

## The Volume Profile for the Aquation Reactions of *trans*-[CoBr(NO<sub>2</sub>)(en)<sub>2</sub>]<sup>+</sup> and *trans*-[CoCl(N<sub>3</sub>)(en)<sub>2</sub>]<sup>+</sup>

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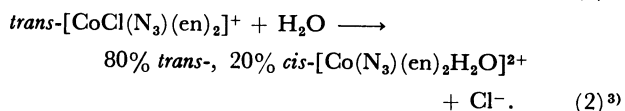
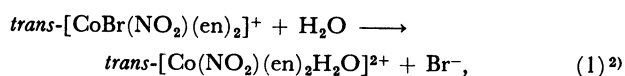
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**Synopsis.** For the aquation of *trans*-[CoBr(NO<sub>2</sub>)(en)<sub>2</sub>]<sup>+</sup>, the activation volume at atmospheric pressure ( $\Delta V^\ddagger$ ) is  $0.3 \pm 0.2$  cm<sup>3</sup> mol<sup>-1</sup> at 10 °C, and the reaction volume ( $\Delta V$ ) is  $-10.4 \pm 0.1$  cm<sup>3</sup> mol<sup>-1</sup> at 7.4 °C, both in pure water. For *trans*-[CoCl(N<sub>3</sub>)(en)<sub>2</sub>]<sup>+</sup>,  $\Delta V^\ddagger$  is  $0.7 \pm 0.6$  cm<sup>3</sup> mol<sup>-1</sup> at 30 °C in 0.011 M HClO<sub>4</sub> (1 M = 1 mol dm<sup>-3</sup>) and  $\Delta V$  is  $-11.0 \pm 0.6$  and  $-11.4 \pm 0.3$  cm<sup>3</sup> mol<sup>-1</sup> at 25 °C in 0.008 M HClO<sub>4</sub>, 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  $\Delta V$  of 14 aquation reactions of the Co<sup>III</sup> complex ion, where the leaving ligand is a monovalent anion.<sup>1)</sup> It has been indicated that the  $\Delta V$ 's for 10 such reactions lie in the relatively limited range from  $-7$  to  $-13$  cm<sup>3</sup> mol<sup>-1</sup> and are typically  $-10$  cm<sup>3</sup> mol<sup>-1</sup>. A general feature that has also been pointed out is that the  $\Delta V^\ddagger$  is large (*ca.* 14 cm<sup>3</sup> mol<sup>-1</sup>) when the initial complex contains the strongly electron-donating NH<sub>2</sub><sup>-</sup> nonlabile ligand; moderate when the initial complex contains a moderately electron-donating Cl<sup>-</sup> or N<sub>3</sub><sup>-</sup>, or moderately electron-withdrawing NO<sub>2</sub><sup>-</sup>, nonlabile ligand, and small (*ca.*  $-9$  cm<sup>3</sup> mol<sup>-1</sup>) and close to the corresponding  $\Delta V$  when the initial complex does not contain any nonlabile ligand with electron-donating or -withdrawing power.

In the present work,  $\Delta V^\ddagger$  and  $\Delta V$  are obtained for two additional reactions, where the initial complex contains a nonlabile NO<sub>2</sub><sup>-</sup> or N<sub>3</sub><sup>-</sup> ligand:



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.<sup>4)</sup> 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<sub>2</sub>)(en)<sub>2</sub>H<sub>2</sub>O]<sup>2+</sup> to the *cis*-isomer is sufficiently slow, and the kinetic course of Reaction 1 is not interrupted by this

isomerization.<sup>5)</sup> The *trans*- and *cis*-[Co(N<sub>3</sub>)(en)<sub>2</sub>H<sub>2</sub>O]<sup>2+</sup> have an isosbestic point at 533 nm, where the velocity of Reaction 2 can be followed spectrophotometrically.<sup>3)</sup>

### Experimental

**Materials.** The *trans*-[CoBr(NO<sub>2</sub>)(en)<sub>2</sub>]ClO<sub>4</sub> (1)<sup>2)</sup> and *trans*-[CoCl(N<sub>3</sub>)(en)<sub>2</sub>]ClO<sub>4</sub> (2)<sup>6)</sup> 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.<sup>1)</sup>

### 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*<sub>0</sub> is the average rate constant at atmospheric pressure.  $\Delta V^\ddagger$  is obtained by the use of  $\Delta V^\ddagger = -RT(d \ln k / dP) = -RTa$ . 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<sub>4</sub> aqueous solution. The rate constants at each pressure are essentially the same in both.

