

Volume Profile for Aquation of $\text{Co(en)}_2(\text{NH}_3)\text{X}^{2+}$ ($\text{X} = \text{trans-Cl}^-$, trans-Br^- , cis-Br^- , cis-NO_3^-)

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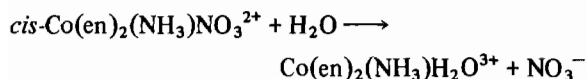
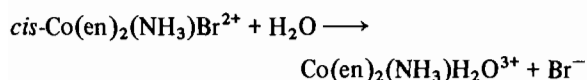
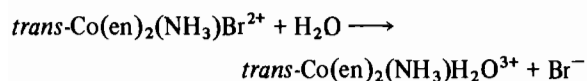
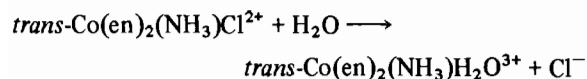
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In a recent report, volume profiles for twenty-four aquation reactions of the anionopentaamminecobalt(III) complex ion were examined [1]. It has been suggested that a correlation (eqn. (1)) exists

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

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



We have also reinvestigated ΔV^\ddagger for the aquation of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{Cl}^-$, Br^- , NO_3^-) at relatively high temperature (40 ~ 65 °C). The resultant volume profiles for the aquations of $\text{Co(en)}_2(\text{NH}_3)\text{X}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ 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*- $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, 526 (48), 454_{sh}, 361 (53) [4]; *trans*- $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Br}]\text{Br}_2 \cdot \text{H}_2\text{O}$, 544 (52), 459_{sh} (28) [5]; *cis*- $[\text{Co}(\text{en})_2(\text{NH}_3)\text{NO}_3](\text{NO}_3)_2$, 488 (80), 345 (71) [4]. *cis*- $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Br}]\text{Br}_2 \cdot \text{H}_2\text{O}$ [6], *trans*- $[\text{Co}(\text{en})_2(\text{NH}_3)\text{H}_2\text{O}](\text{NO}_3)_3$ [7] and the perchlorate salts of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{Cl}^-$, Br^- , NO_3^-) [8] were obtained in previous

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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 $\text{Co(en)}_2(\text{NH}_3)\text{X}^{2+}$ were followed at 300 nm, where the molar extinction coefficients of *trans*- and *cis*- $\text{Co(en)}_2(\text{NH}_3)\text{H}_2\text{O}^{3+}$ 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 $\ln k_{\text{obs}}$ on P was assumed [8]. A negative value of ΔV^\ddagger was obtained typically within error limits of $\pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$.

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 $\pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$. The activation volume at infinite dilution was obtained for the base hydrolysis of $\text{Co(en)}_2(\text{NH}_3)\text{X}^{2+}$ (ΔV_{bh}^0) and for the neutralization of *trans*- $\text{Co(en)}_2(\text{NH}_3)\text{H}_2\text{O}^{3+}$ ($\Delta V_{\text{neut}}^0 = 27.0 \text{ cm}^3 \text{ mol}^{-1}$). The reaction volume for the aquation (ΔV^0) was calculated by $\Delta V^0 = \Delta V_{\text{bh}}^0 - \Delta V_{\text{neut}}^0$. The difference between the partial molar volume (\bar{V}) of *trans*- and *cis*- $\text{Co(en)}_2(\text{NH}_3)\text{H}_2\text{O}^{3+}$ ($0.4 \text{ cm}^3 \text{ mol}^{-1}$) or between \bar{V} of *trans*- and *cis*- $\text{Co(en)}_2(\text{NH}_3)\text{OH}^{2+}$ ($-1.5 \text{ cm}^3 \text{ mol}^{-1}$) was neglected [7].

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

(i) In the case of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{Cl}^-$, Br^- , NO_3^-) the magnitude of ΔV^\ddagger does not depend significantly on the reaction temperature.

(ii) The ΔV^0 for $\text{Co(en)}_2(\text{NH}_3)\text{X}^{2+}$ is close to the ΔV^0 for $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ 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 ΔV^\ddagger for $\text{Co(en)}_2(\text{NH}_3)\text{X}^{2+}$ is close to the ΔV^\ddagger for $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ with the same X. In this connection we discussed before that the former might be larger than the latter by $2 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$ [7]. This description was based on a $\Delta V^\ddagger = -3.2 \text{ cm}^3 \text{ mol}^{-1}$ for the aquation of *cis*- $\text{Co(en)}_2(\text{NH}_3)\text{Cl}^{2+}$ ($C = 5.5 \text{ mM}$, $[\text{HClO}_4] = 100 \text{ mM}$, $t = 75 \text{ }^\circ\text{C}$, $\lambda = 300 \text{ nm}$). However, it may be better not to take this value of ΔV^\ddagger into consideration, because the aquation of *cis*- $\text{Co(en)}_2(\text{NH}_3)\text{Cl}^{2+}$ does not go to completion and it is difficult to obtain an accurate value of ΔV^\ddagger for this reaction.

TABLE 1. Pressure Effect on the Aquation Velocity in 100 mM HClO₄

Complex	C ^a (mM)	t (°C)	λ ^b (nm)	k _{obs} × 10 ⁴ (s ⁻¹) ^c at pressures (MPa) of				
				5	50	100	150	200
Co(NH ₃) ₅ Cl ²⁺	1.0	65.1	282	1.83	2.06	2.30	2.55	2.77
Co(NH ₃) ₅ Br ²⁺	1.0	54.1	310	1.85	2.17	2.39	2.64	2.99
Co(NH ₃) ₅ NO 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

^aComplex concentration; mM = 10⁻³ mol dm⁻³. ^bReaction was followed at this wavelength. ^cMean of three runs. ^dReaction was followed until 40–50% completion [5]. ^eIn 1 mM HClO₄.

TABLE 2. Volume Profiles (cm³ mol⁻¹) for the Aquation Reactions

Complex	ΔV [‡] (t in °C)	ΔV [‡] (at 25 °C)	ΔV ⁰ (at 25 °C)
Co(NH ₃) ₅ Cl ²⁺	-6.0 (65)	-7.9 ^a	-15.6 ^a
Co(NH ₃) ₅ Br ²⁺	-6.4 (54)	-6.7 ^a	-14.4 ^a
Co(NH ₃) ₅ NO 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

^aFrom refs. 9 and 10.

(iv) The ΔV[‡] and ΔV⁰ values for Co(en)₂(NH₃)X²⁺ 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 H₂O and the leaving X participate almost equally to the

transition state. Thus, aquation of Co(en)₂(NH₃)X²⁺ will most probably proceed through an interchange mechanism.

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