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Volume Profile for Aquation of $Co(en)_2Cl_2^+$, $Co(trien)Cl_2^+$ and $Co(edda)Cl_2^-$

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Abstract

Activation volume ($\Delta V^{\ddagger} = -2 \sim +3$ cm^3 mol^{-1}) and reaction volume ($\Delta V = -18 \sim +2$ cm^3 mol^{-1}) were experimentally obtained for seven title reactions. Results are interpreted consistently with the Interchange mechanism. In the case of $Co(en)_2Cl_2^+$ and $Co(trien)Cl_2^+$, the $\Delta V^{\ddagger}$ for *trans* isomers aquating with steric change is slightly ($1 \sim 3$ cm^3 mol^{-1}) larger than the $\Delta V^{\ddagger}$ for *cis* isomers aquating with configuration retention. This tendency parallels the suggestion by Tobe that the $\Delta S^{\ddagger}$ is positive for aquation with steric change.

Introduction

In our recent work, the volume profile for the aquation of the anionopentaamminecobaltate ion was consistently understood in relation to the Interchange mechanism [1–3]. In this work, we investigate the volume profile of the following aquations

trans-$Co(NH_3)_4Cl_2^+ + H_2O =$

45% *trans*-, 55% *cis*-$Co(NH_3)_4(H_2O)Cl^{2+} + Cl^-$ [4]

trans-$Co(en)_2Cl_2^+ + H_2O =$

74% *trans*-, 26% *cis*-$Co(en)_2(H_2O)Cl^{2+} + Cl^-$ [5]

cis-$Co(en)_2Cl_2^+ + H_2O =$ *cis*-$Co(en)_2(H_2O)Cl^{2+} + Cl^-$ [6]

trans-$Co(trien)Cl_2^+ + H_2O =$

cis-β-$Co(trien)(H_2O)Cl^{2+} + Cl^-$ [7]

cis-α-$Co(trien)Cl_2^+ + H_2O =$

cis-α-$Co(trien)(H_2O)Cl^{2+} + Cl^-$ [7]

cis-β-$Co(trien)Cl_2^+ + H_2O =$

cis-β-$Co(trien)(H_2O)Cl^{2+} + Cl^-$ [7]

cis-α-$Co(edda)Cl_2^- + H_2O =$

cis-α-$Co(edda)(H_2O)Cl + Cl^-$

cis-α-$Co(edda)(H_2O)Cl + H_2O =$

cis-α-$Co(edda)(H_2O)_2^+ + Cl^-$

trans-$Co(en)_2Br_2^+ + H_2O =$

85% *trans*-, 15% *cis*-$Co(en)_2(H_2O)Br^{2+} + Br^-$ [5]

The $\Delta V^{\ddagger}$ for *trans*-$Co(en)_2Cl_2^+$ and *trans*-$Co(en)_2Br_2^+$ are reinvestigated, because in previous work they have not been correctly obtained [8]. The $\Delta V^{\ddagger}$ for *cis*-$Co(en)_2Cl_2^+$ and β-$Co(trien)Cl_2^+$ are also reinvestigated extensively [8, 9].

Experimental

Materials

The following complex salts were obtained according to the literature and identified by elemental analysis and UV absorption: α-$[Co(trien)Cl_2]Cl \cdot 0.5H_2O$, β-$[Co(trien)Cl_2]Cl \cdot H_2O$, *trans*-$[Co(trien)Cl_2]ClO_4$ [10]*; α-$H[Co(edda)Cl_2]$, α-$[Co(edda)(H_2O)Cl] \cdot 0.5H_2O$ [11]*; *trans*-$[Co(NH_3)_4Cl_2]HSO_4$ [12]; *trans*-$[Co(en)_2Br_2]Br \cdot 0.5H_2O$ [13]; *trans*-$[Co(en)_2Cl_2]Cl$, *cis*-$[Co(en)_2Cl_2]Cl \cdot H_2O$ [14]. The α-$Co(trien)Cl_2^+$ salt was stored below 0 °C to avoid isomerization, and used within 2 months of identification [15].

Dilatometry

The reacting solution was contained in a glass bulb (39.2 cm^3) fitted with an upright capillary (diameter = 0.0404 cm). This bulb was maintained in a well controlled (±0.001 °C) thermostat and the movement of the meniscus height was followed. Relevant rate constants were used to estimate the progress of aquation and the reaction volume was calculated.

High Pressure Kinetics

Generally, reaction was followed spectrophotometrically *in situ* using a Hawley-Chase type high pressure cell up to 90% completion [16]. Value of

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*trien = triethylenetetramine; H_2edda = ethylenediamine-*N*,*N'*-diacetic acid.

