Inorg. Chem. **1982**, *21*, 3687-3691 **3687**

Contribution from The Research School of Chemistry,
The Australian National University, Canberra 2600, Australia

Activation Volumes for Aquation of Cobalt(III) Pentaammine Complexes with Neutral Leaving Groups[1]

GEOFFREY A. LAWRANCE

Received February 4, 1982

The pressure dependence of the spontaneous aquation of a series of $Co(NH_3)_5L^{3+}$ complexes with L = methanol, ethanol, 2-propanol, formamide, *N*-methylformamide, *N,N*-dimethylformamide, urea, *N*-methylurea, *N,N'*-dimethylurea, and dimethyl sulfoxide has been determined. The activation volume ($\Delta V^{\ddagger}$) lies in the limited range +0.3–+3.8 $cm^3 mol^{-1}$ across the series and is essentially independent of the size of the leaving group. The average $\Delta V^{\ddagger}$ of ~2 $cm^3 mol^{-1}$ is an estimate of the solvent-independent intrinsic component of $\Delta V^{\ddagger}$ and is interpreted as being indicative of a dissociative interchange (I_d) mechanism. Apparent molar volumes of the series of complexes are reported. The "volume profile" approach for a dissociative mechanism has been applied to these and earlier data for both neutral and anionic leaving groups; variation in the estimated molar volume of the putative pentacoordinate intermediate with the type of leaving group is discussed in terms of the limited validity of the volume profile approach when an I_d mechanism operates.

Introduction

The spontaneous aquation reactions of pentaamminecobalt(III) complexes have an extensive research history. Generally, a dissociative mechanism has been supported,[2-5] but it involves some bond making by the entering group, favoring a dissociative interchange (I_d) description. Determinations of activation volumes ($\Delta V^{\ddagger}$) for a range of $Co(NH_3)_5X^{n+}$ complexes, mainly with ionic leaving groups, have been reported over the past decade and support the earlier mechanistic assignments.[6-11]

Where charged leaving groups were involved, observed activation volumes were negative, and it was presumed that solvent electrostriction changes in forming the activated state contributed significantly to $\Delta V^{\ddagger}$.[12] Variations in $\Delta V^{\ddagger}$ values observed for aquation reactions of cationic and anionic complexes with anionic leaving groups are consistent with this concept.[13] Further, where the leaving group is not charged, the determined activation volumes are small and not appreciably dependent on the charge of the precursor complex.[11] This latter observation is consistent with the assumption that changes in electrostriction are minimal where the leaving group is not charged.

As part of a continuing research program on the effect of both leaving groups and nonleaving groups on the observed activation volume, the limited data for aquation of neutral leaving groups in pentaamminecobalt(III) complexes have been extended. Preliminary observations indicated that $\Delta V^{\ddagger}$ is small and positive for neutral leaving groups and relatively independent of the size of the leaving group.[14] Further, the volume profile diagram applied by Palmer and Kelm,[9] and recently reexamined by Sisley and Swaddle,[10] has been applied to the complexes studied in this work and to earlier data, with a view to probing the effect of leaving-group charge on the partial molar volume ($\bar{V}$) estimated for the putative pentacoordinate intermediate, $Co(NH_3)_5^{3+}$.

Experimental Section

Complex Preparations. The precursor complex $[Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ was prepared as previously described.[15] All complexes were prepared by dissolution of this complex in the appropriate AR grade solvent or, in the case of the urea complexes, by reaction in sulfolane with excess ligand. Complexes were usually recrystallized from aqueous solution as trifluoromethanesulfonate, perchlorate, or dithionate salts. The syntheses, except for those of *N*-methylurea and *N,N'*-dimethylurea, have been described previously.[15,16] These two complexes were prepared in a manner identical with the method described for the urea complex.[15] Pentaamminecobalt(III) complexes of methanol ($OHCH_3$), ethanol ($OHCH_2CH_3$), 2-propanol ($OHCH(CH_3)_2$), formamide ($OCHNH_2$), *N*-methylformamide ($OCH(NHCH_3)$), *N,N*-dimethylformamide ($OCH(N(CH_3)_2)$), urea ($OC(NH_2)_2$), *N*-methylurea ($OC(NH_2)(NHCH_3)$), *N,N'*-dimethylurea ($OC(NHCH_3)_2$), and dimethyl sulfoxide ($OS(CH_3)_2$) were prepared and characterized satisfactorily by microanalysis, proton magnetic resonance, and absorption spectroscopy.

Kinetic Measurements. The rates of spontaneous aquation of $Co(NH_3)_5L^{3+}$ complexes were followed at 540 nm with a Varian 635D spectrophotometer equipped with a thermostated (±0.1 °C) high-pressure optical cell. Reaction solutions were distilled water (no added electrolyte) or 0.01 M CF_3SO_3H in water, with complex concentrations typically 0.005 M. Rate constants were computed by the Guggenheim method, or by least-squares fitting to a single exponential term for first-order processes, using data collected over at least 3 half-lives at pressures of up to 1725 bar. The activation volume ($\Delta V^{\ddagger}$) for each reaction was determined from plots of log k_p vs. pressure, as previously described.[17] The temperature dependence of reactions was studied over a temperature range of at least 20 °C, and activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) were obtained from plots of log k_T vs. $1/T$ in the usual manner.

