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The Volume Profile for the Aquation Reactions of *trans*-$[CoBr(NO_2)(en)_2]^+$ and *trans*-$[CoCl(N_3)(en)_2]^+$ †

Yoichi Kitamura,* Shinji Nariyuki, and Toshiaki Kondo††
Department of Chemistry, Faculty of Science, Ehime University, Matsuyama, Ehime 790

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Synopsis. For the aquation of *trans*-$[CoBr(NO_2)(en)_2]^+$, the activation volume at atmospheric pressure ($\Delta V^{\ddagger}$) is 0.3±0.2 $cm^3\,mol^{-1}$ at 10 °C, and the reaction volume (ΔV) is −10.4±0.1 $cm^3\,mol^{-1}$ at 7.4 °C, both in pure water. For *trans*-$[CoCl(N_3)(en)_2]^+$, $\Delta V^{\ddagger}$ is 0.7±0.6 $cm^3\,mol^{-1}$ at 30 °C in 0.011 M $HClO_4$ (1 M=1 mol dm^{-3}) and ΔV is −11.0±0.6 and −11.4±0.3 $cm^3\,mol^{-1}$ at 25 °C in 0.008 M $HClO_4$, thus yielding the trans and the cis aqua products respectively.

In a recent report, one (Y. K.) of the present authors has examined the magnitudes of $\Delta V^{\ddagger}$ and ΔV of 14 aquation reactions of the Co^{III} complex ion, where the leaving ligand is a monovalent anion.[1] It has been indicated that the ΔV's for 10 such reactions lie in the relatively limited range from −7 to −13 $cm^3\,mol^{-1}$ and are typically −10 $cm^3\,mol^{-1}$. A general feature that has also been pointed out is that the $\Delta V^{\ddagger}$ is large (*ca.* 14 $cm^3\,mol^{-1}$) when the initial complex contains the strongly electron-donating NH_2^- nonlabile ligand; moderate when the initial complex contains a moderately electron-donating Cl^- or N_3^-, or moderately electron-withdrawing NO_2^-, nonlabile ligand, and small (*ca.* −9 $cm^3\,mol^{-1}$) and close to the corresponding ΔV when the initial complex does not contain any nonlabile ligand with electron-donating or -withdrawing power.

In the present work, $\Delta V^{\ddagger}$ and ΔV are obtained for two additional reactions, where the initial complex contains a nonlabile NO_2^- or N_3^- ligand:

$$trans\text{-}[CoBr(NO_2)(en)_2]^+ + H_2O \longrightarrow trans\text{-}[Co(NO_2)(en)_2H_2O]^{2+} + Br^-, \quad (1)^{2)}$$

$$trans\text{-}[CoCl(N_3)(en)_2]^+ + H_2O \longrightarrow 80\%\ trans\text{-},\ 20\%\ cis\text{-}[Co(N_3)(en)_2H_2O]^{2+} + Cl^-. \quad (2)^{3)}$$

It is tested whether or not the volume profiles of Reactions 1 and 2 are pertinent to the general tendency and whether or not the previous interpretation of the $\Delta V^{\ddagger}$ is also applicable in these cases. In Reaction 2 the trans configuration of the reactant is not retained. On the basis of this, the geometry of the transition state in Reaction 2 should differ from those in analogous reactions, where the geometries are retained.[4] We are further interested in whether or not this feature of Reaction 2 is remarkable in its $\Delta V^{\ddagger}$. The isomerization velocity of *trans*-$[Co(NO_2)(en)_2H_2O]^{2+}$ to the cis-isomer is sufficiently slow, and the kinetic course of Reaction 1 is not interrupted by this isomerization.[5] The *trans*- and *cis*- $[Co(N_3)(en)_2H_2O]^{2+}$ have an isosbestic point at 533 nm, where the velocity of Reaction 2 can be followed spectrophotometrically.[3]

Experimental

Materials. The *trans*-$[CoBr(NO_2)(en)_2]ClO_4$ (**1**)[2] and *trans*-$[CoCl(N_3)(en)_2]ClO_4$ (**2**)[6] were obtained by the published methods and identified by means of elemental analysis (C, H, N).

