

exchange studies of $\text{Ni}(\text{CO})_4$, in which it may be presumed the observed first-order rate constant involves Ni-CO bond fission to afford $[\text{Ni}(\text{CO})_3]$, the observed entropy of activation is positive,²¹ although those reactions are some 6 orders of magnitude slower than are those reported here.

In contrast, the insensitivity of the rates of reaction of coordinatively unsaturated group VIB metal carbonyls and derivatives to the steric and electronic nature of L, together with evidence which indicates that those reactions take place at rates which approach that of diffusion control,²² have been interpreted as indicating that the coordinatively unsaturated intermediate is geometrically little changed from its coordinatively saturated counterpart. Indeed, the gas-phase IR spectrum of $[\text{Cr}(\text{CO})_5]$ is consistent with this conclusion.²³ It will be of interest to determine volumes of activation corresponding to the rate constants determined in the present study through flash photolysis investigations at various pressures²⁴ to ascertain if there is a correspondence in the entropy of activation and volume of activation

data in these systems and if the latter may be correlated with changes in molecular geometry accompanying coordination of L' to $[\text{Co}(\text{CO})_2\text{NO}]$ and dissociation of THF from $[\text{Co}(\text{CO})_2(\text{THF})\text{NO}]$.

Conclusion

The kinetics results reported here for displacement of the weak nucleophile THF from $\text{Co}(\text{CO})_2(\text{THF})\text{NO}$ by a variety of Lewis bases indicate that the dissociative pathway is significantly more important than for analogous reactions of $\text{Co}(\text{CO})_3\text{NO}$. It is reasonable to presume that the displacement of other weak nucleophiles such as N_2 ,⁷ 1-butene,⁸ H_2 ,⁹ and 1,3-butadiene from their cobalt dicarbonyl nitrosyl complexes, of great current interest, will be mechanistically similar.

Acknowledgment. The support of this research by the National Science Foundation under Grants CHE-84 15153 and CHE-88 00127 is gratefully acknowledged.

Registry No. 2 (L = PPh_3), 118141-73-4; 2 (L = CO), 118141-74-5; 2 (L = $\text{P}(\text{O}i\text{Pr})_3$), 118141-75-6; THF, 109-99-9; $\text{Co}(\text{CO})_3\text{NO}$, 14096-82-3; $\text{Co}(\text{CO})_2(\text{PPh}_3)\text{NO}$, 13681-96-4; $\text{Co}(\text{CO})_2(\text{P}(\text{O}i\text{Pr})_3)\text{NO}$, 14406-76-9; $\text{Co}(\text{CO})_2(\text{P}(\text{O}-i\text{Pr})_3)\text{NO}$, 21494-34-8; $\text{Co}(\text{CO})(\text{P}(\text{O}-i\text{Pr})_3)_2\text{NO}$, 22597-80-4; $\text{Co}(\text{CO})(\text{P}(\text{O}-i\text{Pr})_3)(\text{P}(\text{O}i\text{Pr})_3)\text{NO}$, 118169-83-8; $\text{Co}(\text{CO})(\text{P}(\text{O}-i\text{Pr})_3)(\text{PPh}_3)\text{NO}$, 118141-76-7; $\text{P}(\text{O}-i\text{Pr})_3$, 116-17-6; $\text{P}(\text{O}i\text{Pr})_3$, 101-02-0; $\text{P}(\text{O}i\text{Pr})_3$, 102-85-2; AsPh_3 , 603-32-7; PPh_3 , 603-35-0; 1-hexene, 592-41-6.

Supplementary Material Available: A listing of rate constants for reactions taking place after flash photolysis of cobalt carbonyl complexes in THF and THF/cyclohexane solutions at various temperatures (Appendix) (6 pages). Ordering information is given on any current masthead page.

- (22) (a) Welch, J. A.; Peters, K. S.; Vaida, V. *J. Phys. Chem.* **1982**, *86*, 1941. (b) Simon, J. D.; Peters, K. S. *Chem. Phys. Lett.* **1983**, *98*, 53. (c) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6715. (d) Langford, C. H.; Moralejo, C.; Sharma, D. K. *Inorg. Chim. Acta* **1987**, *126*, L11. (e) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1987**, *91*, 5538.
 (23) For a review of gas-phase IR spectrophotometry of coordinative unsaturated metal carbonyl transients, see: Weitz, E. *J. Phys. Chem.* **1987**, *91*, 3945.
 (24) For a study of the determination of volumes of activation for kinetically labile organometallics produced in solution via flash photolysis, see: Awad, H. H.; Dobson, G. R.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1987**, 1839.

