but analysis of systems involving displacement of charged groups is invariably complicated by electrostriction terms. His interpretation of the data for $Co(NH_3)_5(OH_2)^{3+}$ ($\Delta V^{\ddagger}$ +1.2 cm^3 mol^{-1}) and $Cr(NH_3)_5(OH_2)^{3+}$ ($\Delta V^{\ddagger}$ −5.8 cm^3 mol^{-1}) in terms of a common mechanism is based on an assertion that the coordinated water is more compressed when coordinated to Co(III) than Cr(III), and the latter complex will form stronger hydrogen bonds. Compression of an aqua ligand in the first coordination sphere of a 3+ ion is significant,[23] and unlikely to vary markedly with the ion; nor do we find any great variation in $\Delta V^{\ddagger}$ with size of the neutral donor for either Cr(III) or Co(III) (Table III) with some donors clearly extending further into the solvation shell than others. In any case, a negative activation volume must be taken to imply a more compressed activation state; we can adopt the long-employed conventions and say it is more associated. Whereas steric influences of other ligands are likely to lead to a preference for dissociative (bond-breaking) processes in octahedral complexes, it is apparent that chromium(III) at least has a preference for associative (bond-making) processes, and the operation of an I_a mechanism in aquation reactions of pentaamminechromium(III) in contrast to an I_d mechanism for aquation of pentaamminecobalt(III) compounds seems to have been adequately demonstrated. The reason for this differentiation, however, still remains obscure.

Acknowledgment. G.A.L. thanks the University of Newcastle for support under an outside studies program. R.v.E. gratefully acknowledges financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. $[Cr(NH_3)_5OS(CH_3)_2]^{3+}$, 65821-31-0; $[Cr(NH_3)_5OCHNH_2]^{3+}$, 87564-86-1; $[Cr(NH_3)_5OC(NH_2)_2]^{3+}$, 87564-82-7; $[Cr(NH_3)_5OC(NHCH_3)_2]^{3+}$, 87564-84-9; $[Cr(NH_3)_5OCHN(CH_3)_2]^{3+}$, 62560-25-2; $[Cr(NH_3)_5OC(CH_3)N(CH_3)_2]^{3+}$, 97396-22-0; $[Cr(NH_3)_5OP(OCH_3)_3]^{3+}$, 97396-20-8; $[Cr(NH_3)_5(OH_2)](ClO_4)_3$, 32700-25-7; $[Cr(NH_3)_5(OS(CH_3)_2)](ClO_4)_3$, 65821-32-1; $[Cr(NH_3)_5(OCHNH_2)](CF_3SO_3)(ClO_4)_2$, 97396-24-2; $[Cr(NH_3)_5(OC(NH_2)_2)](S_2O_6)_{3/2}$, 87564-83-8; $[Cr(NH_3)_5(OCHN(CH_3)_2)](ClO_4)_3$, 62560-26-3; $[Cr(NH_3)_5(OC(CH_3)N(CH_3)_2)](ClO_4)_3$, 97396-23-1; $[Cr(NH_3)_5(OP(OCH_3)_3)](ClO_4)_3$, 97396-21-9; $OP(OCH_3)_3$, 512-56-1.

---

(23) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303.

Contribution from the Institute for Inorganic Chemistry,
University of Witten/Herdecke, 5810 Witten, Federal Republic of Germany

Volumes of Activation and Volume Profiles as Mechanistic Criteria for Base Hydrolysis Reactions of Cobalt(III) Amine Complexes

Yoichi Kitamura,[1a] Geoffrey A. Lawrance,[1b] and Rudi van Eldik*,[1c]

Received August 7, 1987

Volumes of activation ($\Delta V^{\ddagger}_{\text{exptl}}$) and reaction volumes ($\Delta \bar{V}_{\text{BH}}$) for the base hydrolysis of 16 different cobalt(III) amine complexes of the type CoL_5X^{3+}, CoL_5X^{2+}, $CoL_4X_2^{+}$, and CoL_4XY^{+} were determined from high-pressure kinetic and dilatometric measurements, respectively. The values of $\Delta V^{\ddagger}_{\text{exptl}}$ range from 43 to 19 cm^3 mol^{-1}, and those for $\Delta \bar{V}_{\text{BH}}$ range from 24 to 9 cm^3 mol^{-1}, depending on the charge on the complex as determined by that on the leaving group X. The data are very consistent with earlier reported data for closely related systems and demonstrate clearly both the minor role played by the nonparticipating ligands L, and the influence of complex charge. The reported results are all in line with a S_N1CB mechanism. However, evidence for apparent cases involving rate-limiting deprotonation rather than the usual rate-determining ligand dissociation process was not forthcoming, since no differentiation on the basis of $\Delta V^{\ddagger}_{\text{exptl}}$ was observed.

Introduction

Base hydrolysis reactions of cobalt(III) amine complexes are one of the most extensively investigated systems in inorganic reaction kinetics.[2] It is generally accepted that such reactions proceed according to a S_N1CB mechanism in which a conjugate base species dissociates in the rate-determining step to produce a 5-coordinate intermediate, which rapidly picks up a solvent molecule (H_2O) to produce the hydrolysis product. An alternative E2 mechanism was suggested[3,4] in which abstraction of an amine proton and loss of the leaving group are concerted processes; i.e., the five-coordinate intermediate is produced directly without the formation of a conjugate base precursor. Subsequent studies have once again confirmed the general validity of the S_N1CB mechanism.[5-7]