TABLE 1. RATE CONSTANTS (*k*/10<sup>-5</sup> s<sup>-1</sup>) OF THE AQUATION REACTION AT EACH PRESSURE (*P*/bar)

1, <sup>a)</sup> <i>trans</i> -[CoBr(NO <sub>2</sub> )(en) <sub>2</sub> ] <sup>+</sup> , 1 mM in H <sub>2</sub> O, <sup>b)</sup> 10 °C, <sup>c)</sup> 376 nm, <sup>d)</sup> $\ln(k/k_0)/P = -(0.12 \pm 0.07) \times 10^{-4} - (1.6 \pm 0.5) \times 10^{-8} P$ <sup>e)</sup>								
<i>P</i>	1	1	400	800	1200	1600	2000	
<i>k</i>	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, <sup>a)</sup> <i>trans</i> -[CoBr(NO <sub>2</sub> )(en) <sub>2</sub> ] <sup>+</sup> , 1 mM in 0.01 M HClO <sub>4</sub> , <sup>b)</sup> 10 °C, <sup>c)</sup> 376 nm, <sup>d)</sup> $\ln(k/k_0)/P = -(0.08 \pm 0.08) \times 10^{-4} - (2.2 \pm 0.7) \times 10^{-8} P$ <sup>e)</sup>								
<i>P</i>	1	1	400	800	1200	1600	2000	
<i>k</i>	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, <sup>a)</sup> <i>trans</i> -[CoCl(N <sub>3</sub> )(en) <sub>2</sub> ] <sup>+</sup> , 2.6 mM in 0.011 M HClO <sub>4</sub> , <sup>b)</sup> 30 °C, <sup>c)</sup> 533 nm, <sup>d)</sup> $\ln(k/k_0)/P = -(0.27 \pm 0.25) \times 10^{-4} - (2.6 \pm 2.0) \times 10^{-8} P$ <sup>e)</sup>								
<i>P</i>	1	1	400	800	1200	1600	2000	
<i>k</i>	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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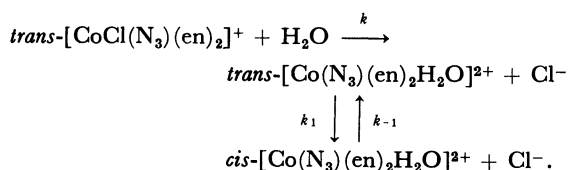
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TABLE 2. VOLUME PROFILE ( $V/\text{cm}^3 \text{ mol}^{-1}$ ) FOR THE AQUATION OF  $[\text{CoXY}(\text{en})_2]^+$ 