Contribution from the Weapons Systems Research Laboratory, Defence Research Centre Salisbury, Adelaide, South Australia 5001, Australia, Department of Chemistry, The University of Newcastle, Newcastle, NSW 2308, Australia, and Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, Federal Republic of Germany

Activation Volumes for Aquation of Chromium(III) Pentaammine Complexes with Neutral Leaving Groups: Comparison with and Mechanistic Differentiation from Cobalt(III) Analogues

Neville J. Curtis,¹ Geoffrey A. Lawrance,^{*2} and Rudi van Eldik^{*3}

Received March 14, 1988

The pressure dependence of the spontaneous aquation of a series of $\text{Cr}(\text{NH}_3)_5\text{L}^{3+}$ complexes with L = formamide, dimethylformamide, urea, *N,N'*-dimethylurea, dimethyl sulfoxide, trimethyl phosphate, and *N,N'*-dimethylacetamide has been determined. The temperature dependence of aquation of the series has also been determined. The activation volume (ΔV^\ddagger) lies in the limited range -3.2 to -8.7 $\text{cm}^3 \text{mol}^{-1}$ and is not related clearly to leaving group size. An approximate correlation between ΔV^\ddagger and activation entropy (ΔS^\ddagger) exists. The average ΔV^\ddagger of ~ -6 $\text{cm}^3 \text{mol}^{-1}$ is an estimate of the solvent-independent intrinsic component of ΔV^\ddagger for reaction of a chromium(III) complex and is interpreted as being indicative of an associative interchange (I_a) mechanism, contrasting with an average ΔV^\ddagger of $\sim +2$ $\text{cm}^3 \text{mol}^{-1}$ in the analogous cobalt(III) series where a dissociative interchange (I_d) mechanism apparently applies. Apparent molar volumes of the series of complexes were determined. The "volume profile" approach applied earlier to the cobalt(III) series yields in the case of the chromium(III) series a different result that supports a mechanistic differentiation between chromium(III) and cobalt(III).

Introduction

Extensive studies of the aquation reactions of pentaammine complexes of cobalt(III) and chromium(III) have appeared over recent decades.⁴⁻⁷ The generally held view from these studies is that reactions in each system are mechanistically distinct, with a dissociative type reaction favored for cobalt(III) and an associative type reaction favored for chromium(III). A limiting

mechanism in either case is not likely, the reactions being distinguished by differing degrees of bond making and bond breaking in the transition state involving the entering and leaving groups. Determinations of activation volumes (ΔV^\ddagger) for a range of complexes, mainly with ionic leaving groups, have been reported over the past 2 decades and have largely been interpreted in terms of these disparate mechanisms.⁸⁻¹⁵

(1) Defence Research Centre Salisbury.

(2) The University of Newcastle.

(3) University of Witten/Herdecke.

(4) *Inorg. React. Mech.* **1971-1980**, 1-7.

(5) Wilkins, R. G. *The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes*; Allyn and Bacon: Boston, MA, 1974.

(6) Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974**, *11*, 47.

(7) Swaddle, T. W. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 95.

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

(9) Jones, W. E.; Carey, L. R.; Swaddle, T. W. *Can. J. Chem.* **1972**, *50*, 2739.

(10) Guastalla, G.; Swaddle, T. W. *Can. J. Chem.* **1973**, *51*, 821.

(11) Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642.

(12) Swaddle, T. W.; Stranks, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 8357.

(13) Lawrance, G. A.; Schneider, K.; van Eldik, R. *Inorg. Chem.* **1984**, *23*, 3922.

(14) Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1977**, *16*, 3139.

Where charged leaving groups were involved, observed activation volumes in all cases were negative, apparently as a consequence of solvent electrostriction changes in forming the transition state contributing significantly to ΔV^\ddagger . This made definition of the mechanistically significant intrinsic component of ΔV^\ddagger difficult and limited the usefulness of the determinations. We recently investigated the aquation reactions of methyl-substituted ammine complexes of cobalt(III) and chromium(III),¹³ and concluded that the importance of bond-making and bond-breaking processes in these systems may change significantly from the pentaammine to the pentakis(methylamine) complex. In this respect, Lay pointed out¹⁶ that both the cobalt(III) and chromium(III) complexes in the latter case may follow an I_d mechanism due to the shortening of the Cr-Cl bond in going from the amine to the methylamine complex, which also accounts for the decrease in reactivity. However, in a preliminary communication,¹⁷ we pointed out that such an assignment is subjected to uncertainties due to the fact that the leaving group was a charged species, which complicates the mechanistic interpretation of observed ΔV^\ddagger values. When neutral leaving groups are involved, electrostriction is not significant, and the determined ΔV^\ddagger then defines the intrinsic volume change at the reaction site more clearly, as demonstrated recently for a series of $\text{Co}(\text{NH}_3)_5\text{L}^{3+}$ complexes.¹⁸

At least for water exchange, the determined ΔV^\ddagger values for $\text{Co}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ of $+1.2 \text{ cm}^3 \text{ mol}^{-1}$ and for $\text{Cr}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ of $-5.8 \text{ cm}^3 \text{ mol}^{-1}$ differ significantly and imply a mechanistic differentiation. As part of a continuing research program on the effect of both leaving and nonleaving groups on the observed activation volume, we have extended the strictly limited comparative data for simple pentaammine systems by investigating a series of pentaamminechromium(III) complexes with neutral leaving groups. Activation parameters and apparent molar volumes for both chromium(III) and cobalt(III) systems have been employed to define mechanistic variations.

