)_5H_2O]^{3+} + OH^- = [Co(NH_3)_5OH]^{2+} + H_2O$

$\Delta V = 20.6$ cm^3 mol^{-1} at 30 °C,

$[Cr(H_2O)_6]^{3+} + OH^- = [Cr(H_2O)_5OH]^{2+} + H_2O$

$\Delta V = 18.3$ cm^3 mol^{-1} at 25 °C,

$[Fe(H_2O)_6]^{3+} + OH^- = [Fe(H_2O)_5OH]^{2+} + H_2O$

$\Delta V = 20.9$ cm^3 mol^{-1}

$[Co(edda)(Hame)]^+ + OH^- = [Co(edda)(ame)]^0 + H_2O$

$\Delta V = 16.9$ cm^3 mol^{-1} at 25 °C.

Then, an average of 19.9 cm^3 mol^{-1} is obtained for the neutralization of a tervalent complex ion. Thus, $\Delta V=18.4$ cm^3 mol^{-1} (average between 19.9 and 16.9 cm^3 mol^{-1}) is appropriate for the neutralization of the 2+ complex ion. By assuming that $\Delta V_{pre}=18.4$ cm^3 mol^{-1}, $\Delta V^{\ddagger}_{cb}$ and ΔV_{cb} are calculated from $\Delta V^{\ddagger}_{b}=33.4$ cm^3 mol^{-1} [25] and $\Delta V_b=9.0$ cm^3 mol^{-1} [23] for $X^-=Cl^-$, and from $\Delta V^{\ddagger}_{b}=32$ cm^3 mol^{-1} [26] and $\Delta V_b=9.8$ cm^3 mol^{-1} [23] for $X^-=Br^-$. Burris and Laidler reported $\Delta V^{\ddagger}_{b}=8.5$ cm^3 mol^{-1} for $X^-=Br^-$;[32] however, this magnitude is mistaken.[26] The present author and others have previously obtained $\Delta V^{\ddagger}_{b}=37$ cm^3 mol^{-1} for $X^-=Br^-$ at 21 °C in 10 mM NH_3–1 mM NH_4ClO_4 (I=1.75 mM).[33]

It can be noticed that the magnitudes of ΔV of Reactions 1—5 and 10—14 are close to each other. When the leaving ligand is Cl^-, they are especially close to one another and have a magnitude of -10.0 ± 1.6 cm^3 mol^{-1}, irrespective of the nonlabile ligands in the complex. When the leaving ligand is Br^-, the ΔV's lie in a relatively small range, from −6.7 to −12.5 cm^3 mol^{-1}. In contrast, the magnitudes of $\Delta V^{\ddagger}$ are distributed over a wide range, from 15 to -10 cm^3 mol^{-1}. This result accords with the expectation that the mechanism is not common throughout Reactions 1—14.[5,6] If the mechanism was the same, the constitutions of their transition states, and hence the magnitudes of $\Delta V^{\neq}$, should be similar to each other. The latter might be anticipated, since the magnitude of ΔV, the volume change for a certain substitution, depends only slightly on the nature of the nonlabile ligand.

From various pieces of evidence and the arguments given in previous reports,[25,27—30] Reactions 13 and 14 can be considered to proceed by means of a limiting dissociative or D mechanism. The transition state is constituted of a five-coordinate intermediate and the leaving ligand, and the $\Delta V^{\neq}$ is the volume change of the reaction:

$$[Co(NH_3)_4(NH_2)X]^+ \longrightarrow [Co(NH_3)_4(NH_2)]^{2+} + X^-, \qquad (iv)$$

where $X^- = Cl^-$ and Br^-.