Tobe et al.[8,9] recently investigated a number of base hydrolysis reactions in which the formation and reprotonation of the conjugate base species interfere with the rate-determining dissociation of the leaving group. If we consider a general S_N1CB mechanism, as outlined in eq 1, it is usually assumed that formation of the

$$\begin{gathered}
Co(L)_5X^{(3-n)+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(L)_4(L{-}H^+)X^{(2-n)+} + H_2O \\
Co(L)_4(L{-}H^+)X^{(2-n)+} \xrightarrow{k_2} Co(L)_4(L{-}H^+)^{2+} + X^{n-} \\
Co(L)_4(L{-}H^+)^{2+} + H_2O \xrightarrow{\text{fast}} Co(L)_5OH^{2+} \qquad (1)
\end{gathered}$$

conjugate base species occurs in a fast preequilibrium, followed by the rate-determining step k_2 (L = amine, $L{-}H^+$ = deprotonated amine). Under such conditions and in the presence of an excess of OH^-, the pseudo-first-order observed rate constant can be expressed as in eq 2, where $K_1 = k_1/k_{-1}$; this reduces to the

$$\begin{aligned}
k_{\text{obsd}} &= k_2K_1[OH^-]/\{1 + K_1[OH^-]\} \\
&\approx k_2K_1[OH^-] \qquad (2)
\end{aligned}$$

simplified form when $K_1[OH^-] \ll 1$.[2] In the *trans*-Co(*RSSR*-

---

(1) (a) On leave from the Department of Chemistry, Ehime University, Matsuyama 790, Japan. (b) On leave from the Department of Chemistry, The University of Newcaste, NSW 2308, Australia. (c) To whom correspondence should be addressed at the University of Witten/Herdecke.

(2) Tobe, M. L. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 1.

(3) Hay, R. W.; Norman, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 734.

(4) Hay, R. W. *Inorg. Chim. Acta* **1980**, *45*, L83.

(5) Jackson, W. G.; Hookey, C. N.; Randall, M. L.; Comba, P.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2473.

(6) Comba, P.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1985**, 51.

(7) Sosa, M. E.; Tobe, M. L. *J. Chem. Soc., Dalton Trans.* **1985**, 475.

(8) Lichtig, J.; Sosa, M. E.; Tobe, M. L. *J. Chem. Soc., Dalton Trans.* **1984**, 581.

(9) Blakeley, C.; Tobe, M. L. *J. Chem. Soc., Dalton Trans.* **1987**, 1775 and references therein.

0020-1669/89/1328-0333$01.50/0 © 1989 American Chemical Society

Table I. Values of k_{obsd} for the Base Hydrolysis of a Series of Cobalt(III) Amine Complexes as a Function of Pressure

complex	hydrolysis product(s)	c,[a] mM	[OH⁻], mM	μ,[b] mM	t,[c] °C	λ,[d] nm	P, MPa	k_{obsd},[e] s^{-1}	$\Delta V^{\ddagger}_{\text{exptl}}$, $\text{cm}^3\ \text{mol}^{-1}$
$Co(NH_3)_5OC(Me)N(Me)_2^{3+}$	$Co(NH_3)_5OH^{2+}$	1.5	25	34	15.4	280	5	0.505	+43.2 ± 1.7
							25	0.324	
							50	0.212	
							74	0.141	
							98.5	0.098	
$Co(NH_2Me)_5Cl^{2+}$	$Co(NH_2Me)_5OH^{2+}$	1	10	13	9.5	280	4	8.06	+32.8 ± 1.7
							25.5	5.31	
							50.5	3.91	
							76	2.93	
							100	2.05	
$Co(NH_2Et)_5Cl^{2+}$	$Co(NH_2Et)_5OH^{2+}$	0.1	1	3	12.2	265	5	3.75	+31.1 ± 0.5
							25	2.88	
							50	2.11	
							75	1.53	
							100	1.07	
cis-$Co(en)_2(NH_3)Cl^{2+}$	78% *cis*-, 22% *trans*-$Co(en)_2(NH_3)OH^{2+}$[f]	2	50	56	25	290	5	0.537	+31.8 ± 0.6
							24.5	0.436	
							50.4	0.304	
							73.7	0.233	
							98.5	0.172	
cis-$Co(en)_2(NH_3)Br^{2+}$	77% *cis*-, 23% *trans*-$Co(en)_2(NH_3)OH^{2+}$[f]	2	50	56	25	305	5	3.56	+30.8 ± 1.0
							25	2.87	
							51	2.19	
							74.5	1.55	
							99	1.18	
trans-$Co(en)_2Cl_2^{+}$	95% *trans*-, 5% *cis*-$Co(en)_2(Cl)OH^{+}$[g]	1	15	16	14.5	285	5	6.52	+24.8 ± 0.5
							26.5	5.08	
							50	4.13	
							75	3.12	
							99	2.49	
		1	15	16	14.5	293	5	5.74	+23.8 ± 0.6
							26	4.90	
							50.5	3.76	
							75	2.94	
							99	2.33	
cis-$Co(en)_2Cl_2^{+}$	37% *cis*-, 63% *trans*-$Co(en)_2(Cl)OH^{+}$[g]	1	50	51	9.7	295	5	1.09	+27.9 ± 0.7
							26.4	0.807	
							50	0.625	
							76	0.472	
							101	0.352	
trans-$Co(en)_2(N_3)Cl^{+}$	77%-*trans*, 23% *cis*-$Co(en)_2(N_3)OH^{+}$[h]	0.4	50	50	15.4	350	5	0.163	+26.7 ± 0.4
							26	0.128	
							50	0.0977	
							75	0.0759	
							99	0.0586	
cis-β-$Co(trien)Cl_2^{+}$[i]	*cis*-β-$Co(trien)(Cl)OH^{+}$[j]	3.8	0.005	100	3.7	310	5	0.887	+35.7 ± 1.2
							25.5	0.813	
							50	0.760	
							74	0.652	
							99	0.621	
trans-Co(*RSSR*-cyclam)Cl_2^{+}	*trans*-Co(*RSSR*-cyclam)$(Cl)OH^{+}$[k]	0.1	1	1	9.4	264.6	4	13.4	+20.1 ± 0.9
							26	11.1	
							48.4	8.92	
							73	7.14	
							96.3	6.20	
		0.1	1	1	9.5	272.5	3.7	17.7	+17.4 ± 0.6
							23.5	15.1	
							50	12.8	
							76	10.6	
							100	8.52	
		0.1	1	3	11.9	272.5	5	40.5	+19.4 ± 0.8
							25	33.0	
							50	26.4	
							75	22.5	
							100	18.5	
cis-$Co(en)_2(NO_2)Cl^{+}$	*cis*-$Co(en)_2(NO_2)OH^{+}$	0.2	50	50	24.4	340	5	0.081	+20.8 ± 0.3
							25	0.070	
							50	0.056	
							75	0.045	
							100	0.037	
cis-$Co(tet)Cl_2^{+}$	*cis*-$Co(tet)(Cl)OH^{+}$	0.1	1	3	12.2	265	5	29.9	+23.1 ± 0.8
							25	23.9	
							50	19.5	
							75	14.6	
							100	11.9	