Experimental Section

Syntheses. The precursor complex $[\text{Cr}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$ was prepared as previously described.¹⁹ The series of pentaammine complexes with formamide, dimethylformamide, urea, *N,N'*-dimethylurea, dimethyl sulfoxide, trimethyl phosphate and *N,N*-dimethylacetamide coordinated were prepared as described previously from the precursor complex.²⁰ All complexes were characterized satisfactorily by microanalysis and infrared and electronic spectroscopies.

Physical Methods. The rates of spontaneous aquation of complexes were followed at a wavelength between 490 and 540 nm with a Varian 635 spectrophotometer or a Zeiss PMQ II spectrophotometer incorporating a thermostated ($\pm 0.1^\circ\text{C}$) high-pressure spectrophotometer cell with sapphire windows. Reactions were followed for at least 3 half-lives in 0.01 M HClO_4 at a wavelength between 490 and 540 nm. Samples were subjected to pressures up to 1725 bar. Rate constants were determined by standard least-squares techniques using the Guggenheim or exponential curve-fitting techniques, while activation volumes were determined from $\log k_{\text{obsd}}$ versus P data as previously described.¹³ Temperature-dependent data, collected by using a standard thermostated cell and a Hitachi 220A spectrophotometer, permitted the determination of activation enthalpy and entropy from $\log k$ versus $1/T$ in the usual manner.

Density measurements were performed by using an Anton Paar DMA02 digital density meter thermostated at $25 (\pm 0.003)^\circ\text{C}$. Triply distilled water and specially cleaned glassware were employed. Densities were measured at a range of concentrations of complex, and apparent molar volumes (ϕ_i) were calculated from eq 1, where d_0 and d_s are the

$$\phi_i = M/d_0 - [1000(d_s - d_0)]/c_s d_0 \quad (1)$$

densities of the solvent and solution, c_s is the molar concentration, and M is the molecular weight of the complex.

Table I. Pressure Dependence of the Rate Constants for Aquation of $\text{Cr}(\text{NH}_3)_5\text{L}^{3+}$ Ions in 0.01 M HClO_4 ^d

P , bar	$10^4 k_p$, s ⁻¹	P , bar	$10^4 k_p$, s ⁻¹
L = OS(CH ₃) ₂ ^a			
50	1.87 ± 0.06	1000	2.11 ± 0.07
500	1.98 ± 0.03		
L = OCHNH ₂ ^a			
50	5.41 ± 0.24	1000	6.33 ± 0.06
500	5.91 ± 0.15	1500	7.12 ± 0.22
L = OC(NH ₂) ₂ ^b			
1	4.37 ± 0.11	1035	5.80 ± 0.20
345	4.80 ± 0.15	1380	6.70 ± 0.16
690	5.43 ± 0.08		
L = OC(NHCH ₃) ₂ ^c			
1	1.90 ± 0.03	1380	2.31 ± 0.05
690	2.08 ± 0.03	1725	2.42 ± 0.04
L = OCHN(CH ₃) ₂ ^a			
50	1.44 ± 0.03	1000	1.88 ± 0.03
500	1.64 ± 0.08		
L = OC(CH ₃)N(CH ₃) ₂ ^a			
50	1.73 ± 0.02	1000	2.17 ± 0.16
500	1.95 ± 0.08		
L = OP(OCH ₃) ₃ ^a			
50	4.39 ± 0.18	1000	6.03 ± 0.35
500	5.12 ± 0.17		

^a 45.0 °C. ^b 50.9 °C. ^c 48.7 °C. ^d All values are the average of at least three independent runs.

Table II. Temperature Dependence of the Rate Constants for Aquation of $\text{Cr}(\text{NH}_3)_5\text{L}^{3+}$ Ions in 0.01 M HClO_4 ^a

temp, °C	$10^4 k_T$, s ⁻¹	temp, °C	$10^4 k_T$, s ⁻¹
L = OS(CH ₃) ₂			
36.5	0.82 ± 0.03	48.8	3.51 ± 0.08
42.5	1.73 ± 0.05	54.1	6.49 ± 0.15
L = OCHNH ₂			
27.3	0.68 ± 0.01	43.6	5.13 ± 0.11
34.0	1.57 ± 0.03	49.9	10.05 ± 0.2
L = OC(NH ₂) ₂			
37.0	0.89 ± 0.02	50.8	4.37 ± 0.11
44.5	2.08 ± 0.05	55.1	6.86 ± 0.20
L = OC(NHCH ₃) ₂			
35.7	0.40 ± 0.01	48.7	1.90 ± 0.03
41.3	0.81 ± 0.02	56.1	4.52 ± 0.10
L = OCHN(CH ₃) ₂			
30.8	0.30 ± 0.01	43.3	1.40 ± 0.03
36.3	0.61 ± 0.01	51.4	3.27 ± 0.07
L = OC(CH ₃)N(CH ₃) ₂			
32.0	0.43 ± 0.01	44.9	1.85 ± 0.03
38.5	0.94 ± 0.02	52.8	4.56 ± 0.08
L = OP(OCH ₃) ₃			
34.4	2.34 ± 0.05	46.3	9.04 ± 0.18
42.0	5.58 ± 0.10	50.4	13.9 ± 0.25

^a Reported rate constants are the average of at least four kinetic runs.