Density Measurements. An Anton Paar DMA02 digital density meter, thermostated at 25 (±0.003) °C, was used. Triply distilled water and specially cleaned glassware were employed. Glassware was soaked overnight in concentrated HCl, rinsed with distilled water, then with glacial acetic acid, and again with distilled water, and then dried. Densities were measured at a minimum of four different complex concentrations over a range (4.0–25.0) × 10^{-3} M. Limited solubilities of complexes restricted the extension of the concentration range and hence caused somewhat larger errors in determined partial molar volumes than is generally the case; errors were typically ±1.0 $cm^3 mol^{-1}$. Densities of the salts $NaCF_3SO_3$ and $Na_2S_2O_6$, and the ligands *N*-methylurea and *N*-methylformamide, were determined over more extensive concentration ranges ((0.5–20) × 10^{-2} M). Apparent molar volumes (Φ_i) were calculated from eq 1[18] where d_0 and d_s are

$$\Phi_i = M/d_0 - [1000(d_s - d_0)]/c_s d_0 \qquad (1)$$

---

(1) Communicated in part at the Royal Australian Chemical Institute Colloquim on Solution Kinetics, Jindabyne, Australia, Feb 1981.

(2) *Spec. Period. Rep.: Inorg. React. Mech.* **1971–1980**, *1–7*.

(3) Langford, C. H.; Gray, H. B. "Ligand Substitution Dynamics"; W. A. Benjamin: New, York, 1965.

(4) Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974**, *11*, 47–104.

(5) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217–268.

(6) Jones, W. E.; Carey, L. R.; Swaddle, T. W. *Can. J. Chem.* **1972**, *50*, 2739–2746. Guastalla, G.; Swaddle, T. W. *Ibid.* **1973**, *51*, 821–827.

(7) Hunt, H.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642–2646.

(8) Gay, D. L.; Nalepa, R. *Can. J. Chem.* **1970**, *48*, 910–912.

(9) Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1977**, *16*, 3139–3143.

(10) Sisley, M. J.; Swaddle, T. W. *Inorg. Chem.* **1981**, *20*, 2799–2803.

(11) Lawrance, G. A.; Suvachittanont, S. *Inorg. Chim. Acta* **1980**, *44*, L61–L62.

(12) Palmer, D. A.; Kelm, H. In "High Pressure Chemistry"; Kelm, H., Ed.; Reidel: Dordrecht, 1978; pp 281–310, 421–434.

(13) Palmer, D. A.; Kelm, H. *Z. Anorg. Allg. Chem.* **1979**, *450*, 50–56.

(14) Lawrance, G. A. *Inorg. Chim. Acta* **1981**, *54*, L225–L226.

(15) Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470–476.

(16) Fairlie, D.; Jackson, W. G., to be submitted for publication.

(17) Lawrance, G. A.; Stranks, D. R. *Acc. Chem. Res.* **1979**, *11*, 403–409.

0020-1669/82/1321-3687$01.25/0

Table I. Pressure Dependence of the Rate of Aquation of $Co(NH_3)_5L^{3+}$ Ions

press., bar	$10^4 k_P$, s^{-1}	press., bar	$10^4 k_P$, s^{-1}
$L = OHCH_3$[a,b]			
1	3.57 ± 0.06 (5)	1100	3.25 ± 0.02 (4)
550	3.41 ± 0.04 (4)	1650	3.10 ± 0.03 (2)
$L = OHCH_2CH_3$[a,b]			
1	4.31 ± 0.04 (3)	1100	3.81 ± 0.04 (4)
550	4.02 ± 0.06 (4)	1650	3.58 ± 0.04 (2)
$L = OHCH(CH_3)_2$[a,c]			
1	3.30 ± 0.04 (3)	1100	2.77 ± 0.05 (2)
550	3.02 ± 0.03 (4)	1650	2.57 ± 0.03 (2)
$L = OC(NH_2)_2$[d,e]			
1	1.80 ± 0.02 (4)	1380	1.73 ± 0.04 (3)
690	1.78 ± 0.04 (3)	1725	1.68 ± 0.03 (2)
$L = OC(NH_2)(NHCH_3)$[d,f]			
1	1.47 ± 0.02 (3)	1100	1.47 ± 0.02 (3)
550	1.48 ± 0.01 (2)	1650	1.45 ± 0.02 (3)
$L = OC(NHCH_3)_2$[d,g]			
1	1.84 ± 0.02 (3)	1100	1.71 ± 0.03 (3)
550	1.79 ± 0.02 (2)	1650	1.67 ± 0.02 (2)
$L = OCH(NH_2)$[a,h]			
1	1.35 ± 0.02 (2)	1100	1.30 ± 0.02 (2)
550	1.32 ± 0.01 (3)	1650	1.26 ± 0.02 (3)
$L = OCH(NHCH_3)$[a,h]			
1	$0.56_2 \pm 0.003$ (3)	1100	0.52 ± 0.005 (3)
550	$0.54_8 \pm 0.008$ (3)	1650	0.50 ± 0.005 (2)
$L = OCH(N(CH_3)_2)$[a,i]			
1	0.42 ± 0.005 (3)	1100	$0.37_7 \pm 0.01$ (3)
550	0.40 ± 0.005 (2)	1650	0.36 ± 0.005 (3)
$L = OS(CH_3)_2$[a,j]			
1	1.75 ± 0.03 (3)	1100	1.59 ± 0.04 (2)
550	1.68 ± 0.02 (3)	1650	1.54 ± 0.02 (3)

[a] Measured in 0.01 M CF_3SO_3H; number of runs in parentheses. [b] 38.2 °C. [c] 24.6 °C. [d] Measured in water (no added electrolyte). [e] 34.5 °C. [f] 34.9 °C. [g] 34.4 °C. [h] 47.9 °C. [i] 49.0 °C. [j] 41.0 °C.