Table I (Continued)

complex	hydrolysis product(s)	c,[a] mM	[OH$^-$], mM	μ,[b] mM	t,[c] °C	λ,[d] nm	P, MPa	k_{obsd},[e] s^{-1}	$\Delta V^{\ddagger}_{\text{exptl}}$, cm^3 mol^{-1}
cis-Co(tet)(Cl)OH$^+$	*cis*-Co(tet)(OH)$_2^+$	0.1	1	3	12.2	265	5	0.097	+25.9 ± 2.1
							25	0.0695	
							50	0.053	
							75	0.041	
							100	0.034	
trans-RS-Co(tet)Cl$_2^+$	*trans-RS*-Co(tet)(Cl)OH$^+$ [l]	0.1	1	3	12.2	265	5	50.8	+22.1 ± 0.7
							25	41.0	
							50	33.9	
							75	25.7	
							100	21.0	
		0.2	2	6	4.7	275	5	29.9	+20.4 ± 0.7
							25	24.2	
							50	20.0	
							75	16.3	
							100	12.6	
trans-RR(*SS*)-Co(tet)Cl$_2^+$	*trans-RS*-Co(tet)(Cl)OH$^+$ [m]	0.2	2	6	5.7	275	5	15.8	+24.4 ± 1.2
							25	12.8	
							50	9.4	
							75	7.2	
							100	5.95	
trans-RS-Co(tet)(Cl)OH$^+$	*trans-RS*-Co(tet)(OH)$_2^+$ [l]	0.1	1	3	12.2	265	5	0.0142	+23.8 ± 0.9
							25	0.0109	
							50	0.0086	
							75	0.0067	
							100	0.0054	

[a] c = [complex]. [b] μ = ionic strength. [c] t = temperature. [d] λ = wavelength. [e] Mean value of more than four runs. [f] Reference 23. [g] Reference 24. [h] Reference 25. [i] Reaction performed in Tris buffer. [j] Reference 26. [k] References 26, 27. [l] Reference 28. [m] Reference 29.

cyclam)Cl$_2^+$ system studied by Tobe et al.[8] (cyclam = 1,4,8,11-tetraazacyclotetradecane) it was found that k_{-1} and k_2 are of similar magnitude at 0 °C and that $k_2 \gg k_{-1}$ above 25 °C. Under such conditions the conjugate base formation step cannot be treated as a rapid preequilibrium, and a steady-state approximation must be applied. This results in the rate law shown in eq 3, which

$$k_{\text{obsd}} = k_1k_2[\text{OH}^-]/(k_{-1} + k_2) \qquad (3)$$

reduces to $k_{\text{obsd}} = k_1[\text{OH}^-]$ for $k_2 \gg k_{-1}$; i.e., the formation of the conjugate base species becomes the rate-determining step of the mechanism. Several examples of this apparent behavior have been reported.[9]

Our general interest in base hydrolysis reactions of cobalt(III) amine complexes has led to detailed studies of the volume profiles for such processes.[10,11] We could on the basis of these measurements estimate the partial molar volume of the common 5-coordinate intermediate $\text{Co(NH}_3)_4(\text{NH}_2)^{2+}$ in the hydrolysis of a series of complexes of the type $\text{Co(NH}_3)_5\text{X}^{(3-n)+}$. In addition, the introduction of alkyl substituents on one ammine ligand created the possibility to gradually increase the size of this intermediate and to investigate the additivity property of the partial molar volumes of 5- and 6-coordinate species. The results for a total of 14 different complexes formed a very consistent picture and underlined the validity of the $\text{S}_\text{N}1\text{CB}$ mechanism.

The volumes of activation for the two limiting forms of the $\text{S}_\text{N}1\text{CB}$ mechanism as discussed above, i.e., where $k_{\text{obsd}} = K_1k_2[\text{OH}^-]$ or $k_{\text{obsd}} = k_1[\text{OH}^-]$, are expected to differ significantly. We have therefore extended our earlier studies to include additional complexes of the general type $\text{Co(L)}_5\text{X}^{(3-n)+}$ or $\text{Co(L)}_4\text{XY}^{(3-n)+}$, and to include several species for which the change in the rate-limiting step was reported.[8,9] Further, we have investigated the influence on $\Delta V^{\ddagger}$ and $\Delta \bar{V}_{\text{BH}}$ of varying the nonparticipating ligands and the precursor charge in this study. The results of this study define the mechanistic sensitivity of volumes of activation and volume profiles for such base hydrolysis processes.

Experimental Section

The cobalt(III) amine complexes used in this study were either obtained as gifts or prepared as described in the literature[12] and were identified by chemical analyses and UV–vis spectroscopy; all spectra agreed with literature data. Chemicals of analytical reagent grade and CO_2-free doubly distilled water were used throughout this study. UV–vis spectra were recorded on Perkin Elmer 555 and Shimadzu UV 250 spectrophotometers.