Results

All chromium(III) complexes exhibited a modest acceleration of rate of aquation with increasing pressure (Table I). The temperature dependence of the aquation reactions has also been determined for comparative purposes (Table II). Calculated activation parameters from the latter data (ΔH^\ddagger , ΔS^\ddagger) are included in Table III, together with the determined or extrapolated rate of aquation of the complexes at 25 °C. Previously determined data for water exchange on $\text{Cr}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ also appear in that table.

Activation volumes (ΔV^\ddagger) determined from the pressure dependences are all negative, and span a range from -3.8 to -8.7

(15) Sisley, M. J.; Swaddle, T. W. *Inorg. Chem.* **1981**, *20*, 2799.

(16) Lay, P. A. *Inorg. Chem.* **1987**, *26*, 2144.

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

(18) Lawrence, G. A. *Inorg. Chem.* **1982**, *21*, 3687.

(19) Dixon, N. E.; Lawrence, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2940.

(20) Curtis, N. J.; Lawrence, G. A. *Inorg. Chim. Acta.* **1985**, *100*, 275.

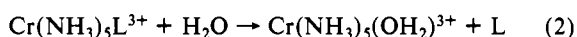
Table III. Activation Parameters and Comparative Rates for Aquation of $M(\text{NH}_3)_5\text{L}^{3+}$ Ions

L	$10^5 k,^a$ s ⁻¹	$\Delta H^\ddagger, \text{kJ}$ mol ⁻¹	$\Delta S^\ddagger, \text{J}$ K ⁻¹ mol ⁻¹	$\Delta V^\ddagger, \text{cm}^3$ mol ⁻¹
M = Cr(III) ^b				
OH ₂ ^c	5.2	97.0	0.0	-5.8
OS(CH ₃) ₂	1.95	95.3 ± 0.8	-15 ± 3	-3.2 ± 0.1
OCHNH ₂	5.1	94.0 ± 1.7	-12 ± 5	-4.8 ± 0.3
OC(NH ₂) ₂	2.0	93.5 ± 1.4	-22 ± 4	-8.2 ± 0.5
OC(NHCH ₃) ₂	1.0	97.5 ± 0.5	-14 ± 2	-3.8 ± 0.2
OCHN(CH ₃) ₂	1.45	93.1 ± 1.8	-25 ± 5	-7.4 ± 0.1
OC(CH ₃)N(CH ₃) ₂	1.9	91.9 ± 2.0	-30 ± 6	-6.2 ± 0.4
OP(OCH ₃) ₂	6.0	89.7 ± 0.9	-23 ± 3	-8.7 ± 0.1
M = Co(III) ^d				
OH ₂	0.59	111	+28	+1.2
OS(CH ₃) ₂	1.8	103	+10	+2.0
OCHNH ₂	0.58	107	+12	+1.1
OC(NH ₂) ₂	5.5	94	-10	+1.3
OC(NHCH ₃) ₂	5.1	102	+17	+1.5
OCHN(CH ₃) ₂	0.16	111	+16	+2.6
OHCH ₃	6.5	98	+5	+2.2
OHCH ₂ CH ₃	8.5	99	+9	+2.9
OHCH(CH ₃) ₂	33.6	98	+16	+3.8
OC(NH ₂)(NHCH ₃)	4.1	98	+2	+0.3
OCH ₂ (NHCH ₃)	0.25	108	+13	+1.7

^a Aquation rate at 25 °C. ^b This work. ^c Reference 12. ^d Reference 18.

cm³ mol⁻¹ (Table III). There is no obvious relationship between the size of ΔV^\ddagger and the partial molar volume of the neutral leaving group or precursor ion (Table IV). While ΔV^\ddagger increased from -4.8 cm³ mol⁻¹ for OCHNH₂ to -7.4 cm³ mol⁻¹ for OCHN(CH₃)₂ as the size of the leaving group increases, the opposite result occurred in going from urea (-8.2 cm³ mol⁻¹) to *N,N'*-dimethylurea (-3.8 cm³ mol⁻¹). The value for dimethylacetamide is also more positive than that for dimethylformamide, while the previously reported value¹² for water exchange is a little larger than ΔV^\ddagger values observed here for some larger leaving groups. Overall, the value of ΔV^\ddagger is not particularly sensitive to the size or type of the leaving group, but the variations observed are somewhat larger than those seen with a greater range of leaving groups in the analogous cobalt(III) series.