Table II. Temperature Dependence of the Rate of Aquation of $Co(NH_3)_5L^{3+}$ Ions[a]

temp, °C	$10^4 k_T$, s^{-1} [b]	temp, °C	$10^4 k_T$, s^{-1} [b]
$L = OHCH_3$			
21.6	0.40 ± 0.01	35.1	2.45 ± 0.03
27.6	0.94 ± 0.02	39.8	4.42 ± 0.10
$L = OHCH_2CH_3$			
19.4	$0.37_5 \pm 0.01$	33.5	2.62 ± 0.05
26.2	1.02 ± 0.03	39.6	5.60 ± 0.20
$L = OHCH(CH_3)_2$			
9.1	$0.35_5 \pm 0.01$	25.0	3.36 ± 0.04
17.0	1.11 ± 0.01	32.0	8.77 ± 0.15
$L = OC(NH_2)_2$			
20.0	$0.27_5 \pm 0.01$	40.2	3.62 ± 0.07
26.9	$0.74_5 \pm 0.01$	47.0	8.07 ± 0.08
34.5	$1.79_5 \pm 0.03$		
$L = OC(NH_2)(NHCH_3)$			
19.8	0.19 ± 0.005	42.0	3.60 ± 0.05
26.7	0.52 ± 0.01	48.9	8.23 ± 0.20
34.1	1.36 ± 0.04		
$L = OC(NHCH_3)_2$			
19.9	0.24 ± 0.005	41.4	4.75 ± 0.05
26.6	0.63 ± 0.01	49.2	12.0 ± 0.15
33.9	1.78 ± 0.02		

[a] Temperature dependences of aquation rates for dimethyl sulfoxide and the amide complexes have been determined recently, under similar conditions.[9,16] [b] Average of three independent runs; solvents were the same as employed in the high-pressure kinetics.

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

Results

All complexes displayed a small deceleration of aquation rate with increasing pressure (Table I). The calculated activation volumes are included in Table III and were all small, positive, and pressure-independent over the available range of pressures. The variation in spontaneous aquation rate at any one temperature for the alcohol, urea, amide, and sulfoxide complexes required that, for experimental convenience, pressure-dependent rates be determined at different temperatures for the series of complexes. However, the temperature span across the ten complexes studied was <25 °C; since $\Delta V^{\ddagger}$ is usually not appreciably temperature dependent,[17] it is unlikely that these minor temperature variations would alter $\Delta V^{\ddagger}$ values appreciably, particularly in view of the small size of the observed values. For comparative purposes, the temperature dependence of the aquation reactions has been determined (Table II) where values have not been reported previously under similar conditions. Calculated activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) are included in Table III, together with the determined or extrapolated rate of aquation of the complexes at 25 °C.

Apparent molar volumes of compounds determined in this study are collected in Table IV. Within experimental error, no concentration dependences of Φ_i for the complex ions were observed over the limited range available. The mean values of Φ_i should closely approximate the partial molar volumes at infinite dilution, $\bar{V}$. The absolute molar volumes of individual ions have been calculated from the conventional molar volumes, by assuming $\bar{V} = -4.5$ $cm^3\ mol^{-1}$ for the hydrogen ion.[18] Although this approach has been adopted previously in this area,[9] the necessity and validity of this calculation have been questioned.[10] However, since comparison will be made later between cationic complexes with both anionic and neutral leaving groups, the molar volumes of the latter being "absolute" values, it is felt that a determination of absolute molar volumes of the ionic compounds is justified. The extensive literature related to estimation of $\bar{V}(H^+)$ has been reviewed,[18] and it seems likely that the "best estimate" employed here is adequately determined.

For the overall aquation reaction

$$Co(NH_3)_5L^{3+} + OH_2 \rightarrow Co(NH_3)_5(OH_2)^{3+} + L \quad (2)$$

the available molar volume data allowed estimation of the reaction volume (ΔV°) for each reaction, since all the molar volumes in eq 3 have been determined. Although experimental

$$\Delta V^{\circ} = [\bar{V}(Co(NH_3)_5OH_2^{3+}) + \bar{V}(L)] - [\bar{V}(Co(NH_3)_5L^{3+}) + \bar{V}(OH_2)] \quad (3)$$

errors are compounded in this analysis, the determined ΔV° values are all small and similar to $\Delta V^{\ddagger}$ values in each case (Table III). During the study, activation volumes and molar volumes were determined under similar low ionic strength conditions, in order to strengthen the validity of comparisons and calculations involving these terms.

While the molar volume of the leaving group varied from 18 $cm^3\ mol^{-1}$ $(OH)_2$ to 80.0 $cm^3\ mol^{-1}$ $(OC(NHCH_3)_2)$, the activation volumes were small and positive in all cases and spanned a range from +0.3 to +3.8 $cm^3\ mol^{-1}$ only. The determined $\Delta V^{\ddagger}$ values are therefore insensitive to the size or type of neutral leaving group. For $Co(NH_3)_5(OHR)^{3+}$, where R = H, CH_3, CH_2CH_3, or $CH(CH_3)_2$, a trend whereby the observed $\Delta V^{\ddagger}$ increases slightly with $\bar{V}$ of the leaving group (and also, in this case, with aquation rate) was observed. A

---

(18) Millero, F. J. *Chem. Rev.* **1971**, *71*, 147–176.