In the dilatometric studies a Carlsberg dilatometer with a capillary diameter of 0.0448 cm was used according to the procedures outlined before.[10,13] The temperature was controlled to ±0.001 °C. Kinetic measurements were performed on a thermostated (±0.1 °C) high-pressure stopped-flow instrument.[10] The observed rate constants were calculated over 2–3 half-lives with the aid of a fitted infinity value in order to eliminate the effect of secondary base hydrolysis and isomerization reactions.

Results

Kinetic Measurements. The pseudo-first-order hydrolysis rate constants were measured under the conditions indicated in Table I. The contribution of spontaneous aquation is negligible under the selected conditions. The values of k_{obsd} decrease significantly with increasing pressure for all the studied systems. For a general base hydrolysis reaction with second-order rate constants k_B and, at infinite dilution, $k_\text{B}°$, eq 4 can be derived where Y_C, Y_{OH}, and

$$k_{\text{obsd}} = k_\text{B}[\text{OH}^-] = k_\text{B}°[\text{OH}^-]Y_\text{c}Y_{\text{OH}}/Y_{\ddagger} \qquad (4)$$

$Y_{\ddagger}$ are the activity coefficients of the reactant complex, OH$^-$, and transition state, respectively. Plots of ln k_{obsd} versus pressure are linear within the experimental error limits for all the studied systems up to 1 kbar. For the majority of cases $\Delta V^{\ddagger}_{\text{expt}}$ was calculated by using eq 5. Only for the hydrolysis of *cis*-β-Co-

$$\Delta V^{\ddagger}_{\text{exptl}} = -RT\left(\frac{\text{d} \ln k_\text{B}°}{\text{d}p}\right)_T = -RT\left(\frac{\text{d} \ln k_{\text{obsd}}}{\text{d}p}\right)_T + RT\frac{\text{d}}{\text{d}p}\left(\ln \frac{Y_\text{C}Y_{\text{OH}}}{Y_{\ddagger}}\right)_T \qquad (5)$$

---

(10) Kitamura, Y.; van Eldik, R.; Kelm, H. *Inorg. Chem.* **1984**, *23*, 2038.

(11) van Eldik, R.; Kitamura, Y.; Piriz Mac-Coll, C. P. *Inorg. Chem.* **1986**, *25*, 4252.

(12) Shibata, M.; Uehara, A. *Shinzikkenkagakukoza*; Maruzen: Tokyo, 1977; Vol. 8-III, Chapters 12–15. Lawrance G. A.; Schneider, K. J.; van Eldik, R. *Inorg. Chem.* **1984**, *23*, 3922. Staples, P. J.; Tobe, M. L. *J. Chem. Soc.* **1960**, 4812. Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1967**, *6*, 787. Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102. Cooksey, C. J.; Tobe, M. L. *Inorg. Chem.* **1978**, *17*, 1558.

(13) Kitamura, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3453.

Table II. Dilatometrically Determined Reaction Volumes for the Base Hydrolysis of a Series of Cobalt(III) Amine Complexes at 25 °C

complex	$\Delta\bar{V}_{obsd}$, cm^3 mol^{-1}	$\Delta\bar{V}_{cor}$, cm^3 mol^{-1}	$\Delta\bar{V}_{BH}$,^{a} cm^3 mol^{-1}
$Co(NH_3)_5OC(Me)N(Me)_2^{3+}$	22.1	−1.8	23.9
$Co(NH_2Me)_5Cl^{2+}$	12.2, 12.7	0	12.5
$Co(NH_2Et)_5Cl^{2+}$	12.1^b	0	12.1
cis-$Co(en)_2(NH_3)Cl^{2+}$	9.3	0	9.3
cis-$Co(en)_2(NH_3)Br^{2+}$	10.9	0	10.9
trans-$Co(en)_2Cl_2^+$	9.3, 8.1	−0.1	8.8
trans-Co(*RSSR*-cyclam)Cl_2^+	11.1, 10.9^c	−0.1	11.1
trans-Co(*RS*-2,3,2-tet)Cl_2^+	8.6^b	−0.1	8.7
cis-Co(2,3,2-tet)Cl_2^+	14.7^b	−0.1	14.8
cis-$Co(en)_2(NO_2)Cl^+$	8.9	−0.1	9.0

$^a\Delta\bar{V}_{BH} = \Delta\bar{V}_{obsd} - \Delta\bar{V}_{cor}$. ^{b}At 10 °C. ^{c}At 20 °C.

(trien)Cl_2^+, for which a tris buffer was used, ΔV^*_{exptl} was calculated by using eq 6. The pressure dependence of Y_c, Y_{OH}, and Y_* were

$$\Delta V^*_{exptl} = -RT\left(\frac{d \ln k_{obsd}}{dp}\right) - 2.3RT\frac{d}{dp}(pOH) + RT\frac{d}{dp}\left(\ln \frac{Y_c}{Y_*}\right) \quad (6)$$

estimated using the Debye–Hückel limiting law.[14] The contribution of the last terms in eq 5 and 6 are very small indeed: between 0 and 1.4 cm^3 mol^{-1}. The term $-2.3RTd(pOH)/dp$ in eq 6, however, has a value of 26.3 cm^3 mol^{-1} when a reaction volume of 4.3 cm^3 mol^{-1} at infinite dilution and 25 °C is used for the acid dissociation of the Tris buffer[15] (Tris = tris(hydroxymethyl)aminomethane). The determined ΔV^* for *cis*-*β*-Co(trien)Cl_2^+ is anomalously high compared with other like-charged ions, but the validity of the result is impaired by necessary assumptions employed in the calculation in this one case. Direct reaction with hydroxide ion is the prefered and generally employed method.