Apparent molar volumes of the complexes (ϕ_i) were determined (Table IV); data for the *N,N'*-dimethylurea complex alone is not reported, since minor decomposition in the solid state over a relatively short period of time invalidated these results. The values of ϕ_i recorded from data collected over a limited concentration range were essentially independent of concentration, and the mean value of ϕ_i reported should approach very closely the partial molar volume at infinite dilution (\bar{V}). Absolute molar volumes of individual ions reported in Table IV have been calculated from the conventional molar volumes, assuming $\bar{V} = -4.5$ cm³ mol⁻¹ for the hydrogen ion. This procedure has been adopted to permit comparison with other complex cations reported previously and with the neutral leaving groups. The estimated $\bar{V}(\text{H}^+)$ employed appears the best estimate, based on an extensive literature.²¹ Since molar volumes are available for all components of the overall reaction (2) in Table IV, estimation of the reaction volume (ΔV°)



for each reaction is possible by application of eq 3. While errors

$$\Delta V^\circ = [\bar{V}(\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}) + \bar{V}(\text{L})] - [\bar{V}(\text{Cr}(\text{NH}_3)_5\text{L}^{3+}) + \bar{V}(\text{H}_2\text{O})] \quad (3)$$

in this analysis are compounded, the determined ΔV° values are small and positive and not comparable with ΔV^\ddagger values but nevertheless indicate a consistent trend whereby the transition state is of smaller volume than the precursor and product states. All ΔV° values lie near 10 cm³ mol⁻¹, which is larger than expected

Table IV. Apparent Molar Volumes of Salts and Partial Molar Volumes of Ions and Ligands in Aqueous Solution at 25 °C

compd	$\phi_i,^a$ cm ³ mol ⁻¹
[Cr(NH ₃) ₅ (OH ₂)](ClO ₄) ₃	215.5 ^c
[Cr(NH ₃) ₅ (OS(CH ₃) ₂)](ClO ₄) ₃	256.0
[Cr(NH ₃) ₅ (OCH ₂ NH ₂)](CF ₃ SO ₃)(ClO ₄) ₂	258.6
[Cr(NH ₃) ₅ (OC(NH ₂) ₂)](S ₂ O ₆) _{3/2}	187.0
[Cr(NH ₃) ₅ (OCHN(CH ₃) ₂)](ClO ₄) ₃	263.0
[Cr(NH ₃) ₅ (OC(CH ₃)N(CH ₃) ₂)](ClO ₄) ₃	277.0
[Cr(NH ₃) ₅ (OP(OCH ₃) ₂)](ClO ₄) ₃	301.1
ion or ligand	$\bar{V},^b$ cm ³ mol ⁻¹
Cr(NH ₃) ₅ (OH ₂) ³⁺	69.7 ^c
Cr(NH ₃) ₅ (OS(CH ₃) ₂) ³⁺	106.2
Cr(NH ₃) ₅ (OCHNH ₂) ³⁺	81.0
Cr(NH ₃) ₅ (OC(NH ₂) ₂) ³⁺	84.0
Cr(NH ₃) ₅ (OCHN(CH ₃) ₂) ³⁺	117.2
Cr(NH ₃) ₅ (OC(CH ₃)N(CH ₃) ₂) ³⁺	131.2
Cr(NH ₃) ₅ (OP(OCH ₃) ₂) ³⁺	155.3
OH ₂	18.0
OS(CH ₃) ₂	68.8 ^d
OCHNH ₂	39.2 ^e
OC(NH ₂) ₂	44.2 ^f
OCHN(CH ₃) ₂	76.0 ^e
OC(CH ₃)N(CH ₃) ₂	88.9 ^e
OP(OCH ₃) ₂	116.0

^a ϕ_i (conv) values; standard error <0.5%. ^b Calculated by assuming $\bar{V}(\text{H}^+) = -4.5$ cm³ mol⁻¹, $\bar{V}(\text{ClO}_4^-) = 48.6$ cm³ mol⁻¹, $\bar{V}(\text{CF}_3\text{SO}_3^-) = 80.4$ cm³ mol⁻¹, and $\bar{V}(\text{S}_2\text{O}_6^{2-}) = 68.7$ cm³ mol⁻¹; see ref 18. ^c Reference 15. ^d Reference 14. ^e Herskovits, T. T.; Kelly, T. M. *J. Phys. Chem.* 1973, 77, 381. ^f Gucker, F. E.; Moser, C. E. *J. Am. Chem. Soc.* 1938, 60, 2582. ^g Values for Co(III) analogues in parentheses; see ref 18.

after the near-zero data reported for cobalt(III) analogues.