Table III. Activation Parameters and Comparative Rates for Aquation of $Co(NH_3)_5L^{3+}$ Ions

L	10^5k, s^{-1} [a]	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta V°_{calcd}$,[b] cm^3 mol^{-1}
OH_2	0.59	111 ± 1	+28 ± 4	+1.2 ± 0.2	0.0
$OHCH_3$	6.5	98 ± 1	+5 ± 2	+2.2 ± 0.2	1.6
$OHCH_2CH_3$	8.5	$99 \pm 1._5$	+9 ± 4	+2.9 ± 0.3	2.2
$OHCH(CH_3)_2$	33.6	98 ± 1	+16 ± 3	+3.8 ± 0.2	2.9
$OC(NH_2)_2$	5.5	$94 \pm 1._5$	−10 ± 5	+1.3 ± 0.5	1.2
$OC(NH_2)(NHCH_3)$	4.1	98 ± 1	+2 ± 3	+0.3 ± 0.3	−1.6
$OC(NHCH_3)_2$	5.1	102 ± 1	+17 ± 3	+1.5 ± 0.3	−0.6
$OCH(NH_2)$	0.58	107 ± 3[c]	+12 ± 9[c]	+1.1 ± 0.3	0.5
$OCH(NHCH_3)$	0.25	108 ± 3[c]	+13 ± 8[c]	+1.7 ± 0.3	1.5
$OCH(N(CH_3)_2)$	0.16	111 ± 4[d]	+16 ± 8[d]	+2.6 ± 0.4	2.9
$OS(CH_3)_2$	1.8	$103 \pm 2._5$[e]	+10 ± 7[e]	−1.7 ± 0.7[e]	
				+2.0 ± 0.4	3.1

[a] Aquation rate at 25 °C. [b] Calculated by using eq 3. [c] Reference 16. [d] Reynolds, W. L.; Knoll, M. A. *Int. J. Chem. Kinet.* 1976, *8*, 389. [e] Reference 9.

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

compd	Φ_i,[a] cm^3 mol^{-1}	compd	Φ_i,[a] cm^3 mol^{-1}
$[Co(NH_3)_5(OHCH_3)](CF_3SO_3)_3$	320.0	$[Co(NH_3)_5(OCH(NH_2))](ClO_4)_3$	226.8
$[Co(NH_3)_5(OHCH_2CH_3)](CF_3SO_3)_3$	336.4	$[Co(NH_3)_5(OCH(NHCH_3))](S_2O_6)_{3/2}$	201.4
$[Co(NH_3)_5(OHCH(CH_3)_2)](CF_3SO_3)_3$	352.5	$[Co(NH_3)_5(OCH(N(CH_3)_2))](ClO_4)_3$	261.2
$[Co(NH_3)_5(OC(NH_2)_2)](S_2O_6)_{3/2}$	188.3	$[Co(NH_3)_5(OS(CH_3)_2)](ClO_4)_3$	253.8
$[Co(NH_3)_5(OC(NH_2)(NHCH_3))](S_2O_6)_{3/2}$	209.1	$Na_2(S_2O_6)$	57.3
$[Co(NH_3)_5(OC(NHCH_3)_2)](S_2O_6)_{3/2}$	225.9	$Na(CF_3SO_3)$	74.7

ion	$\overline{V}$, cm^3 mol^{-1} [b]	L	$\overline{V}$, cm^3 mol^{-1} [c]	ion	$\overline{V}$, cm^3 mol^{-1} [b]	L	$\overline{V}$, cm^3 mol^{-1} [c]
$Co(NH_3)_5(OH_2)^{3+}$	60.3[d]	OH_2	18	$Co(NH_3)_5(OS(CH_3)_2)^{3+}$	108.0	$OS(CH_3)_2$	68.8[d]
$Co(NH_3)_5(OHCH_3)^{3+}$	78.8	$OHCH_3$	38.1[f]	$Co(NH_3)_5(OCH(NH_2))^{3+}$	81.0	$OCH(NH_2)$	39.2[l]
$Co(NH_3)_5(OHCH_2CH_3)^{3+}$	95.2	$OHCH_2CH_3$	55.1[g]	$Co(NH_3)_5(OCH(NHCH_3))^{3+}$	98.3	$OCH(NHCH_3)$	57.5[j]
$Co(NH_3)_5(OHCH(CH_3)_2)^{3+}$	111.3	$OHCH(CH_3)_2$	71.9[h]	$Co(NH_3)_5(OCH(N(CH_3)_2))^{3+}$	115.4	$OCH(N(CH_3)_2)$	76.0[l]
$Co(NH_3)_5(OC(NH_2)_2)^{3+}$	85.3	$OC(NH_2)_2$	44.2[i]	$CF_3SO_3^-$	80.4		
$Co(NH_3)_5(OC(NH_2)(NHCH_3))^{3+}$	106.0	$OC(NH_2)(NHCH_3)$	62.1[j]	$S_2O_6^{2-}$	68.7		
$Co(NH_3)_5(OC(NHCH_3)_2)^{3+}$	122.9	$OC(NHCH_3)_2$	80.0[k]	ClO_4^-	48.6[e]		