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the first order rate constant of aquation k_{obs} was calculated by the Guggenheim method. In the case of α-Co(edda)(H_2O)Cl and *trans*-Co(en)$_2$Cl$_2^+$, aliquots were taken out from the high pressure vessel and analysed spectrophotometrically [2]. In the former, the reaction was followed to completion and k_{obs} was calculated from the $\ln(D_t - D_\infty)$ *versus* t plot, where D_t and D_∞ are the optical density at reaction time t and at 8 half lives. In the latter, the reaction was followed to 80% completion and k_{obs} was calculated with the aid of a fitted D_∞ value.

TABLE 1. Values of $10^4 \times k_{obs}$ (s^{-1}) for Aquation of α-Co(edda)Cl$_2^-$ at Normal Pressure^a

T (℃)	[HClO$_4$] (M)			
	0.001	0.01	0.1	0.5
25.1			2.72	
30.5	4.53	4.90	5.17	4.92
35.4	9.38		9.53	
40.5			18.3	

Concentration of the complex (C) = 3.7 mM. $\Delta H^{\ddagger} = 22.4 \pm 0.4$ kcal mol^{-1}. $\Delta S^{\ddagger} = 0.2 \pm 1.4$ cal K^{-1} mol^{-1}. M = mol dm^{-3}. mM = 10^{-3} M. ^{a}Mean of duplicate runs.

TABLE 2. Values of $10^4 \times k_{obs}$ (s^{-1}) for Aquation of α-Co(edda)(H_2O)Cl at Normal Pressure^a

T (℃)	[HClO$_4$] (M)		
	0.001	0.01	0.1
35.0		0.384	
40.6		0.711	
45.1	1.33	1.29	1.24
49.6		2.36	

C = 2.8 mM. $\Delta H^{\ddagger} = 23.9 \pm 0.6$ kcal mol^{-1}. $\Delta S^{\ddagger} = -1.1 \pm 1.9$ cal K^{-1} mol^{-1}. ^{a}Mean of duplicate runs.

Results

Aquation of α-Co(edda)Cl$_2^-$

The spectral change of α-Co(edda)Cl$_2^-$ in acidic aqueous solution maintains isosbestic points at 480 and 571 nm in its early stage. These are isosbestic points between α-Co(edda)Cl$_2^-$ and α-Co(edda)(H_2O)Cl [11]. Thus, the first chloride liberation proceeds with configuration retention. This reaction was followed at an isosbestic point 353.5 nm of the second chloride liberation. The results are summarized in Table 1. The value of k_{obs} is independent of the acid concentration.

Aquation of α-Co(edda)(H_2O)Cl

The spectral change of α-Co(edda)(H_2O)Cl in acidic aqueous solution maintains isosbestic points at 353.5, 381, 459 and 549 nm. The final spectrum coincides with the spectrum of α-Co(edda)(H_2O)$_2^+$. Thus, aquation proceeds with configuration retention. This reaction was followed at 292 nm. The results are summarized in Table 2. The value of k_{obs} is independent of the acid concentration.

High Pressure Kinetic Results

The results are summarized in Table 3. In every case, k_{obs} depends slightly on pressure. Linear dependence of $\ln k_{obs}$ on P was assumed. The value of $\Delta V^{\ddagger}$ was calculated by

$$\Delta V^{\ddagger} = -RT \frac{d \ln k_{obs}}{dP}$$

typically within an error limit of ±0.3 cm^3 mol^{-1}. In the case of *trans*-Co(en)$_2$Cl$_2^+$ and *trans*-Co(en)$_2$Br$_2^+$, aquation velocity is comparable with the subsequent *trans* ⇌ *cis* isomerization velocity of the product complex Co(en)$_2$(H_2O)Cl^{2+} or Co(en)$_2$(H_2O)Br^{2+} [5]. Therefore, the first halide liberation should be followed at a certain isosbestic point of the subsequent isomerization, where the molar extinction coeffi-