Discussion

While charged leaving groups display an effect on observed ΔV^\ddagger ascribed to variation in charge separation and solvent electrostriction in forming the transition state,⁸ an effect illustrated clearly by the variation of ΔV^\ddagger from -18.3 cm³ mol⁻¹ (Co(NH₃)₅(SO₄)⁺, 2- leaving group)⁹ to -10.6 cm³ mol⁻¹ (Co(NH₃)₅Cl²⁺, 1- leaving group)¹⁵ to +1.2 cm³ mol⁻¹ (Co(NH₃)₅(OH₂)³⁺, neutral leaving group),¹¹ dissociation of a neutral ligand from a complex cation is far less complicated by these effects. It is convenient for discussion to separate ΔV^\ddagger into the two components $\Delta V^\ddagger_{\text{intr}}$ (the intrinsic contribution arising from nuclear displacements at the reaction centre) and $\Delta V^\ddagger_{\text{solv}}$ (arising from rearrangement of solvent molecules about the reacting site and dominated by changes in solvent electrostriction ($\Delta V^\ddagger_{\text{el}}$) when charged leaving groups are present).¹⁴ A like conceptualization may be applied to ΔS^\ddagger . Large negative ΔV^\ddagger values observed when anionic leaving groups depart a cationic complex and large positive ΔV^\ddagger values observed when anionic leaving groups depart an anionic complex are entirely consistent with domination of the observed ΔV^\ddagger by $\Delta V^\ddagger_{\text{el}}$ terms. These latter terms arise from events somewhat remote from the reaction site and can mask the mechanistically significant terms. While mechanistic information can still be forthcoming from reactions involving charged leaving groups, it is with neutral leaving groups that the firmest conclusions can be drawn.

A study of a series of Co(NH₃)₅L³⁺ complexes revealed ΔV^\ddagger in the limited range +0.3 to +3.8 cm³ mol⁻¹ for a range of leaving groups of variable size, and the average ΔV^\ddagger of ≈ 2 cm³ mol⁻¹ was argued to be an estimate of the solvent-independent intrinsic component of ΔV^\ddagger for an I_d mechanism.¹⁸ More recently, ΔV^\ddagger values for several Co(NH₂CH₃)₅L³⁺ were reported²² and larger average values of ≈ 6 cm³ mol⁻¹ interpreted in an analogous manner, allowing for less participation of the incoming water molecule in this sterically more crowded system. Here, we observe consistently negative ΔV^\ddagger values for the chromium(III) pentaamine system, with average $\Delta V^\ddagger \approx -6$ cm³ mol⁻¹. If the same type of arguments are applied here as for the cobalt(III) systems,

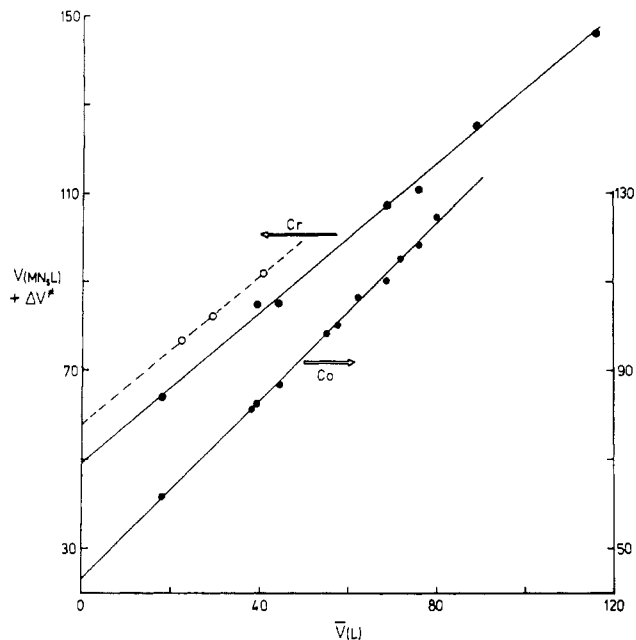
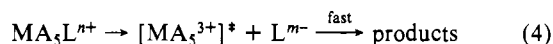


Figure 1. Comparative plots of $[V(M(NH_3)_5L) + \Delta V^\ddagger]$ versus $V(L)$ for chromium(III) complexes and cobalt(III) complexes in units of $\text{cm}^3 \text{mol}^{-1}$. Full circles denote neutral leaving groups, and open circles denote 1- leaving groups. The slope for the Cr(III) data (left-hand lines) is clearly less than the unit slope for the Co(III) data (right-hand line).

these more negative ΔV^\ddagger values require that we must assert a greater participation of incoming water in the transition state in the chromium(III) system. In terms of commonly employed mechanistic convention, we could assign an I_a mechanism to the chromium(III) complexes aquation process. The validity of this assignment requires discussion.