[a] Φ_i(conv) values; standard error <0.5%. [b] Calculated by assuming $\overline{V}(H^+) = -4.5$ cm^3 mol^{-1}. [c] Mainly literature values from determinations in water. [d] Reference 9; recalculated by using $\overline{V}(ClO_4^-)$ from ref 18. [e] Reference 18. [f] Friedman, M. E.; Scheraga, H. A. *J. Phys. Chem.* **1965**, *69*, 3795. [g] Franks, F.; Johnson, H. H. *Trans. Faraday Soc.* **1962**, *58*, 656. [h] Høiland, H.; Vikingstad, E. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 182. [i] Gucker, F. T., Jr.; Gage, F. W.; Moser, C. E. *J. Am. Chem. Soc.* **1938**, *60*, 2582. [j] This work. [k] Philip, P. R.; Perron, G.; Desnoyers, J. E. *Can. J. Chem.* **1974**, *52*, 1709. [l] Herskovits, T. T.; Kelly, T. M. *J. Phys. Chem.* **1973**, *77*, 381.

similar trend applied with the amides but was not observed for the urea complexes. Given the small magnitude of the effects, and the fact that data for determining $\Delta V^{\ddagger}$ were collected at different temperatures for the various alcohol complexes at least, a detailed analysis of this minor effect is unwarranted.

Throughout, the small positive $\Delta V^{\ddagger}$ values were paralleled by the observation of small and usually positive $\Delta S^{\ddagger}$ values. This observation is consistent with the previously established correlation of these parameters for aquation reactions,[19] although a perfect correlation is not expected[17] nor observed.

The pressure dependence of the $Co(NH_3)_5(OH_2)^{3+}$ solvent exchange, and of the $Co(NH_3)_5(OS(CH_3)_2)^{3+}$ aquation, has been studied previously.[8,9] A reinvestigation of the $(CH_3)_2SO$ complex was undertaken in the light of two observations. First, the reported molar volume of the complex ion yielded, on application of eq 3, a $\Delta V°$ markedly different from $\Delta V^{\ddagger}$, which differed from the behavior for all other 3+ complex ions studied. Second, $\Delta V^{\ddagger}$ had been determined under different ionic strength conditions, and a small negative value had been reported.[9] While the value of $\Delta V^{\ddagger}$ determined in this work does not differ markedly from the literature value (Table I), given the different ionic strengths and temperatures employed, the $\bar{V}(Co(NH_3)_5(OS(CH_3)_2)^{3+})$ determined here (108.0 cm^3 mol^{-1}) is appreciably different from the literature value (125.2 cm^3 mol^{-1}). Determinations using two analytically pure samples of complex, prepared by different routes,[15,20] gave in this case the same $\bar{V}$ value of 108.0 (±1.1) cm^3 mol^{-1}. Since the determined $\bar{V}$ of the $(CH_3)_2SO$ complex was similar to those values measured for complexes of other ligands with similar molar volumes (Table IV) and fitted the generally observed relationship $\Delta V° \sim \Delta V^{\ddagger}$, it is likely that the initial determination was erroneous.[21] The variation in the observed $\Delta V^{\ddagger}$ with ionic strength and temperature (of 3.7 ± 1.1 cm^3 mol^{-1}) is not unreasonable. Minor variations in $\Delta V^{\ddagger}$ with temperature have been observed before and can be exemplified by the 1.4 cm^3 mol^{-1} variation in $\Delta V^{\ddagger}$ with a 20 °C change in temperature of the determinations recently reported for the acid-independent aquation pathway of $Co(NH_3)_5(SO_4)^+$;[10] small dependences of $\Delta V^{\ddagger}$ on ionic strength for reactions involving neutral aqua ligand release in the activated state have also been observed.[22] These observations serve to illustrate the importance, when data are compared, of maintaining the conditions as constant as is experimentally feasible across a series. Further, the change in sign of $\Delta V^{\ddagger}$ between the two determinations suggests that a small positive $\Delta V^{\ddagger}$ is not necessarily expected for aquation of a neutral ligand from ammine-

---

(19) Twigg, M. V. *Inorg. Chim. Acta* **1977**, *24*, L84–L86.

(20) Piriz Mac-Coll, C. R.; Beyer, L. *Inorg. Chem.* **1973**, *12*, 7–11.

(21) The method employed by Palmer and Kelm[9] reportedly yields the perchlorate dihydrate salt. The complex isolated via the facile trifluoromethanesulfonate route[15] was analyzed repeatedly as the perchlorate salt without any waters of crystallization. Samples prepared via the earlier method[20] gave variable analyses in our hands, suggesting that purity of the complex prepared via this route may be more difficult to achieve.

(22) See, for example: Lawrance, G. A.; Suvachittanont, S. *Aust. J. Chem.* **1980**, *33*, 1649–1658.

cobalt(III) complexes, although it appears to be a consistent observation at low ionic strengths.