TABLE 3. Pressure Effect on Aquation Velocity

Complex	C (mM)	[HClO$_4$] (mM)	T (℃)	λ^a (nm)	$10^4 \times k_{obs}$ (s^{-1})^b at P (MPa)					
					5	40	80	120	160	200
cis-Co(en)$_2$Cl$_2^+$	0.36	1.1	30.1	281	4.78	4.80	4.79	4.90	4.86	
trans-Co(trien)Cl$_2^+$	1	1	10.5	330	4.43	4.49	4.34	4.32	4.30	4.01
α-Co(trien)Cl$_2^+$	1	10	31.6	310	3.47	3.60	3.69	3.86	3.90	3.99
β-Co(trien)Cl$_2^+$	1	1	15	310	4.07	4.13	4.16	4.18	4.14	4.11
α-Co(edda)Cl$_2^-$	3.7	9.6	30.6	353.5	4.29	4.23	4.13	3.80	3.52	
trans-Co(en)$_2$Br$_2^+$	0.35	10	25.3	342	3.74	3.73	3.78	3.66	3.54	3.44
					5	50	100	150	200	
trans-Co(en)$_2$Cl$_2^+$	0.36	1	40.3	281	1.83	1.87	1.82	1.73	1.75	
α-Co(edda)(H_2O)Cl	2.8	1	47.1	292	1.61	1.61	1.57	1.53	1.53	

^{a}Reaction was followed at this wavelength. ^{b}Mean of two or three runs.

TABLE 4. Dilatometrically Obtained Reaction Volume for Aquation

Complex	T (℃)	Solvent	C (mM)	ΔV (cm^3 mol^{-1})[a]
trans-$Co(NH_3)_4Cl_2^+$	16	water	10	-9.9[b]
trans-$Co(en)_2Cl_2^+$	25	7.6 mM HNO_3	10	-12.0[c], -14.0[d]
cis-$Co(en)_2Cl_2^+$	25	7.6 mM HNO_3	10	-9.1
trans-$Co(trien)Cl_2^+$	10	1 mM $HClO_4$	4	-18.6
α-$Co(trien)Cl_2^+$	25	10 mM $HClO_4$	15	-8.8
β-$Co(trien)Cl_2^+$	10	1 mM $HClO_4$	5	-10.0
α-$Co(edda)Cl_2^-$	25	10 mM $HClO_4$	10	1.9 ± 0.8
α-$Co(edda)(H_2O)Cl$	40	1 mM $HClO_4$	2.5	-7.4

[a] Mean of duplicate runs. [b] Difference between $\bar{V}$ of *trans* and *cis* chloroaqua products was neglected. [c] For the *trans* product, result of single run. [d] For the *cis* product, result of single run.

TABLE 5. Volume Profile for Aquation

Complex	Steric change (%)	$\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1})	$\Delta V^{\ddagger}$ (cm^3 mol^{-1})	ΔV (cm^3 mol^{-1})
trans-$Co(NH_3)_4Cl_2^+$	55	9[a]	-1.7[b]	-9.9
trans-$Co(en)_2Cl_2^+$	26	14[c]	1.8	-12.0
cis-$Co(en)_2Cl_2^+$	0	-5[c]	-0.3	-9.1
trans-$Co(trien)Cl_2^+$	100	16[d]	1.1	-18.6
α-$Co(trien)Cl_2^+$	0	-6[d]	-1.9	-8.7
β-$Co(trien)Cl_2^+$	0	-3[d]	-0.1	-10.0
α-$Co(edda)Cl_2^-$	0	0	3.2	1.9
α-$Co(edda)(H_2O)Cl$	0	-1	0.8	-7.3
trans-$Co(en)_2Br_2^+$	15	15[e]	1.0	
$Co(NH_3)_5Cl^{2+}$		-9[f]	-7.9[g]	-15.6[g]

[a] Ref. 4. [b] Ref. 8. [c] Ref. 18. [d] Ref. 7. [e] Ref. 19. [f] Ref. 20. [g] Ref. 1.

cients of the dihalogeno and halogenoaqua complexes differ significantly (Table 3). Daffner *et al.* followed incorrectly the aquation of *trans*-$Co(en)_2Cl_2^+$ at 301 and 530 nm and that of *trans*-$Co(en)_2Br_2^+$ at 490 and 351 nm [8]. These wavelengths are not the isosbestic point for the isomerization of the products [5, 17].

Dilatometric Results

The results are summarized in Table 4.