In the extreme dissociative (D) limit, the activation volume can be written for



as

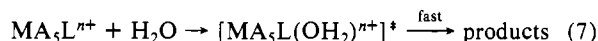
$$\Delta V^\ddagger = [\bar{V}(MA_5^{3+}) + \bar{V}(L^{m-})] - \bar{V}(MA_5L^{n+}) \quad (5)$$

which on rearrangement assigns the intermediate of reduced coordination number a volume

$$\bar{V}(MA_5^{3+}) = \Delta V^\ddagger + \bar{V}(MA_5L^{n+}) - \bar{V}(L^{m-}) \quad (6)$$

where all the right-hand parameters are experimentally accessible. A graph of $\Delta V^\ddagger + \bar{V}(MA_5L^{n+})$ versus $\bar{V}(L^{m-})$ should be linear, with unit slope, and an intercept $\bar{V}(MA_5^{3+})$. This has been observed for $Co(NH_3)_5X^{n+}$ complexes, except the intercept depends on the charge on X, and this has been related to the very limited lifetime of the intermediate of reduced coordination number.¹⁸ A short-lived intermediate (if, indeed, one can assert the presence of such a species at all) would retain the solvent sheath of its precursor largely, and this would be reflected in different apparent molar volumes for the intermediates from different parents.

If eq 6 is not strictly correct for dissociative cobalt(III), it is likely to be less applicable for a system presumed to be associative in nature. The data for the chromium(III) system with neutral leaving groups fits an approximate line, but the slope is not 1. The data for the cobalt(III) and chromium(III) systems are compared in Figure 1. Again, data for the halide aquation reactions fits a different line, apparently of the same slope, although the data for SCN^- as a leaving group does not fit with this data (perhaps because protonation may be involved in the dissociation process in that case). If eq 4-6 have any validity at all, then the present observation suggests that variation from cobalt(III) to chromium(III) systems is not enormous. For a limiting associative mechanism, eq 7, the activation volume can be written as in eq



8, where the intermediate of increased coordination number,

$$\Delta V^\ddagger = \bar{V}(MA_5L(OH_2)^{n+}) - [\bar{V}(MA_5L^{n+}) + \bar{V}(H_2O)] \quad (8)$$

$\bar{V}(MA_5L(OH_2)^{n+})$ in eq 9, should not be obtainable from the same

$$\bar{V}(MA_5L(OH_2)^{n+}) = \Delta V^\ddagger + \bar{V}(MA_5L^{n+}) - \bar{V}(H_2O) \quad (9)$$

graphical approach predicted for the D mechanism. However, since $\bar{V}(MA_5L^{n+})$ will increase as $\bar{V}(L^{m-})$ in any case, it is not surprising that some approximately linear response is seen in Figure 1. Consequently, the mechanistic value of a graph such as Figure 1 is limited and perhaps restricted to the significance of the slope as a mechanistic indicator.

Previous investigation of the behavior of cobalt(III) and chromium(III) pentaamines with ionic leaving groups reported differing slopes for the graphs of ΔV^\ddagger versus ΔV° .¹⁴ A slope of 1.0 for cobalt compared with a slope of 0.59 for chromium was observed, and this was tied to apparently less separation of X^- from the metal ion in the transition state in the latter case. That analysis, applicable for charged leaving groups, clearly implies the same mechanistic differentiation as observed in this case for neutral leaving groups. Evidently, in these simple systems, we are dealing with variations that are defined by the metal ion, but may be affected also by nonleaving groups in more complex systems.

Even in aqueous base, where intermediates of reduced coordination number are apparently stabilized, lifetimes of intermediates for simple cobalt(III) amines at least are very short, probably in the picosecond range.⁷ It is clear, therefore, that limiting mechanisms with defined intermediates are not expected for aquation reactions of simple pentaamines. Thus we are dealing with differing degrees of bond making and bond breaking involving the leaving group and the incoming water molecule. A study of aquation of $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_2CH_3)_5Cl^{2+}$ indicated that the interplay of these effects is subtle, with data in the latter suggesting that dissociation is much more important in that case than in the less sterically crowded pentaamine.¹³

The values of ΔV^\ddagger and ΔV° for the aquation of $M(NH_3)_5L^{3+}$ complexes show no particular dependence on the size of the leaving group L. ΔV^\ddagger is throughout the series of complexes between 5 and 10 $\text{cm}^3 \text{mol}^{-1}$ smaller for $M = Cr(III)$ than for $M = Co(III)$, whereas ΔV° is throughout ca. 10 $\text{cm}^3 \text{mol}^{-1}$ larger for $M = Cr(III)$ than for $M = Co(III)$. The overall volume increase of ca. 16 $\text{cm}^3 \text{mol}^{-1}$ between the transition and final states during the aquation of the Cr(III) complexes must be due to the release of L on going from a semi-7-coordinate transition state to the final products. Furthermore, the transition state in the case of the Cr(III) complexes is significantly more compact than for the Co(III) complexes due to the associative nature of the interchange process. The fact that ΔV^\ddagger and ΔV° are so independent of L for these systems is in our opinion, a characteristic property of an interchange process. The degree of bond formation/bond breakage will depend on the nature of M and L, producing a well-balanced transition state (on a volume basis) and constant volume parameters. This is not the case for limiting A and D processes.