Dilatometric Measurements. Throughout these measurements a 15 cm^3 10 mM complex solution was mixed with a 3 cm^3 50 mM NaOH solution at 25 °C. For the complexes $Co(NH_3)_5OC(Me)N(Me)_2^{3+}$, *cis*-$Co(en)_2(NH_3)Cl^{2+}$, and *cis*-$Co(en)_2(NH_3)Br^{2+}$, the change in volume was measured 15 min after mixing, at which point the hydrolysis reaction had gone to completion. In the case of the $Co(NH_2Me)_5Cl^{2+}$ complex, the meniscus height was recorded 2–4 min after mixing, since subsequent precipitation interferes at longer times. For *cis*-$Co(en)_2(NO_2)Cl^+$ the movement of the meniscus was followed for 47 min after mixing during which the base hydrolysis proceeded to 97% completion. The progress of aquation (21.6%) during the time (28 min) from dissolution of the complex to mixing with base was taken into account by using a $\Delta\bar{V}$ for the neutralization of *cis*-$Co(en)_2(NO_2)H_2O^{2+}$ of 18.9 cm^3 mol^{-1}.[18] For *trans*-$Co(en)_2Cl^{2+}$ and *trans*-Co(*RSSR*-cyclam)Cl_2^+, the volume increase on mixing is followed by a slow decrease in volume, which corresponds to the hydrolysis of the second chloride ligand. The results for the hydrolysis of the $Co(NH_2Me)_5Cl^{2+}$ and *trans*-$Co(en)_2Cl_2^+$ complexes were corrected for a small contribution resulting from spontaneous aquation. A further correction was introduced throughout the series of complexes to account for the change in ionic strength during mixing, in the way described before.[10] The dilatometric results are summarized in Table II.

Discussion

On the basis of our previous experience with base hydrolysis reactions of cobalt(III) amine complexes,[10,11] the reaction volume profile for the S_N1CB mechanism outlined in eq 1 can be presented schematically as in Figure 1. The experimental results in Tables I and II underline the general validity of this volume profile. ΔV^*_{exptl} and $\Delta\bar{V}_{BH}$ are positive for all the studied systems, and both exhibit a significant dependence on the nature, especially the charge, of the precursor complex and the leaving group, i.e., the change in electrostriction during the reaction.[10,11] The large volume collapse from the transition to the product state, i.e., $\Delta V^*_{exptl} - \Delta\bar{V}_{BH}$, is mainly due to the binding of a water molecule[10,11] during the final step of the process (see eq 1). The large, positive value of ΔV^*_{exptl} can be ascribed to the sum of two components, $\Delta V^*_{exptl} = \Delta\bar{V}(K_1) + \Delta V^*(k_2)$, both of which are positive due to charge neutralization and the release of a solvent molecule in the former case and ligand dissociation in the latter case.

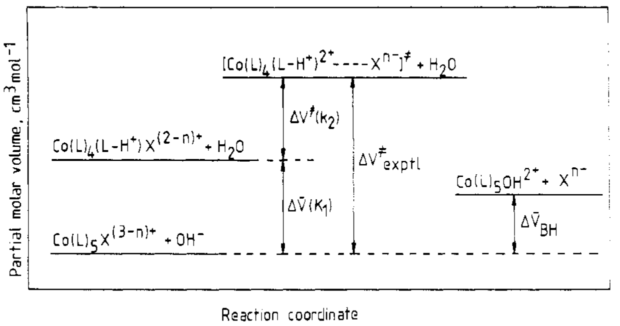

Figure 1. Volume profile for the base hydrolysis mechanism outlined in eq 1.

The results for the systems investigated in this study are all in line with the general concepts of the S_N1CB mechanism and the results reported before.[10,11] This becomes obvious from an overall comparison of all the available data for the base hydrolysis of different cobalt(III) amine complexes given in Table III. For instance, the results for $Co(NH_2R)_5Cl^{2+}$ (R = Me or Et) and *cis*-$Co(en)_2(NH_3)Cl^{2+}$ are in close agreement with those for $Co(NH_3)_5Cl^{2+}$ and the series of $Co(NH_3)_4(NH_2X)Cl^{2+}$ species (see Table III) and clearly show the minor influence of the nonleaving groups. The formation of different isomers as hydrolysis products in some cases does not affect the treatment of the data since the partial molar volumes of such isomers are indeed very similar.[16] It follows in general that the nature and size of the nonparticipating (spectator) ligands play a minor role in depicting the intimate nature of the hydrolysis mechanism as revealed by the parameters.[17] Averaged ΔV^*_{exptl} values for 3+ ions (42 cm^3 mol^{-1}), 2+ ions (30 cm^3 mol^{-1}), and 1+ ions (24 cm^3 mol^{-1}) follow a modest trend with precursor charge. Notable is the observation that the data range for complexes of the type $CoL_4X_2^+$ (19.4–27.9 cm^3 mol^{-1}) is lower than that for the CoL_5X^{2+} species (26.4–33.0 cm^3 mol^{-1}), but rather surprisingly not well separated. By comparison, ΔV^* for the highest CoL_5X^{2+} species is over 7 cm^3 mol^{-1} lower than values for CoL_5X^{3+} species. A closer analysis of the data reveals the reason for this behavior.

As mentioned before, the absolute values of ΔV^*_{exptl} and $\Delta\bar{V}_{BH}$ strongly depend on the changes in electrostriction during the reaction. The systems in Table III can be subdivided into four groups of reactions based on the overall change in charge of the system as determined by the ionic nature of the precursor complex and the hydroxide group and the product complex and the leaving group. The different volume parameters in Figure 1 were averaged for each of these groups and may be summarized as a function of ΔZ^2, i.e., the change in charge during the reaction. Such data are subjected to large error limits in cases where only a few data points are available. Nevertheless, the results clearly demonstrate the decrease in the volume parameter with increasing ΔZ^2, i.e., with increasing electrosctriction.[17] These trends are presented schematically in Figure 2 and agree with the correlation found for a series of neutralization reactions[18] and our general understanding of electrostriction effects.[17] Furthermore, these correlations enable us to understand the similarity in particularly $\Delta\bar{V}_{BH}$ for the CoL_5X^{2+} and $CoL_4X_2^+$ systems since ΔZ^2 has the same value (zero) for both systems. Since $\Delta\bar{V}_{BH}$ and ΔZ^2 both relate

---

(14) Hamann, S. D. *J. Chem. Soc. Faraday Trans. 1* **1984**, *80*, 2541.