In the volume profiles of Reactions 10—12, it is clear that the $\Delta V^{\neq}$ is close to the corresponding ΔV. Then, the constitution of the transition state of Reactions 10—12 should be similar to that of the final state. In the transition state, one water molecule should have already been incorporated into the coordination sphere; it is from this fact that the remarkably smaller magnitudes of $\Delta V^{\neq}$ of Reactions 10—12 than those of Reactions 13 and 14 must result. The transition state of Reactions 10—12 is an ion pair between the product, $[Co(NH_3)_5H_2O]^{3+}$, and the leaving ligand. Only the separation of this ion pair is necessary to complete the reaction; this explains the experimentally obtained volume decrease $\Delta V^{\neq} - \Delta V \simeq 1$ cm^3 mol^{-1} for Reactions 10—12. This interpretation of the transition state of Reactions 10—12 is virtually similar to that given by Jones *et al.*.[22] They have indicated that the transition state of Reactions 10—12 is an ion pair with a momentarily enhanced solvational sphere. The transition state has been denoted as: $\{Co(NH_3)_5{}^{3+}, X^-, yH_2O\}$, where X^- remains in the first solvation sphere of the complex and where y is large enough to permit the full solvation of both $Co(NH_3)_5{}^{3+}$ and X^-. They have also estimated the excess number of water molecules in the first solvation sphere over the average at the moment of the transition state as 4, 4, and 2 for $X^- = Cl^-$, Br^-, and NO_3^- respectively. They have explained that the transition state occurs when a wide excursion of a Co–X vibration coincides with the transient excess solvation caused by the fluctuation of the water molecules in the first solvation sphere. In practice, one can not discriminate this solvation-enhanced ion pair from an ordinary ion pair between the product and the leaving ligand, $\{[Co(NH_3)_5H_2O]^{3+}, X^-\}$. The latter is preferable because of its simplicity.

For Reactions 1—9, the magnitudes of $\Delta V^{\neq}$ are intermediate between those for Reactions 13 and 14 and those for Reactions 10—12. Then, in Reactions 1—9, the transition state is composed of an ion pair between the leaving ligand and the unstable five-coordinate intermediate, $[Co(AA)_2Y\cdots OH_2]^{2+}$, where AA=en, bpy, phen, (dtcd)/2; $Y^- = NO_2^-$, N_3^-, Cl^-. The water molecule is half-way between the vacant coordination site and the first solvation sphere. Thus, the mechanism is a dissociative interchange or I_d for Reactions 1—12.

The essential point of the D or I_d mechanism is that the transition state occurs with the widest excursion of the Co–X bond vibration. However, every widest excursion does not give rise to the transition state. A factor which contributes to the emergence of the transition state is the simultaneous intrusion of one water molecule from the solvation into the coordination sphere. When the initial complex contains the strongly electron-donating NH_2^- ligand, the complex will be unstable, according to Ingold *et al.*, and only a slight intrusion will be enough.[5,6] When the initial complex contains a moderately electron-donating N_3^- or Cl^- ligand, or a moderately electron-withdrawing NO_2^- ligand, the complex will be moderately stable and some further intrusion will be needed. When the initial complex does not contain any ligand with electron-donating or -withdrawing power, the complex will be stable and only a sufficient intrusion of a water molecule will give rise to the transition state.

The widest excursion of the leaving ligand will cause a volume increase (ΔV_d) and the intrusion of a water molecule will accompany a volume decrease ($\alpha \Delta V_{inc}$), where ΔV_{inc} is the volume change for the full incorporation of one water molecule into the five-coordinate intermediate and where α is the degree of the intrusion. According to this model, $\Delta V^{\neq}$ is expressed as $\Delta V^{\neq} = \Delta V_d + \alpha \Delta V_{inc}$. By assuming $\alpha = 0$ for Reactions 13 and 14, ΔV_d and ΔV_{inc} can be estimated from the experimentally obtained volume profiles: $\Delta V_d = \Delta V^{\neq} = 13$—15 cm^3 mol^{-1} and $\Delta V_{inc} = \Delta V - \Delta V^{\neq} = -22$—$-25$ cm^3 mol^{-1}. These magnitudes of ΔV_d and ΔV_{inc} give $\Delta V^{\neq} = -12$—-7 cm^3 mol^{-1} for $\alpha = 1$, which is in agreement with the magnitude of $\Delta V^{\neq}$ experimentally obtained for Reactions 10—12. In a previous report, the intrinsic and the solvational components of ΔV_d and the content of ΔV_{inc} have been considered.[25] The absolute value of the solvational component of ΔV_{inc} can be expected formally to be small, since the incorporation of a solvent molecule is not accompanied by a change in the ionic valence. In Reactions 1—9, α takes a value between 0 and 1. The completion of the intrusion of the water molecule and the separation of the ion pair are necessary to complete the reaction, which explains the experimentally obtained volume decrease, $\Delta V^{\neq} - \Delta V = 18$—10 cm^3 mol^{-1}, for Reactions 1—5.