Reaction No.	Reactant	Configuration <sup>a)</sup>	$\Delta V^*$ ( $T/^\circ\text{C}$ , solvent)	$\Delta V$ ( $T/^\circ\text{C}$ , solvent)
1 <sup>b)</sup>	<i>trans</i> - $[\text{CoBr}(\text{NO}_2)(\text{en})_2]^+$	100% <i>trans</i>	$0.3 \pm 0.2$ (10, $\text{H}_2\text{O}$ ) $0.2 \pm 0.2$ (10, 10 mM $\text{HClO}_4$ )	$-10.4 \pm 0.1$ (7.4, $\text{H}_2\text{O}$ )
2 <sup>b)</sup>	<i>trans</i> - $[\text{CoCl}(\text{N}_3)(\text{en})_2]^+$	80% <i>trans</i> , 20% <i>cis</i>	$0.7 \pm 0.6$ (30, 11 mM $\text{HClO}_4$ )	$-11.0 \pm 0.6$ (25, 8 mM $\text{HClO}_4$ ) <sup>c)</sup> $-11.4 \pm 0.3$ (25, 8 mM $\text{HClO}_4$ ) <sup>d)</sup>
3 <sup>e)</sup>	<i>trans</i> - $[\text{CoCl}(\text{NO}_2)_2(\text{en})_2]^+$	100% <i>trans</i>	0.1 (15, $\text{H}_2\text{O}$ )	$-10.4$ (15, $\text{H}_2\text{O}$ )
4 <sup>e)</sup>	<i>cis</i> - $[\text{CoCl}(\text{NO}_2)_2(\text{en})_2]^+$	100% <i>cis</i>	0.9 (30, $\text{H}_2\text{O}$ )	$-9.3$ (25, $\text{H}_2\text{O}$ )
5 <sup>f)</sup>	<i>cis</i> - $[\text{CoCl}_2(\text{en})_2]^+$	100% <i>cis</i>	$-0.3 \pm 0.4$ (30, 10 mM $\text{HNO}_3$ ) <sup>g)</sup>	$-14.2$ (25, $\text{H}_2\text{O}$ )
6 <sup>f)</sup>	<i>trans</i> - $[\text{CoCl}_2(\text{en})_2]^+$	65% <i>trans</i> , 35% <i>cis</i>	$-1.7 \pm 1.1$ (25, $\text{H}_2\text{O}$ )	$-13.9$ (25, $\text{H}_2\text{O}$ )

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 ( $\text{NaClO}_4$ ).

**Dilatometric Results.** Reaction 1 was followed at  $7.4^\circ\text{C}$  in a 4.0 mM aqueous solution of **1** from a 52 to a 99% completion.  $\Delta V$  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  $h_\infty$  value is calculated from  $h_t$ 's, and  $k=40.7 \times 10^{-5} \text{ s}^{-1}$  is obtained from this plot. The volume change in a 4.0 mM solution of **2** in 0.008 M  $\text{HClO}_4$  was followed at  $25^\circ\text{C}$  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:<sup>3)</sup>



We used the literature rate constants at  $25^\circ\text{C}$  in an 0.01 M  $\text{HClO}_4$  aqueous solution ( $k=22.0 \times 10^{-5} \text{ s}^{-1}$ ,  $k_1=7.2 \times 10^{-5} \text{ s}^{-1}$ ,  $k_{-1}=2.6 \times 10^{-5} \text{ s}^{-1}$ ).<sup>3)</sup> The  $\Delta V$ '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.  $\Delta V$  is  $-10.7 \pm 0.5$  and  $-11.3 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$  for the *trans* product, and  $-11.4 \pm 0.3$  and  $-11.3 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$  for the *cis* product. These results indicate that the difference between the  $\bar{V}_i$ 's of *trans*- $[\text{Co}(\text{N}_3)(\text{en})_2\text{H}_2\text{O}]^{2+}$  and of *cis*- $[\text{Co}(\text{N}_3)(\text{en})_2\text{H}_2\text{O}]^{2+}$  is small enough. Assuming this difference as zero,  $k=21.2 \times 10^{-5}$  and  $21.9 \times 10^{-5} \text{ s}^{-1}$  are obtained from the Guggenheim plots of the dilatometric data, which agree well with

that in the literature.<sup>3)</sup> 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  $\Delta V^*$ 's are close to zero and the  $\Delta V$ 's are close to  $-10 \text{ cm}^3 \text{ mol}^{-1}$ . Thus, the volume profiles of Reactions 1 and 2 are quite pertinent to the general tendency indicated in the previous report.<sup>1)</sup> 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,  $[\text{Co}(\text{NO}_2)(\text{en})_2 \cdots \text{OH}_2]^{2+}$  or  $[\text{Co}(\text{N}_3)(\text{en})_2 \cdots \text{OH}_2]^{2+}$ , 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  $\Delta V^*$  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  $\Delta V$ 's of Reaction 2 are quite similar in both cases where *cis* and *trans* aqua products are formed. It seems that neither  $\Delta V^*$  nor  $\Delta V$  is sensitive to the stereochemical course of the reaction.

## References

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