The Volumes of Activation for Aquation Reactions of Acidopenta-amminecobalt (III) Complexes

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Summary The volumes of activation for aquation of representative complexes of the series $Co(NH_3)_5X^{3-n+}$ are equal (within experimental uncertainty) to the molar-volume changes for the respective completed reactions.

THE effects of hydrostatic pressure p up to 4,000 atmospheres upon the pseudo-first-order rate coefficients k for the aquation of acidopenta-amminecobalt (III) complexes

$$Co(NH_3)_5X^{(3-n)+} + H_2O \longrightarrow Co(NH_3)_5OH_2^{3+} + X^{n-} \qquad (1)$$

where X^{n-} is Cl^-, Br^-, NO_3^-, and SO_4^{2-}, have been studied using a pressurized-syringe apparatus similar to that described by Whalley *et al.*[1,2] The data have been analysed using a least-squares computer programme, in terms of the equation[3]

$$\ln k = a + bp + cp^2 \qquad (2)$$

from which $\Delta V_0^{\ddagger}$, the volume of activation at zero pressure, can be derived:

$$b = (\partial \ln k/\partial p)_T = -\Delta V_0^{\ddagger}/\boldsymbol{R}T. \qquad (3)$$

Values of $\Delta V_0^{\ddagger}$ are presented in the Table, together with the molar volume of reaction, ΔV, for the completed reactions (1), as determined by Spiro *et al.*[4] The striking feature of the data is that $\Delta V_0^\ddagger$ and ΔV are essentially *equal*, if due allowance is made for the experimental uncertainty ($\pm 0{\cdot}5$ ml. in $\Delta V_0^\ddagger$, and $\pm 0{\cdot}4$ ml. in ΔV with the exception of SO_4^{2-} for which the uncertainty is increased by ion-pairing[4]) and for the small effects of temperature and ionic strength differences.[4]

TABLE

Volumes of activation and volumes of reaction for the aquation of $Co(NH_3)_5X^{(3-n)+}$

X^{n-}	$\Delta V_0^\ddagger$, ml. mole$^{-1\,a}$	ΔV, ml. mole$^{-1\,b}$
NO_3^-	− 5·9	− 6·0
Br^-	− 8·6	− 9·6
Cl^-	− 9·7	−10·4
SO_4^{2-}	−16·9	−15·2

[a] 25°; ionic strength $0{\cdot}1M$ ($HClO_4$–$LiClO_4$; $[HClO_4] = 5 \times 10^{-5}M$).
[b] 30°; ionic strength $1{\cdot}0M$ ($NaClO_4$); (from ref. 4).

This phenomenon provides independent support for the mechanism suggested by Langford[5] for reaction (1), according to which the role of X^{n-} in the transition state is closely similar to its role in the product, *viz.*, that of a fully solvated anion, while the entering aqua ligand is at most only weakly bound in the transition state. For ionogenic solvolyses in general, contributions to $\Delta V_0^\ddagger$ from bond-making and bond-breaking are small compared with that from electrostriction of solvent by the developing charges.[6] It would appear that electrostriction of water is as extensive in the transition state of reaction (1) as it is for the completed reaction, since a plot of $\Delta V_0^\ddagger$ against ΔV is essentially a straight line of slope 1·0.

The fact that $\Delta V_0^\ddagger$ is not merely related but virtually *equal* to ΔV can be naïvely rationalised if it is postulated that successful completion of reaction, beyond the formation of a transition-state consisting of the solvated ions $Co(NH_3)_5^{3+}$ and X^{n-}, merely involves the transfer of a water molecule from the solvation sheath of $Co(NH_3)_5^{3+}$ to its first co-ordination sphere. This process would occur with only a very small decrease in volume (as compared with the experimental uncertainty), since the water molecule in question is already under compression arising from an effective pressure of several thousand atmospheres created by electrostriction,[7] and even the volume change associated with the co-ordination of water to Co^{III} from bulk solvent is small.[8]

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[1] A. R. Osborn and E. Whalley, *Canad. J. Chem.*, 1961, **39**, 1094.
[2] J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, 1959, **55**, 809.
[3] H. S. Golinkin, W. G. Laidlaw, and J. B. Hyne, *Canad. J. Chem.*, 1966, **44**, 2193.
[4] T. G. Spiro, A. Revesz, and J. Lee, *J. Amer. Chem. Soc.*, 1968, **90**, 4000.
[5] C. H. Langford, *Inorg. Chem.*, 1965, **4**, 265.
[6] C. T. Burris and K. J. Laidler, *Trans. Faraday Soc.*, 1955, **51**, 1497.
[7] A. J. Ellis, *J. Chem. Soc.* (*A*), 1968, 1138.
[8] H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 2642.