Discussion

Dissociation of a neutral ligand from a cationic complex is not complicated by the effects of charge separation that occur upon dissociation of an anionic ligand. Variation in the observed $\Delta V^{\ddagger}$ for aquation of $Co(NH_3)_5(SO_4)^+$ (−18.3 cm^3 mol^{-1}),[10] $Co(NH_3)_5Cl^{2+}$ (−10.6 cm^3 mol^{-1}),[6] and $Co(NH_3)_5(OH_2)^{3+}$ (+1.2 cm^3 mol^{-1}),[8] where the molar volumes of the leaving groups are similar yet the charge varies from 2− to 1− to 0, can be ascribed to variation in charge separation in the activated state. The conceptual division of the experimental $\Delta V^{\ddagger}$ for reactions of coordination complexes into two components has been proposed;[9] $\Delta V^{\ddagger}_{intr}$ represents the intrinsic contribution arising from nuclear displacement at the reaction center in forming the activated state, and $\Delta V^{\ddagger}_{solv}$ results from the rearrangement of solvent molecules about the reacting species. For charged or highly polar molecules, changes in electrostriction ($\Delta V^{\ddagger}_{el}$) dominate the $\Delta V^{\ddagger}_{solv}$ term. Subsequently, the increasingly negative $\Delta V^{\ddagger}$ values from OH_2 to Cl^- to SO_4^{2-}, for example, can be ascribed to increase in the $\Delta V^{\ddagger}_{el}$ term, for a process which is dissociative. This concept is supported by the observation of positive $\Delta V^{\ddagger}$ values in reactions of $Co(CN)_5X^{3-}$, where a decrease in electrostriction in the dissociated transition state is anticipated.[13]

In the absence of significant variation in specific, nonelectrostatic solute–solvent interactions, $\Delta V^{\ddagger}$ for dissociation of a neutral ligand should be dominated by the $\Delta V^{\ddagger}_{intr}$ term. The observation of similar $\Delta V^{\ddagger}$ values ($\sim$+2 cm^3 mol^{-1}) for a range of neutral leaving groups of different molar volumes and geometries is consistent with this proposal. Further, calculated ΔV° values are all small, consistent with minor solvation changes from reactants to products. Earlier, $\Delta V^{\ddagger}$ for dissociation of urea from cationic and neutral complexes was shown to be similar,[11] a result which supports the minor role of $\Delta V^{\ddagger}_{solv}$ terms. Further, solvent self-exchange of $Co(NH_3)_5(OCHN(CH_3)_2)^{3+}$ exhibited a $\Delta V^{\ddagger}$ of +3.2 cm^3 mol^{-1},[23] similar to $\Delta V^{\ddagger}$ of +2.6 cm^3 mol^{-1} for spontaneous aquation, despite the variation from aprotic to protic solvent. Subsequently, unidentate ligand dissociation from an amminecobalt(III) complex is asserted to be characterized by a small, positive $\Delta V^{\ddagger}_{intr}$ term ($\sim$+2 cm^3 mol^{-1}). It is likely that the $\Delta V^{\ddagger}_{intr}$ term will be relatively constant for all unidentate leaving groups, with the observed $\Delta V^{\ddagger}$ affected markedly however by associated changes in electrostriction ($\Delta V^{\ddagger}_{el}$, important for charged leaving groups) and to a lesser extent by changes in specific, nonelectrostatic solute–solvent interactions. The arguments for variation in $\Delta V^{\ddagger}$ for $Co(NH_3)_5L^{n+}$ (L = OH_2, Cl^-, SO_4^{2-}) advanced earlier accord with the above discussion. In terms of the established mechanistic concepts, a small positive $\Delta V^{\ddagger}_{intr}$ term for spontaneous aquation is most consistent with the operation of an I_d mechanism.[12]

In the same way that eq 3 can be applied to define the reaction volume (ΔV°), the activation volume in the extreme dissociative (D) limit, i.e.

$$Co(NH_3)_5L^{n+} \rightarrow [Co(NH_3)_5^{3+}]^{\ddagger} + L^{m-} \xrightarrow[\text{fast}]{} \text{products} \quad (4)$$

can be written as[9]

$$\Delta V^{\ddagger} = \bar{V}(Co(NH_3)_5^{3+}) + \bar{V}(L^{m-}) - \bar{V}(Co(NH_3)_5L^{n+}) \quad (5)$$

The intermediate of reduced coordination number may be assigned a molar volume, since rearrangement of eq 5 yields

$$\bar{V}(Co(NH_3)_5^{3+}) = \Delta V^{\ddagger} + \bar{V}(Co(NH_3)_5L^{n+}) - \bar{V}(L^{m-}) \quad (6)$$

where all the parameters on the right-hand side can be determined by experiment. The existence of a five-coordinate intermediate in base hydrolysis reactions has been carefully probed,[24] with competition experiments supporting the existence of a $Co(NH_3)_4(NH_2)^{2+}$ intermediate at least trapped in a cage of solvent and competitors, with sufficient lifetime to allow for selective entry of anionic competitors into the coordination sphere of the intermediate. Observed competition is almost independent of the leaving group. For spontaneous aquation reactions, competition by anions is appreciably less and shows considerable dependence on leaving group.[25] The implication is that the intermediate $Co(NH_3)_5^{3+}$ has an appreciably shorter lifetime or does not exist as a separate entity; in fact there is evidence for bond making by entering groups. Consequently, the validity of eq 5 in the context of spontaneous aquation is impaired, since the activated state probably includes some bond making with water in addition to bond breaking or stretching of the leaving-group bond. However, it is instructive to examine the implications of eq 5 and to see if it can serve to provide some mechanistic insight. Aspects of this "volume profile" approach have been presented previously[9] and were recently reinvestigated.[10]