(15) Kitamura, Y.; Itoh, T. *J. Solution Chem.* **1987**, *16*, 715.

(16) Kitamura, Y.; Takamoto, T.; Yoshitani, K. *Inorg. Chem.* **1988**, *27*, 1382.

(17) van Eldik, R. In *Inorganic High Pressure Chemistry: Kinetics and Mechanisms*; van Eldik, R., Ed.; Elsevier: Amsterdam, 1986; Chapter 1.

(18) Kitamura, Y.; van Eldik, R. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 418.

Table III. Summary of Activation and Reaction Volume Data for the Base Hydrolysis of a Series of Cobalt(III) Amine Complexes[a]

complex	$\Delta V^{\ddagger}_{\mathrm{exptl}}$, cm^3 mol^{-1}	$\Delta \bar{V}_{\mathrm{BH}}$,[b] cm^3 mol^{-1}	$\Delta V^{\ddagger}_{\mathrm{exptl}} - \Delta \bar{V}_{\mathrm{BH}}$, cm^3 mol^{-1}	$\Delta \bar{V}(K_1)$,[c] cm^3 mol^{-1}	$\Delta V^{\ddagger}(k_2)$,[d] cm^3 mol^{-1}	ref
$Co(NH_3)_5Me_2SO^{3+}$	40.2 ± 0.5	21.2	19.0	27	13.2	10
$Co(NH_3)_5OC(Me)N(Me)_2^{3+}$	43.2 ± 1.7	23.9	19.3	27	16.2	*e*
$Co(NH_3)_5F^{2+}$	26.4 ± 1.0	7.4	19.0	22	4.4	10
$Co(NH_3)_5Cl^{2+}$	33.0 ± 0.8	9.9	23.1	22	11.0	10
$Co(NH_3)_5Br^{2+}$	32.5 ± 1.4	11.1	21.4	22	10.5	10
$Co(NH_3)_5I^{2+}$	33.6 ± 1.0	15.5	18.1	22	11.6	10
$Co(NH_3)_5NO_3^{2+}$	31.0 ± 0.8	13.2	17.8	22	9.0	10
$Co(NH_3)_4(NH_2X)Cl^{2+}$						
X: cis, Me	29.4 ± 0.4	9.8	19.6	22	7.4	11
trans, Me	28.6 ± 1.3	10.4	18.2	22	6.6	11
trans, Et	28.3 ± 1.4	10.1	18.2	22	6.3	11
cis, *n*-Pr	26.4 ± 1.5	11.4	15.0	22	4.4	11
trans, *n*-Pr	29.9 ± 1.2			22	7.9	11
trans, *n*-Bu	28.7 ± 0.7	11.9	16.8	22	6.7	11
trans, *i*-Bu	28.5 ± 1.2	12.0	16.5	22	6.5	11
$Co(NH_2Me)_5Cl^{2+}$	32.8 ± 1.7	12.5	20.3	22	10.8	*e*
$Co(NH_2Et)_5Cl^{2+}$	31.1 ± 0.5	12.1	19.0	22	9.1	*e*
cis-$Co(en)_2(NH_3)Cl^{2+}$	31.8 ± 0.6	9.3	22.5	22	9.8	*e*
cis-$Co(en)_2(NH_3)Br^{2+}$	30.8 ± 1.0	10.9	19.9	22	8.8	*e*
cis-$Co(en)_2Cl_2^{+}$	27.9 ± 0.7			17	10.9	*e*
trans-$Co(en)_2Cl_2^{+}$	24.3 ± 0.5	8.8	15.5	17	7.3	*e*
cis-β-$Co(trien)Cl_2^{+}$	35.7 ± 1.2			17	18.7	*e*
trans-Co(*RSSR*-cyclam)Cl_2^{+}	18.8 ± 1.3	11.1	7.7	17	1.8	*e*
trans-$Co(en)_2(N_3)Cl^{+}$	26.7 ± 0.4			17	9.7	*e*
cis-$Co(en)_2(NO_2)Cl^{+}$	20.8 ± 0.3	9.0	11.8	17	3.8	*e*
cis-$Co(tet)Cl_2^{+}$	23.1 ± 0.8	14.8	8.3	17	6.1	*e*
cis-$Co(tet)(OH)Cl^{+}$	25.9 ± 2.1			17	8.9	*e*
trans-RS-$Co(tet)Cl_2^{+}$	21.3 ± 0.9	8.7	12.6	17	4.3	*e*
trans-RR(*SS*)-$Co(tet)Cl_2^{+}$	24.4 ± 1.2			17	7.4	*e*
trans-RS-$Co(tet)(OH)Cl^{+}$	23.8 ± 0.9			17	6.8	*e*
$Co(NH_3)_5SO_4^{+}$	22.2 ± 0.7	−3.9	26.1	17	5.2	10

[a] For experimental conditions see original work. tet = 1,9-diamine-3,7-diazanonane; en = 1,2-diaminoethane; trien = 1,8-diamino-3,6-diazaoctane; cyclam = 1,4,8,11-tetraazacyclotetradecane. [b] Determined dilatometrically for overall base hydrolysis (BH). [c] Calculated from the expression[18] $\Delta \bar{V}(K_1) = 14.5 - 2.5\Delta Z^2$, where $\Delta Z^2 = (Z-1)^2 - Z^2 = 1 - 2Z$. [d] $\Delta V^{\ddagger}(k_2) = \Delta V^{\ddagger}_{\mathrm{exptl}} - \Delta \bar{V}(K_1)$. [e] This work.