In Reactions 1—5, the *trans*- and *cis*-configuration is retained during the reaction.[7,14] This fact can be interpreted as indicating that, in their transition state, the entering water molecule has already occupied its position to some extent, in accordance with the explanation given above.

For Reaction 1, $\Delta V^{\neq}$ is obtained at three temperatures. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are calculated at each pressure [given as P/kg cm^{-2}, $\Delta H^{\neq}$/kJ mol^{-1}, $\Delta S^{\neq}$/J K^{-1} mol^{-1}]: 1, 91.8, 7.1; 400, 91.4, 5.2; 800, 90.6, 3.3; 1200, 94.1, 13.9; 1600, 89.7, -1.6; 2000, 91.4, 5.2. The value of $(\partial \Delta S^{\neq}/\partial P)_T$ at normal pressure and 15 °C can be calculated from the $\Delta S^{\neq}$'s at 1, 400, and 800 kg cm^{-2} as -0.05 cm^3 K^{-1} mol^{-1}. On the other hand, $(\partial \Delta V^{\neq}/\partial T)_P$ at normal pressure is obtained as 0.06 cm^3 K^{-1} mol^{-1} (Table 2). Thus, the thermodynamic relation $(\partial \Delta S^{\neq}/\partial P)_T = -(\partial \Delta V^{\neq}/\partial T)_P$ is satisfied; this is consistent with the postulation of the equilibrium between the initial and transition states.[2,3] For Reaction 1, $\Delta V^{\neq} = 0.9$ cm^3 mol^{-1} can be obtained at 30 °C by extrapolation. The coincidence of $\Delta V^{\neq}$ at 30 °C of Reactions 1 and 2 is rather surprising in view of the different initial configurations of the two isomers. Langford has pointed out that the bond distances between the nonlabile ligands and the metal ion might contract during the activation process.[35] However, if the Co–N bond distances of the two en ligands changed considerably in the activation process, some differences in the magnitude of $\Delta V^{\neq}$ might be expected, since these two isomers have different initial configurations, and so different solvational spheres. For Reactions 1 and 2, the activation energies are also equal (86.7 kJ mol^{-1}), while the activation entropies differ only slightly (Table 2).[8] Thus, the low reaction velocity of the *cis*-$[\mathrm{Co(en)_2NO_2Cl}]^+$ is due to the rare chance of the intrusion of a water molecule attributable to the existence of the $\mathrm{NO_2^-}$ ligand in a position *cis* to the attacking water molecule.

The existence of a parallel correlation between $\Delta S^{\neq}$ and $\Delta V^{\neq}$ has sometimes been indicated.[36] Recently, Palmer and Kelm have examined this relation for 35 coordination reactions and pointed out that the parallelism is only of a qualitative nature.[3] Lawrance and Suvachittanont have indicated that the parallelism does not hold for Reactions 6 and 7.[21] From the present results (Table 2), it is clear that the parallelism is not satisfied for Reactions 3—5, either. The entropy change (ΔS_{pre}) for the preequilibrium ii of the base-hydrolysis can not be known. It is assumed, therefore, that ΔS_{pre} is approximately equal to the $\Delta S°$ of the analogous Equilibrium i. Then the activation entropies ($\Delta S^{\neq}_{\mathrm{cb}}$) of Reactions 13 and 14 are calculated by the use of $\Delta S^{\neq}_{\mathrm{cb}} = \Delta S^{\neq}_{\mathrm{b}} - \Delta S_{\mathrm{pre}}$, where the activation entropies of the base-hydrolysis ($\Delta S^{\neq}_{\mathrm{b}}$) are 140 and 187 J K^{-1} mol^{-1} for $[\mathrm{Co(NH_3)_5Cl}]^{2+}$ and $[\mathrm{Co(NH_3)_5Br}]^{2+}$ respectively.[24] For Reactions 10—14, the parallelism seems to be roughly satisfied. On the other hand, it is surprising that rather a reverse relation seems to hold for Reactions 1—9: $\Delta V^{\neq}$ is large when $\Delta S^{\neq}$ is small. It is difficult at present to give any reasonable explanation of this.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 464195 from the Ministry of Education, Science and Culture. The high-pressure optical cell was constructed with the financial support of the Japan Society for the Promotion of Science.

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