While both pentaamine systems lie in the interchange regime, there appears to be a distinct preference for bond breaking with cobalt and bond making with chromium. This effectively means that, in the rapid vibration-like exchange, M-L extension is greater and M-OH₂ formation weaker with cobalt, while with chromium M-L extension is less and the M-OH₂ approach closer. To define this distinction simply, it seems reasonable to describe the mechanisms in terms of the well-worn I_d and I_a mechanisms, respectively. However, there seems no special reason to forbid either mechanism to operate for a particular metal ion if circumstances direct it. Metal ion, leaving group, nonleaving groups, and solvent will all play a role in determining the operating mechanism within a spectrum of possibilities. Lay¹⁶ has argued for a common mechanism for aquation of pentaamine complexes with certain (particularly ionic) leaving groups, with kinetic differences asserted to be the result of ground-state differences. We have earlier pointed out that a dissociative mechanism is not unacceptable for chromium(III) under certain circumstances.¹³

but analysis of systems involving displacement of charged groups is invariably complicated by electrostriction terms. His interpretation of the data for $\text{Co}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ ($\Delta V^\ddagger + 1.2 \text{ cm}^3 \text{ mol}^{-1}$) and $\text{Cr}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ ($\Delta V^\ddagger - 5.8 \text{ cm}^3 \text{ mol}^{-1}$) in terms of a common mechanism is based on an assertion that the coordinated water is more compressed when coordinated to $\text{Co}(\text{III})$ than $\text{Cr}(\text{III})$, 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 ΔV^\ddagger with size of the neutral donor for either $\text{Cr}(\text{III})$ or $\text{Co}(\text{III})$ (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. $[\text{Cr}(\text{NH}_3)_5\text{OS}(\text{CH}_3)_2]^{3+}$, 65821-31-0; $[\text{Cr}(\text{NH}_3)_5\text{OCHNH}_2]^{3+}$, 87564-86-1; $[\text{Cr}(\text{NH}_3)_5\text{OC}(\text{NH}_2)_2]^{3+}$, 87564-82-7; $[\text{Cr}(\text{NH}_3)_5\text{OC}(\text{NHCH}_3)_2]^{3+}$, 87564-84-9; $[\text{Cr}(\text{NH}_3)_5\text{OCHN}(\text{CH}_3)_2]^{3+}$, 62560-25-2; $[\text{Cr}(\text{NH}_3)_5\text{OC}(\text{CH}_3)\text{N}(\text{CH}_3)_2]^{3+}$, 97396-22-0; $[\text{Cr}(\text{NH}_3)_5\text{OP}(\text{OCH}_3)_3]^{3+}$, 97396-20-8; $[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)](\text{ClO}_4)_3$, 32700-25-7; $[\text{Cr}(\text{NH}_3)_5(\text{OS}(\text{CH}_3)_2)](\text{ClO}_4)_3$, 65821-32-1; $[\text{Cr}(\text{NH}_3)_5(\text{OCHNH}_2)](\text{CF}_3\text{SO}_3)(\text{ClO}_4)_2$, 97396-24-2; $[\text{Cr}(\text{NH}_3)_5(\text{OC}(\text{NH}_2)_2)](\text{S}_2\text{O}_6)_{3/2}$, 87564-83-8; $[\text{Cr}(\text{NH}_3)_5(\text{OCHN}(\text{CH}_3)_2)](\text{ClO}_4)_3$, 62560-26-3; $[\text{Cr}(\text{NH}_3)_5(\text{OC}(\text{CH}_3)\text{N}(\text{CH}_3)_2)](\text{ClO}_4)_3$, 97396-23-1; $[\text{Cr}(\text{NH}_3)_5(\text{OP}(\text{OCH}_3)_3)](\text{ClO}_4)_3$, 97396-21-9; $\text{OP}(\text{OCH}_3)_3$, 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}

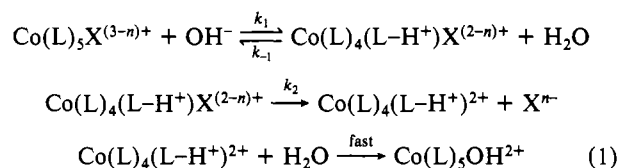
Received August 7, 1987

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 $\text{CoL}_5\text{X}^{3+}$, 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 $\text{cm}^3 \text{ mol}^{-1}$, and those for $\Delta \bar{V}_{\text{BH}}$ range from 24 to 9 $\text{cm}^3 \text{ mol}^{-1}$, 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 $\text{S}_{\text{N}}1\text{CB}$ 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 $\text{S}_{\text{N}}1\text{CB}$ 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 $\text{S}_{\text{N}}1\text{CB}$ 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 $\text{S}_{\text{N}}1\text{CB}$ mechanism, as outlined in eq 1, it is usually assumed that formation of the



conjugate base species occurs in a fast preequilibrium, followed by the rate-determining step k_2 (L = amine, $\text{L}-\text{H}^+$ = 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

$$\begin{aligned} k_{\text{obsd}} &= k_2 K_1 [\text{OH}^-] / \{1 + K_1 [\text{OH}^-]\} \\ &\approx k_2 K_1 [\text{OH}^-] \end{aligned} \quad (2)$$

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

- (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 Newcastle, 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.