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Volume Profile for Aquation of $Co(en)_2(NH_3)X^{2+}$ (X = *trans*-Cl^-, *trans*-Br^-, *cis*-Br^-, *cis*-NO_3^-)

Y. KITAMURA*, S. TANEDA and K. KURODA

Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790, Japan

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In a recent report, volume profiles for twenty-four aquation reactions of the anionopentaamminecobalt(III) complex ion were examined [1]. It has been suggested that a correlation (eqn. (1)) exists

$$\Delta V^{\ddagger} = (0.48 \pm 0.02)\Delta V + (1.5 \pm 0.3) \qquad (1)$$

between their activation volume ($\Delta V^{\ddagger}$) and the reaction volume (ΔV). In the present work, we have investigated the volume profiles of the title reaction:

$$trans\text{-}Co(en)_2(NH_3)Cl^{2+} + H_2O \longrightarrow trans\text{-}Co(en)_2(NH_3)H_2O^{3+} + Cl^-$$

$$trans\text{-}Co(en)_2(NH_3)Br^{2+} + H_2O \longrightarrow trans\text{-}Co(en)_2(NH_3)H_2O^{3+} + Br^-$$

$$cis\text{-}Co(en)_2(NH_3)Br^{2+} + H_2O \longrightarrow Co(en)_2(NH_3)H_2O^{3+} + Br^-$$

$$cis\text{-}Co(en)_2(NH_3)NO_3^{2+} + H_2O \longrightarrow Co(en)_2(NH_3)H_2O^{3+} + NO_3^-$$

We have also reinvestigated $\Delta V^{\ddagger}$ for the aquation of $Co(NH_3)_5X^{2+}$ ($X = Cl^-$, Br^-, NO_3^-) at relatively high temperature (40 ~ 65 °C). The resultant volume profiles for the aquations of $Co(en)_2(NH_3)X^{2+}$ and $Co(NH_3)_5X^{2+}$ are compared.

Experimental

The following three complex salts were obtained according to the literature and identified by elemental analysis and UV absorption [2, 3] [λ_{max} (in nm) (ϵ)]: *trans*-$[Co(en)_2(NH_3)Cl]Cl_2 \cdot H_2O$, 526 (48), 454_{sh}, 361 (53) [4]; *trans*-$[Co(en)_2(NH_3)Br]Br_2 \cdot H_2O$, 544 (52), 459_{sh} (28) [5]; *cis*-$[Co(en)_2(NH_3)NO_3](NO_3)_2$, 488 (80), 345 (71) [4]. *cis*-$[Co(en)_2(NH_3)Br]Br_2 \cdot H_2O$ [6], *trans*-$[Co(en)_2(NH_3)H_2O](NO_3)_3$ [7] and the perchlorate salts of $Co(NH_3)_5X^{2+}$ ($X = Cl^-$, Br^-, NO_3^-) [8] were obtained in previous work. Kinetic measurements at high pressure and dilatometry were carried out as described elsewhere [1, 8].

Results and Discussion

Kinetic results are summarized in Table 1. Aliquots of reacting solution were taken from the high pressure vessel and analysed spectrophotometrically. The aquations of $Co(en)_2(NH_3)X^{2+}$ were followed at 300 nm, where the molar extinction coefficients of *trans*- and *cis*-$Co(en)_2(NH_3)H_2O^{3+}$ are approximately equal [5]. Generally, reaction was followed over two or three half-lives. In every case, the rate constant increased with an increase in pressure. Linear dependence of $\ln k_{obs}$ on P was assumed [8]. A negative value of $\Delta V^{\ddagger}$ was obtained typically within error limits of ±0.3 $cm^3\ mol^{-1}$.

Dilatometry was carried out at 25 °C by mixing a 10 mM aqueous solution of the complex salt with an equivalent amount of 50 mM NaOH. Duplicate runs were performed. Error limits were typically ±0.2 $cm^3\ mol^{-1}$. The activation volume at infinite dilution was obtained for the base hydrolysis of $Co(en)_2(NH_3)X^{2+}$ (ΔV^0_{bh}) and for the neutralization of *trans*-$Co(en)_2(NH_3)H_2O^{3+}$ ($\Delta V^0_{neut} = 27.0$ $cm^3\ mol^{-1}$). The reaction volume for the aquation (ΔV^0) was calculated by $\Delta V^0 = \Delta V^0_{bh} - \Delta V^0_{neut}$. The difference between the partial molar volume ($\bar{V}$) of *trans*- and *cis*-$Co(en)_2(NH_3)H_2O^{3+}$ (0.4 $cm^3\ mol^{-1}$) or between $\bar{V}$ of *trans*- and *cis*-$Co(en)_2(NH_3)OH^{2+}$ (−1.5 $cm^3\ mol^{-1}$) was neglected [7].