Kinetic Measurements and Dilatometry. The procedures were the same as in the previous report except that a Heise high-pressure gauge was used.[1]

Results and Discussion

Kinetic Results. The rate constants at each pressure are shown in Table 1. The *k*-values at each pressure are fitted to $\ln(k/k_0)/P=a+bP$ by the least-squares method, where k_0 is the average rate constant at atmospheric pressure. $\Delta V^{\ddagger}$ is obtained by the use of $\Delta V^{\ddagger}=-RT(\mathrm{d}\ln k/\mathrm{d}P)=-RTa$. The rate constants are rather independent of the pressure, and the resultant $\Delta V^{\ddagger}$'s are close to zero (Table 2). Reaction 1 was followed in pure water and in an 0.01 M $HClO_4$ aqueous solution. The rate constants at each pressure are essentially the same in both.

Table 1. Rate constants ($k/10^{-5}\,s^{-1}$) of the aquation reaction at each pressure (P/bar)

1,[a] *trans*-$[CoBr(NO_2)(en)_2]^+$, 1 mM in H_2O,[b] 10 °C,[c] 376 nm,[d] $\ln(k/k_0)/P=-(0.12\pm0.07)\times10^{-4}-(1.6\pm0.5)\times10^{-8}P$[e]

P	1	1	400	800	1200	1600	2000
k	58.2	56.3	56.2	55.2	55.2	53.0	53.5
	55.8	57.8	56.7	56.2	54.8	54.5	51.2

1,[a] *trans*-$[CoBr(NO_2)(en)_2]^+$, 1 mM in 0.01 M $HClO_4$,[b] 10 °C,[c] 376 nm,[d] $\ln(k/k_0)/P=-(0.08\pm0.08)\times10^{-4}-(2.2\pm0.7)\times10^{-8}P$[e]

P	1	1	400	800	1200	1600	2000
k	58.5	57.5	58.2	57.0	55.2	53.8	53.7
	59.2	56.8	57.2	55.8	55.5	53.7	52.3

2,[a] *trans*-$[CoCl(N_3)(en)_2]^+$, 2.6 mM in 0.011 M $HClO_4$,[b] 30 °C,[c] 533 nm,[d] $\ln(k/k_0)/P=-(0.27\pm0.25)\times10^{-4}-(2.6\pm2.0)\times10^{-8}P$[e]

P	1	1	400	800	1200	1600	2000
k	37.7	35.5	35.3	34.8	33.3	32.8	32.3
	36.5	36.3	37.2	33.5	33.2	33.0	32.7

a) Reaction number. b) Concentration of the complex. c) Reaction temperature. d) Reaction was followed at this wavelength. e) Standard deviations are indicated.

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†† Present address: Kawanoe High School, Kawanoe, Ehime 799-01.

TABLE 2. VOLUME PROFILE (V/cm^3 mol^{-1}) FOR THE AQUATION OF [CoXY(en)$_2$]$^+$

Reaction No.	Reactant	Configuration[a]	$\Delta V^{\neq}$ (T/°C, solvent)	ΔV (T/°C, solvent)
1[b]	*trans*-[CoBr(NO$_2$)(en)$_2$]$^+$	100% trans	0.3±0.2 (10, H_2O) 0.2±0.2 (10, 10 mM $HClO_4$)	−10.4±0.1 (7.4, H_2O)
2[b]	*trans*-[CoCl(N$_3$)(en)$_2$]$^+$	80% trans, 20% cis	0.7±0.6 (30, 11 mM $HClO_4$)	−11.0±0.6 (25, 8 mM $HClO_4$)[c] −11.4±0.3 (25, 8 mM $HClO_4$)[d]
3[e]	*trans*-[CoCl(NO$_2$)$_2$(en)$_2$]$^+$	100% trans	0.1 (15, H_2O)	−10.4 (15, H_2O)
4[e]	*cis*-[CoCl(NO$_2$)$_2$(en)$_2$]$^+$	100% cis	0.9 (30, H_2O)	−9.3 (25, H_2O)
5[f]	*cis*-[CoCl$_2$(en)$_2$]$^+$	100% cis	−0.3±0.4 (30, 10 mM HNO_3)[g]	−14.2 (25, H_2O)
6[f]	*trans*[CoCl$_2$(en)$_2$]$^+$	65% trans, 35% cis	−1.7±1.1 (25, H_2O)	−13.9 (25, H_2O)

a) Configuration of the aqua product. b) This work. c) For the trans aqua product. d) For the cis aqua product. e) Ref. 1. f) Ref. 7. g) Ionic strength = 0.1 M ($NaClO_4$).