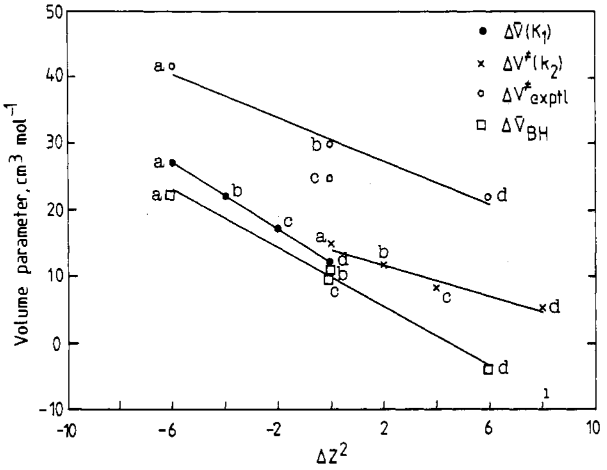

Figure 2. Plot of volume parameter versus ΔZ^2. The letters a, b, and c refer to averaged data for 3+, 2+, and 1+ complexes with neutral (a) or 1− leaving groups (b, c), whereas d refers to a 1+ complex with a 2− leaving group.

to the overall reaction, the similarity for 2+ and 1+ ions is anticipated to be greater than in the case of $\Delta V^{\ddagger}_{\mathrm{exptl}}$, where different electrostriction effects will operate in the transition state. This is seen in the greater average variation between $\Delta V^{\ddagger}_{\mathrm{exptl}}$ for the two systems compared with $\Delta \bar{V}_{\mathrm{BH}}$ data in Figure 2. In addition, with the help of a predicted value for $\Delta \bar{V}(K_1)$,[18] the trends in $\Delta V^{\ddagger}(k_2)$ can be interpreted in a similar way (see Figure 2).

It is very encouraging to see that the volume data for so many different systems can be treated in a systematic way. The volume collapse ($\Delta V^{\ddagger}_{\mathrm{exptl}} - \Delta \bar{V}_{\mathrm{BH}}$) has in many cases a value of ca. 20 cm^3 mol^{-1}. This means that the partial molar volume of the 5-coordinate transition state species, viz. $Co(L)_4(L-H^+)^{2+}$, is very similar to that of the 6-coordinate hydrolysis product.[10,11] Furthermore, this volume collapse can be ascribed to the ionization of water (accompanied by a volume decrease of 22 cm^3 mol^{-1} [18]) in order for it to bind as H^+ and OH^- in the final product. In this respect we notice that the data for the cyclam complex does not fit the reported trends well, although $\Delta V^{\ddagger}_{\mathrm{exptl}}$ is not markedly smaller than the average value found for the other $CoL_4X_2^+$ species. The value of $\Delta \bar{V}_{\mathrm{BH}}$ for the cyclam complex is apparently normal, indicating that the observed deviation in $\Delta V^{\ddagger} - \Delta \bar{V}_{\mathrm{BH}}$ has its basis in the kinetics. This deviation is an indication for a possible change in rate-determining step within the concept of the S_N1CB mechanism.

As mentioned in the Introduction, Tobe et al.[8] have reported that the rate law in eq 3 applies to the cyclam system. In the case where k_{-1} and k_2 are of similar magnitude, the pressure dependence of k_1, k_{-1}, and k_2 must be taken into account in the interpretation of $\Delta V^{\ddagger}_{\mathrm{exptl}}$. Tobe et al.[8] reported a value of 0.79 for k_2/k_{-1} at 0 °C and of ca. 8 at 25 °C. For our measurements at 9.4 °C, we assumed k_2/k_{-1} to be ca. 4. Under such conditions, $k_{-1} + k_2 \approx k_2$ and eq 3 reduces to $k_{\mathrm{obsd}} = k_1[OH^-]$, such that $\Delta V^{\ddagger}_{\mathrm{exptl}} \approx \Delta V^{\ddagger}(k_1)$. A changeover in the rate-determining step may account for the smaller value found for $\Delta V^{\ddagger}_{\mathrm{exptl}}$, viz. ca. 19 cm^3 mol^{-1}. This value is close to that expected for $\Delta \bar{V}(K_1)$, viz. 17 cm^3 mol^{-1}, indicating that $\Delta V^{\ddagger}(k_{-1}) \ll \Delta V^{\ddagger}(k_1)$ and is close to zero. We are not aware of any direct measurement to underline this latter conclusion, but it seems to be in good agreement with a recently reported value of −4.7 cm^3 mol^{-1} for the reaction of a water molecule with $Co(en)_2(hfac)^{2+}$ to produce $Co(en)_2(hfac{\cdot}OH)^+$ and a proton.[19] However, $\Delta V^{\ddagger}_{\mathrm{exptl}}$ for the cyclam system at a higher temperature (11.9 °C), where k_2/k_{-1} would be expected to change and influence the determination somewhat, was not different. This could indicate that $\Delta V^{\ddagger}_{\mathrm{exptl}}$ is not a sensitive indicator of a change in rate-determining step in the present system, although it was previously predicted that a changeover in the rate-determining step from k_2 to k_1 should be accompanied by a significant decrease in $\Delta V^{\ddagger}_{\mathrm{exptl}}$.[11] It is notable that like-charged complex ions such

---

(19) Kitamura, Y.; van Eldik, R. *Inorg. Chem.* **1987**, *26*, 2907.