The $\Delta V^{\ddagger}$ and ΔV^0 values are summarized in Table 2. From this Table the following can be inferred:

(i) In the case of $Co(NH_3)_5X^{2+}$ ($X = Cl^-$, Br^-, NO_3^-) the magnitude of $\Delta V^{\ddagger}$ does not depend significantly on the reaction temperature.

(ii) The ΔV^0 for $Co(en)_2(NH_3)X^{2+}$ is close to the ΔV^0 for $Co(NH_3)_5X^{2+}$ with the same X. This underlines the independence of the reaction volume of the Co(III) complex on the kind of non-labile ligand [11].

(iii) The $\Delta V^{\ddagger}$ for $Co(en)_2(NH_3)X^{2+}$ is close to the $\Delta V^{\ddagger}$ for $Co(NH_3)_5X^{2+}$ with the same X. In this connection we discussed before that the former might be larger than the latter by 2 ± 1 $cm^3\ mol^{-1}$ [7]. This description was based on a $\Delta V^{\ddagger} = -3.2$ $cm^3\ mol^{-1}$ for the aquation of *cis*-$Co(en)_2(NH_3)Cl^{2+}$ ($C = 5.5$ mM, $[HClO_4] = 100$ mM, $t = 75$ °C, $\lambda = 300$ nm). However, it may be better not to take this value of $\Delta V^{\ddagger}$ into consideration, because the aquation of *cis*-$Co(en)_2(NH_3)Cl^{2+}$ does not go to completion and it is difficult to obtain an accurate value of $\Delta V^{\ddagger}$ for this reaction.

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*Author to whom correspondence should be addressed.

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TABLE 1. Pressure Effect on the Aquation Velocity in 100 mM $HClO_4$

Complex	C^a (mM)	t (°C)	λ^b (nm)	$k_{obs} \times 10^4$ $(s^{-1})^c$ at pressures (MPa) of				
				5	50	100	150	200
$Co(NH_3)_5Cl^{2+}$	1.0	65.1	282	1.83	2.06	2.30	2.55	2.77
$Co(NH_3)_5Br^{2+}$	1.0	54.1	310	1.85	2.17	2.39	2.64	2.99
$Co(NH_3)_5NO_3^{2+}$	1.0	40.1	270	1.72	2.00	2.22	2.40	2.68
trans-$Co(en)_2(NH_3)Cl^{2+d}$	2.5	69.7	300	0.641	0.696	0.775	0.834	0.900
trans-$Co(en)_2(NH_3)Br^{2+e}$	1.0	60.1	300	1.10	1.11	1.22	1.27	1.35
cis-$Co(en)_2(NH_3)Br^{2+}$	0.9	60.0	300	0.956	1.06	1.18	1.29	1.42
cis-$Co(en)_2(NH_3)NO_3^{2+}$	6.0	45.2	300	1.15	1.26	1.43	1.65	1.78

[a] Complex concentration; mM = 10^{-3} mol dm^{-3}. [b] Reaction was followed at this wavelength. [c] Mean of three runs. [d] Reaction was followed until 40–50% completion [5]. [e] In 1 mM $HClO_4$.

TABLE 2. Volume Profiles (cm^3 mol^{-1}) for the Aquation Reactions

Complex	$\Delta V^{\ddagger}$ (t in °C)	$\Delta V^{\ddagger}$ (at 25 °C)	ΔV^0 (at 25 °C)
$Co(NH_3)_5Cl^{2+}$	−6.0 (65)	-7.9^a	-15.6^a
$Co(NH_3)_5Br^{2+}$	−6.4 (54)	-6.7^a	-14.4^a
$Co(NH_3)_5NO_3^{2+}$	−5.7 (40)	-4.9^a	-12.3^a
trans-$Co(en)_2(NH_3)Cl^{2+}$	−5.0 (70)		−17.3
trans-$Co(en)_2(NH_3)Br^{2+}$	−3.1 (60)		−14.7
cis-$Co(en)_2(NH_3)Br^{2+}$	−5.6 (60)		−16.1
cis-$Co(en)_2(NH_3)NO_3^{2+}$	−6.1 (45)		−13.2

[a] From refs. 9 and 10.

(iv) The $\Delta V^{\ddagger}$ and ΔV^0 values for $Co(en)_2(NH_3)X^{2+}$ approximately satisfy eqn. (1). This means that the $\bar{V}$ of the transition state is close to the corresponding mean $\bar{V}$ of the initial and final state. It may be interpreted that the entering H_2O and the leaving X participate almost equally to the transition state. Thus, aquation of $Co(en)_2(NH_3)X^{2+}$ will most probably proceed through an interchange mechanism.

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