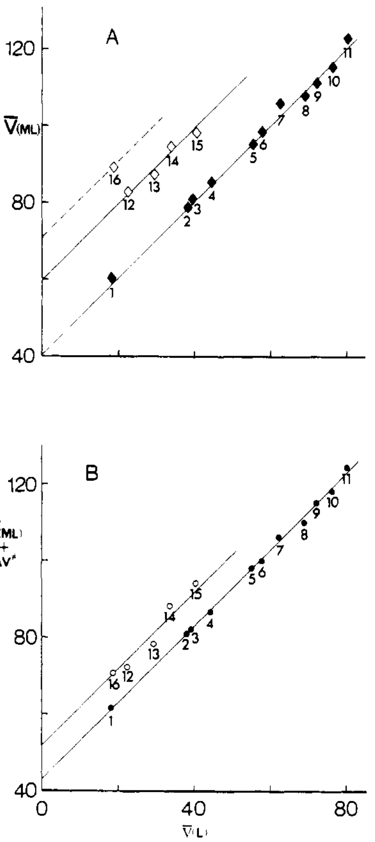

Figure 1. (A) Graph of partial molar volumes of complex ions vs. partial molar volumes of leaving groups. (B) Graph, from eq 5, of $\bar{V}$(complex ion) + $\Delta V^{\ddagger}$ vs. $\bar{V}$(leaving group). Ligands in the pentaamminecobalt(III) complexes: (1) OH_2; (2) $OHCH_3$; (3) $OCH(NH_2)$; (4) $OC(NH_2)_2$; (5) $OHCH_2CH_3$; (6) $OCH(NHCH_3)$; (7) $OC(NH_2)(NHCH_3)$; (8) $OS(CH_3)_2$; (9) $OHCH(CH_3)_2$; (10) $OCHN(CH_3)_2$; (11) $OC(NHCH_3)_2$; (12) Cl^-; (13) Br^-; (14) NO_3^-; (15) SCN^-; (16) SO_4^{2-}.

A requirement of eq 5 is that a graph of $\bar{V}(Co(NH_3)_5L^{n+})$ + $\Delta V^{\ddagger}$ vs. $\bar{V}(L^{m-})$ should be linear, with unit slope and an intercept of $\bar{V}(Co(NH_3)_5^{3+})$. If the D mechanism applies and a common intermediate $Co(NH_3)_5^{3+}$ exists, the intercept $\bar{V}$ for this entity should be independent of the size and charge

---

[23] Ho, S. T. D.; Sisley, M. J.; Swaddle, T. W. *Can. J. Chem.* **1978**, *56*, 2609–2615.

[24] Sargeson, A. M. *Pure Appl. Chem.* **1973**, *33*, 527–544. Dixon, N. E.; Jackson, W. G.; Marty, W.; Sargeson, A. M. *Inorg. Chem.*, in press.

[25] Jackson, W. G., personal communication of unpublished observations.

of the leaving group. Analysis for the 11 complexes of the type $Co(NH_3)_5L^{3+}$ yielded a line of unit slope and an intercept of 43 cm^3 mol^{-1}, with an excellent correlation (Figure 1B). However, it is notable that a similar, though arguably slightly worse, correlation between $\bar{V}(Co(NH_3)_5L^{3+})$ and $\bar{V}(L)$ applies, with intercept of 40.5 cm^3 mol^{-1} (Figure 1A). Further, application of eq 5 to data for complexes with charged leaving groups (X^- and Y^{2-}) yields a line different from that obtained for the neutral leaving groups, and in this case the intercept is 52 cm^3 mol^{-1} (Figure 1B).[26] The limited data for $\bar{V}(Co(NH_3)_5X^{2+})$ vs. $\bar{V}(X^-)$ again fit a line different from the $\bar{V}(Co(NH_3)_5L^{3+})$ vs. $\bar{V}(L)$ graph; the one data point for $\bar{V}(Co(NH_3)_5Y^+)$ vs. $\bar{V}(Y^{2-})$ suggests that, with a similar slope, the variation extends to that set (Figure 1A). Of course, errors in $\bar{V}$ of the complex ions, determined from the composite Φ_i term, may be quite large and impinge on the validity of the variations in Figure 1. However, the correlations observed are sufficiently good to suggest that the differences are valid.

It has been argued[10] that the assertion[27] that $\bar{V}(Co(NH_3)_5^{3+}) \simeq \bar{V}(Co(NH_3)_6^{3+})$, i.e., that the hexaamminecobalt(III) ion ($\bar{V}$ = 61.3 cm^3 mol^{-1}) is a good volume model for the pentacoordinate intermediate, is in error. The calculations of Palmer and Kelm,[9] based mainly on 1− leaving groups, seemed to confirm the earlier proposition; however, reanalysis of Sisley and Swaddle[10] suggested a difference of as much as 17–20 cm^3 mol^{-1}. The present analysis indicates, for neutral leaving groups, the difference $\bar{V}(Co(NH_3)_6^{3+}) - \bar{V}(Co(NH_3)_5^{3+})$ = 18.3 cm^3 mol^{-1}, in good agreement with the recent estimate.[10] However, for anionic leaving groups, the apparent difference is 9.3 cm^3 mol^{-1}.

