Enthalpy Changes in the Base Hydrolysis of the Halogenopentamminecobalt(III) Ions: Evidence for a Dissociative Mechanism

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THE energies of activation (E_a) (and hence the enthalpies of activation, ΔH_a) for the reactions

$$\mathrm{Co(NH_3)_5X^{2+} + OH^- = Co(NH_3)_5OH^{2+} + X^-}\ (\mathrm{X = Cl, Br, I})$$

have been determined from kinetic data (Table). We have measured the enthalpy changes, ΔH_R, for the above reactions by calorimetry.

With reference to a simple reaction co-ordinate profile (Figure), the transition enthalpy $\Delta H_T = \Delta H_a - \Delta H_R$ permits the calculation of the heat content of the transition-state species with respect to the enthalpy of formation of the common reaction product $\mathrm{Co(NH_3)_5OH^{2+}}$. In a substitution reaction proceeding *via* a five-co-ordinate transition state (dissociative mechanism)

$$\Delta H_T = \Delta H_f\{[\mathrm{Co(NH_3)_4(NH_2)}]^{2+}_{\mathrm{aq}}\} - \Delta H_f\{[\mathrm{Co(NH_3)_5OH}]^{2+}_{\mathrm{aq}}\} + \Delta H_f\,(\mathrm{H_2O})$$

$$\Delta H_T = \Delta H_f\{[\mathrm{Co(NH_3)_5}]^{3+},\ \mathrm{OH^-}\} - \Delta H_f\{[\mathrm{Co(NH_3)_5OH}]^{2+}_{\mathrm{aq}}\}$$

for the conjugate base[1] or S_N1 ion-pair[2] mechanism respectively, and is independent of the leaving group, X.

However, for a reaction proceeding *via* a seven-co-ordinate transition state (associative or concerted mechanism),

$$\Delta H_T = \Delta H_f\{[\mathrm{Co(NH_3)_5X(OH)}]^+_{\mathrm{aq}}\} - \Delta H_f(\mathrm{X}^-_{\mathrm{aq}}) - \Delta H_f\{[\mathrm{Co(NH_3)_5OH}]^{2+}_{\mathrm{aq}}\}$$

and will vary with the nature of the leaving group, X, that is unless the sum of the first two terms is constant. This sum may be constant if the leaving group is functioning very nearly as a solvated anion in the transition state, *i.e.* bond breaking is almost complete and the transition state approximates more closely to a five-co-ordinate system. However, for the S_N2 limiting case, this sum could vary considerably. [The $\Delta H_f(\mathrm{X}^-_{\mathrm{aq}})$ values are −40·0, −28·9 and −13·4 kcal.mole^{-1} for Cl^-, Br^-, and I^- respectively,[3] whereas the $\Delta H_f\{[\mathrm{Co(NH_3)_5X(OH)}]^+_{\mathrm{aq}}\}$ values may be more similar because of the uniform large size of the complex ions and therefore similar hydration enthalpies.]

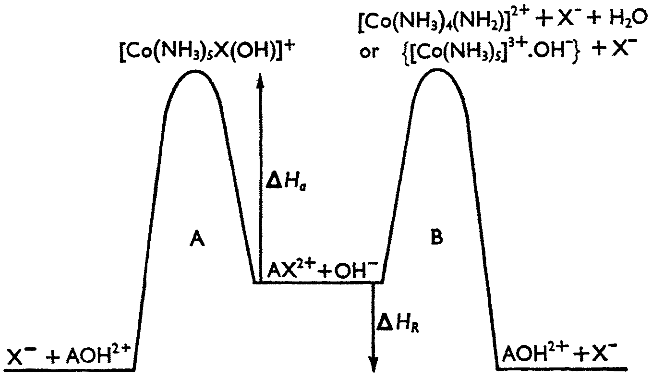

FIGURE. *A simplified reaction-co-ordinate profile for the base hydrolysis of* $\mathrm{AX^{2+}}$ [A = $\mathrm{Co(NH_3)_5}$; X = Cl, Br, I] *assuming seven-* (A) *or five-co-ordinate* (B) *transition states.*

Enthalpy data (kcal.mole^{-1}) for the reaction

$$\mathrm{Co(NH_3)_5X^{2+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^-}$$

X	Cl	Br	I
ΔH_R[a]	−6·0	−5·6	−4·4
E_a	27·2[b]	28·2[c]	28·9[c]
ΔH_a[d]	26·6	27·6	28·3
ΔH_T	32·6	33·2	32·7

[a] At 298°K, ionic strength 0·1 M; estimated error ± 0·2.

[b] G. C. Laylor and G. W. Bushnell, *J. Inorg. Nuclear Chem.*, 1968, **30**, 219.

[c] S. C. Chan, K. Y. Hui, K. Miller, and W. S. Tsang, *J. Chem. Soc.*, 1965, 3207.

[d] $\Delta H_a = E_a - RT = E_a - 0{\cdot}59$ at 289°K.

The constancy of the reported ΔH_T values (Table), confirms a dissociative mechanism involving a common five-co-ordinate transition state.[1] Results from competition reactions[4] involving mixtures of nucleophiles also support such a mechanism.

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[2] S. C. Chan, *J. Chem. Soc.* (*A*), 1967, 2103.
[3] N.B.S. Circular 500 (1952), "Selected Values of Chemical Thermodynamic Properties".
[4] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1966, **88**, 5443; 1967, **89**, 5129; 1968, **90**, 6539, 6654.