as *cis*-$Co(en)_2(NO_2)Cl^+$ exhibit low $\Delta V^{\ddagger}_{\text{exptl}}$ like *trans*-Co(cyclam)Cl_2^+, yet rate-determining deprotonation does not appear to apply in the former case. The validity of $\Delta V^{\ddagger}_{\text{exptl}}$ as an indicator of a change in rate-determining step during base hydrolysis was probed further by studying the *trans*-dichloro complexes of 1,9-diamino-3,7-diazanonane with *RS* or *RR*(*SS*) geometry, where rate-limiting deprotonation has been suggested.[9] We find that $\Delta V^{\ddagger}_{\text{exptl}}$ does not change significantly with temperature, nor do the values differ notably from values for other 1+ systems with chloride as the leaving group. Despite expectations of a clearly smaller $\Delta V^{\ddagger}_{\text{exptl}}$ when rate-limiting deprotonation apparently operates,[11] the experimental data do not underline this. This either indicates that $\Delta V^{\ddagger}_{\text{exptl}}$ is insensitive to a change in rate-determining step in such base hydrolysis reactions or that a common mechanism, in which dissociation of the conjugate species is rate-determining, operates in all cases. We expect that $\Delta V^{\ddagger}$ for conjugate base formation should be smaller than $\Delta\bar{V}(K_1)$. This process involves the neutralization of charge and the production of a water molecule, which will both be accompanied by volume increases. Similarly, the reverse process involves the disappearance of a water molecule and the creation of charge, such that a decrease in volume is expected for both contributions. It follows that the transition state of this process should be located between that of the reactant and product (conjugate base) species. On the basis of these arguments $\Delta V^{\ddagger}$ for conjugate base formation as rate-determining step should be significantly smaller than $\Delta\bar{V}(K_1)$, i.e., ca. 17 $cm^3\ mol^{-1}$. Since $\Delta V^{\ddagger}_{\text{exptl}}$ is at least as large as $\Delta\bar{V}(K_1)$ in all the studied systems, we are forced to believe on the basis of the reported data that conjugate base formation cannot be the rate-determining step. This conclusion contradicts earlier arguments in favor of such a rate-limiting process[9] and deserves further thought.

What does appear to hold is that those systems of like charge that exhibit little isomerization during base hydrolysis, such as *trans*-Co(cyclam)Cl_2^+ and *cis*-$Co(en)_2(NO_2)Cl^+$, exhibit slightly lower $\Delta V^{\ddagger}_{\text{exptl}}$ values than systems such as *trans*-$Co(en)_2(N_3)Cl^+$ and the $Co(en)_2Cl_2^+$ compounds where mixtures of isomers result. This may imply a greater degree of ligand rearrangement in forming the transition state in the latter case, with concomitant greater disturbance of the electrostricted solvation sheath. Such effects, if they operate, may also act to mask the anticipated differences from a change in rate-determining step, since the compounds studied here that should exhibit rate-determining deprotonation do not usually isomerize during the first hydrolysis.

The results of this investigation do demonstrate how activation volume data can be treated in a rather systematic manner. This is rare for an activation parameter associated with structural and solvational changes. Similar conclusions were reached for an extended series of activation volume data for the aquation of $Co(NH_3)_5L^{3+}$, $Cr(NH_3)_5L^{3+}$, and $Co(N)_4XY^{n+}$,[20-22] further demonstrating the validity of this statement.

Acknowledgment. We thank Prof. M. L. Tobe for providing unpublished results and Dr. D. A. Palmer for some of the samples used in this investigation. Y.K. wishes to thank the Department of Education of Japan for a research fellowship enabling him to work at the University of Frankfurt. G.A.L. thanks the University of Newcastle for support under an outside studies program. R.v.E. gratefully acknowledges financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. $Co(NH_3)_5OC(Me)N(Me)_2^{3+}$, 45020-86-8; $Co(NH_2Me)_5Cl^{2+}$, 30051-70-8; $Co(NH_2Et)_5Cl^{2+}$, 32424-81-0; *cis*-$Co(en)_2(NH_3)Cl^{2+}$, 15392-82-2; *cis*-$Co(en)_2(NH_3)Br^{2+}$, 21563-61-1; *trans*-$Co(en)_2Cl_2^+$, 14403-91-9; *cis*-$Co(en)_2Cl_2^+$, 14875-15-1; *trans*-$Co(en)_2(N_3)Cl^+$, 20487-55-2; *cis*-*β*-Co(trien)Cl_2^+, 33865-59-7; *trans*-Co((*RSSR*)-cyclam)Cl_2^+, 118101-01-2; *cis*-$Co(en)_2(NO_2)_2Cl^+$, 16884-74-5; *cis*-Co(tet)Cl_2^+, 118101-02-3; *cis*-Co(tet)(Cl)OH^+, 118017-97-3; *trans*-*RS*-Co(tet)Cl_2^+, 46239-28-5; *trans*-*RR*(*SS*)-Co(tet)Cl_2^+, 46239-27-4; *trans*-*RS*-Co(tet)(Cl)OH^+, 118101-03-4.

---

(20) Lawrance, G. A. *Inorg. Chem.* **1982**, *21*, 3687.

(21) Lawrance, G. A.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1987**, 1105.

(22) Kitamura, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3625.

(23) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 6654.

(24) Chan, S. C.; Tobe, M. L. *J. Chem. Soc.* **1962**, 4531.

(25) Jackson, W. G.; Begbie, C. M. *Inorg. Chem.* **1984**, *23*, 659.

(26) Tobe, M. L. *Acc. Chem. Res.* **1970**, *3*, 377.

(27) Lichtig, J.; Tobe, M. L. *Inorg. Chem.* **1978**, *17*, 2442.

(28) Marangoni, G.; Panayotou, M.; Tobe, M. L. *J. Chem. Soc., Dalton Trans.* **1973**, 1989.

(29) Ahmed. E.; Tobe, M. L. *Inorg. Chem.* **1974**, *13*, 2956.