The observed difference between the results for neutral and ionic leaving groups deserves further comment. It can be argued that the activated intermediate does not have sufficient time to reorganize its solvation shell completely before capturing another ligand. Consequently, the activated state for aquation of a $Co(NH_3)_5L^{3+}$ ion will retain the solvation environment of its 3+ precursor, while the activated state for aquation of a $Co(NH_3)_5X^{2+}$ ion will retain the solvent environment of its 2+ precursor[14] or perhaps achieve a solvation sheath intermediate between that of formally 2+ and 3+ ions. Since the intercept molar volume for hexacoordinate 2+ precursors is larger than that for 3+ precursors (Figure 1A), this difference should be reflected in the related activated intermediates, and this is observed. The variation in molar volume differences of the 3+/2+ precursors (19.5 cm^3 mol^{-1}) and the 3+/"3+" activated complexes (9 cm^3 mol^{-1}) is consistent with a view of the solvation of the activated complex from the $Co(NH_3)_5X^{2+}$ ions approaching but not achieving the solvation sheath of a true 3+ ion. Since we are dealing with the situation in the activated state, and not with subsequent steps along the reaction profile, the above analysis requires that any solvent rearrangement processes occur in the activation step, and not subsequent to it. For a well-defined intermediate, it is likely that the activation step is shifted along the reaction profile axis so that complete rearrangement of the solvent sheath occurs in the activation step. This would require $\bar{V}(Co(NH_3)_5^{3+})$ to be independent of the charge on the precursor complex, and this is not observed.

The volume of the supposed pentacoordinate intermediate is therefore not independent of the charge of the leaving group but is independent of the volume of the leaving group in any series. The implication is that eq 5 and 6 are not strictly correct; i.e., the spontaneous aquation mechanism is not a limiting dissociative (D) process. For leaving groups of the same charge a consistent mechanism is implied by the common intercept and unit slope. An attempt to apply eq 5 to the limited data[9] for the presumably associative mechanism operating in $Cr(NH_3)_5X^{2+}$ ($X = Cl^-, Br^-, I^-, NCS^-$) gave no consistent result. In fact, the line of best fit has a slope of ~0.8, rather than the unit slope required for a dissociative mechanism. This type of variation may indicate that a dissociative mechanism does not operate in that system, although a more extensive study would be revealing. For the $Co(NH_3)_5L^{n+}$ complexes, where some of the expectations of eq 5 apply, a mechanism with the characteristics of the favored[5] dissociative interchange (I_d) description is supported. It is likely that a small, positive $\Delta V^{\ddagger}_{intr}$ component, which can be equated with the observed $\Delta V^{\ddagger}$ for neutral leaving groups, may be a valid indicator of the operation of such a mechanism.

Acknowledgment. Professor L. Nichol and Dr. P. Jeffrey, John Curtin School of Medical Research, ANU, are thanked for making available an Anton Paar DMA02 digital density apparatus. Dr. W. G. Jackson and Mr. D. Fairlie are thanked for communication of results prior to publication. I also thank Professor A. M. Sargeson for useful and pertinent discussion.

Registry No. $Co(NH_3)_5(OHCH_3)^{3+}$, 63388-96-5; $Co(NH_3)_5(OHCH_2CH_3)^{3+}$, 63388-97-6; $Co(NH_3)_5(OHCH(CH_3)_2)^{3+}$, 75522-56-4; $Co(NH_3)_5(OC(NH_2)_2)^{3+}$, 31253-57-3; $Co(NH_3)_5(OC(NH_2)(NHCH_3))^{3+}$, 82555-44-0; $Co(NH_3)_5(OC(NHCH_3)_2)^{3+}$, 82555-45-1; $Co(NH_3)_5(OS(CH_3)_2)^{3+}$, 44915-85-7; $Co(NH_3)_5(OCH(NH_2))^{3+}$, 44819-96-7; $Co(NH_3)_5(OCH(NHMe))^{3+}$, 82555-46-2; $Co(NH_3)_5(OCH(N(CH_3)_2))^{3+}$, 31125-61-8.

---

(26) Molar volumes of $Co(NH_3)_5X^{2+}$ and $Co(NH_3)_5(SO_4)^+$ cations have been calculated from the redetermined data of ref 10, where available, or from ref 9, by using $\bar{V}(ClO_4^-)$ = 48.6 cm^3 mol^{-1} and $\bar{V}(NO_3^-)$ = 33.3 cm^3 mol^{-1}. However, the value of Φ_v = 168.8 cm^3 mol^{-1} in ref 10 for chloropentaamminecobalt(III) perchlorate differs from both the redetermined value of von Jouanne and Kelm, who obtained Φ_v = 180 cm^3 mol^{-1}, and a value of 179 cm^3 mol^{-1} determined in our laboratories; the latter determinations have been used here. The reasons for the discrepancy in this case are not clear, since the compound employed in our study was both microanalytically and chromatographically pure. Values of Φ_v used (cm^3 mol^{-1}): $[Co(NH_3)_5Cl](ClO_4)_2$, 180.0; $[Co(NH_3)_5Br](ClO_4)_2$, 184.6; $[Co(NH_3)_5(NO_3)](NO_3)_2$, 161.1; $[Co(NH_3)_5(NCS)](ClO_4)_2$, 195.3; $[Co(NH_3)_5(SO_4)](ClO_4)$, 137.7.

(27) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303–323.