Dilatometric Results. Reaction 1 was followed at 7.4 °C in a 4.0 mM aqueous solution of **1** from a 52 to a 99% completion. ΔV was obtained from the intercept at $t=0$ of the $\ln(h_t - h_\infty)$ *vs.* t plot, where h_t is the meniscus height at the reaction time (t). The h_∞ value is calculated from h_t's, and $k=40.7\times10^{-5}\,s^{-1}$ is obtained from this plot. The volume change in a 4.0 mM solution of **2** in 0.008 M $HClO_4$ was followed at 25 °C from a 40 to a 90% completion. The total volume (V) of the solution is related to the partial molal volume ($\bar{V}_i$) and the mole number (n_i) of each component (i) in the solution as: $V=\sum n_i\bar{V}_i$. At several stages of Reaction 2, n_i's were calculated according to the following scheme, where the initial product of the aquation consists of 80% trans and 20% cis aqua complex:[3]

$$\begin{tikzcd} \textit{trans}\text{-[CoCl(N}_3\text{)(en)}_2]^+ + H_2O \arrow[r, "k"] & \textit{trans}\text{-[Co(N}_3\text{)(en)}_2H_2O]^{2+} + Cl^- \arrow[d, shift right, "k_1"'] \\ & \textit{cis}\text{-[Co(N}_3\text{)(en)}_2H_2O]^{2+} + Cl^-. \arrow[u, shift right, "k_{-1}"'] \end{tikzcd}$$

We used the literature rate constants at 25 °C in an 0.01 M $HClO_4$ aqueous solution ($k=22.0\times10^{-5}\,s^{-1}$, $k_1=7.2\times10^{-5}\,s^{-1}$, $k_{-1}=2.6\times10^{-5}\,s^{-1}$).[3] The ΔV's of Reaction 2 were obtained for the trans aqua and the cis aqua products respectively by solving a set of simultaneous equations for several reaction stages. Two independent runs were performed. ΔV is −10.7±0.5 and −11.3±0.6 cm^3 mol^{-1} for the trans product, and −11.4±0.3 and −11.3±0.3 cm^3 mol^{-1} for the cis product. These results indicate that the difference between the $\bar{V}_i$'s of *trans*-[Co(N$_3$)(en)$_2$H$_2$O]$^{2+}$ and of *cis*-[Co(N$_3$)(en)$_2$H$_2$O]$^{2+}$ is small enough. Assuming this difference as zero, $k=21.2\times10^{-5}$ and $21.9\times10^{-5}\,s^{-1}$ are obtained from the Guggenheim plots of the dilatometric data, which agree well with that in the literature.[3] The results are summarized in Table 2, along with four volume profiles of analogous reactions.

Discussion. It can be noticed that, in Reactions 1 and 2, the $\Delta V^{\neq}$'s are close to zero and the ΔV's are close to −10 cm^3 mol^{-1}. Thus, the volume profiles of Reactions 1 and 2 are quite pertinent to the general tendency indicated in the previous report.[1] Therefore, these volume profiles can be interpreted along the previous line of arguments. The transition state is composed of an ion pair between the leaving ligand and the five-coordinate intermediate, [Co(NO$_2$)(en)$_2$···OH$_2$]$^{2+}$ or [Co(N$_3$)(en)$_2$···OH$_2$]$^{2+}$, where the entering water molecule is halfway between the vacant coordination site and the first solvation sphere. The volume profiles of Reactions 1—6 are quite similar to each other. The magnitudes of $\Delta V^{\neq}$ are not affected by the geometrical difference in the transition state between those for Reactions 2 and 6 and those for Reactions 1, 3, 4, and 5. This is further in accordance with the fact that the ΔV's of Reaction 2 are quite similar in both cases where cis and trans aqua products are formed. It seems that neither $\Delta V^{\neq}$ nor ΔV is sensitive to the stereochemical course of the reaction.

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