Discussion

The resultant volume profile is summarized in Table 5. Except for the case of *trans*-$Co(trien)Cl_2^+$, the ΔV depends in the main on the charge number (Z) on the reactant complex. The ΔV (cm^3 mol^{-1}) (Z) is approximately: $-16\,(+2) < -10\,(+1) < -7\,(0) < 2\,(-1)$. This tendency can be understood qualitatively by the change ($\Delta \bar{V}_{el}$) of the electrostriction volume ($\bar{V}_{el}$) of the complex during aquation. Assuming $\bar{V}_{el} = -2.5$ (charge number on the complex)^2 cm^3 mol^{-1} [21] $\Delta \bar{V}_{el} = -2.5\,(Z+1)^2 + 2.5\,Z^2$. $\Delta \bar{V}_{el}$ (cm^3 mol^{-1}) (Z) will be: $-12.5\,(+2) < -7.5\,(+1) < -2.5\,(0) < 2.5\,(-1)$. This order in $\Delta \bar{V}_{el}$ accords with the order in ΔV. $\Delta V = -18.6$ cm^3 mol^{-1} for aquation of *trans*-$Co(trien)Cl_2^+$ is exceptionally small. The partial molal volume ($\bar{V}$) of *trans*-$Co(trien)Cl_2^+$ will be larger by 8.6 cm^3 mol^{-1} than the $\bar{V}$ of β-$Co(trien)Cl_2^+$, because the final states of both aquations are the same. This large difference in the $\bar{V}$ of the isomers is rather exceptional. Generally isomers of Co(III) complexes have a similar value of $\bar{V}$ within ±3 cm^3 mol^{-1} [22].

The $\Delta V^{\ddagger}$s for dichlorotetraamine complexes range near zero and are more or less larger than a half of their ΔV (Table 5). The dissociative–associative character of $\Delta V^{\ddagger}$ might be clarified by comparing the $\Delta V^{\ddagger}$ of *trans*-$Co(NH_3)_4Cl_2^+$ with that of $Co(NH_3)_5Cl^{2+}$, because these two complexes contain only monodentate NH_3 and Cl^- ligands. In the case of $Co(NH_3)_5Cl^{2+}$, the $\Delta V^{\ddagger}$ is approximately a half of its ΔV and the partial molal volume of the transition state ($\bar{V}^{\ddagger}$) is close to the mean $\bar{V}$ of the initial and the final state. This situation is consistent with the Interchange mechanism, where the entering H_2O and the leaving Cl^- participate almost equally to the transition state [1]. In the case of *trans*-$Co(NH_3)_4Cl_2^+$, the $\Delta V^{\ddagger}$ is larger than a half of its ΔV and the $\bar{V}^{\ddagger}$ is slightly above the mean $\bar{V}$ of the initial and final state. The latter situation may correspond to an

Interchange mechanism, which is somewhat more dissociative than in the case of $Co(NH_3)_5Cl^{2+}$ [2]. This interpretation accords with the weak labilizing power of the nonlabile Cl^- ligand [23].

In the case of $Co(en)_2Cl_2^+$ and $Co(trien)Cl_2^+$, the $\Delta V^\ddagger$s for the *trans* isomers are slightly larger than the $\Delta V^\ddagger$s for the *cis* isomers. These *trans* isomers accompany steric change during aquation, whereas the *cis* isomers do not. Tobe has pointed out that in the aquation of the dichlorotetraaminecobaltate complex $\Delta S^\ddagger$ is positive when steric change is accompanied, whereas $\Delta S^\ddagger$ is negative when configuration is retained (Table 5) [18]. Although the observed difference in $\Delta V^\ddagger$ is small, this slightly larger $\Delta V^\ddagger$ for the aquation of the *trans* isomers with steric change parallels their positive value of $\Delta S^\ddagger$. It satisfies the formal correlation between $\Delta S^\ddagger$ and $\Delta V^\ddagger$ [24]. It seems that the configurational distortions of nonlabile ligands in the transition state cause a fairly remarkable entropy increase but only a small volume increase. In the case of *trans*-$Co(NH_3)_4Cl_2^+$, the amine ligand has no chelate. So the configurational distortion might not give rise to a volume increase. In the case of α-$Co(edda)Cl_2^-$ and α-$Co(edda)(H_2O)Cl$, the $\Delta V^\ddagger$ is slightly larger than a half of their ΔV. So these complexes may also be considered to aquate through the Interchange mechanism which is more or less dissociative. Their $\Delta V^\ddagger$ might be compared with those of *cis* isomers aquating with configuration retention. The order $\Delta V^\ddagger$ (*cis*-$Co(en)_2Cl_2^+$ or α-, β-$Co(trien)Cl_2^+$) $<$ $\Delta V^\ddagger$ (α-$Co(edda)(H_2O)Cl$) $<$ $\Delta V^\ddagger$ (α-$Co(edda)Cl_2^-$) is analogous to the order in their ΔV. It may be interpreted that charge separation occurs to a certain extent in the transition state. The $\Delta V^\ddagger$ for *trans*-$Co(en)_2Br_2^+$ is similar to that for *trans*-$Co(en)_2Cl_2^+$. Its mechanistic implication might be analogous to the latter.

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