## THE AQUATION OF ACIDOPENTAAQUOCHROMIUM(III) COMPLEXES: A CONSIDERATION OF TRANSITION ENTHALPIES

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The aquation reaction

$$Cr(H_2O)_5X^{2+} + H_2O \to Cr(H_2O)_6^{3+} + X^-$$
 (1)

is known to proceed by both acid-dependent and acid-independent paths. When HX is a strong acid ( $X_{-}^{-} = NO_{3}^{-}$ , Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NCS<sup>-</sup>) the rate expression is

rate =  $[complex](k_0 + k_{-1}[H^+]^{-1} + ...)$ 

with the two specific rate constants corresponding to the reactants  $Cr(H_2O)_5X^{2+}$ and  $Cr(H_2O)_4(OH)X^+$  respectively.<sup>1-4</sup> In this paper we consider the "transition enthalpies" for the acid-independent aquation reaction and discuss the nature of the transition state species.

For reaction (1) the transition enthalpy  $\Delta H_{\rm T}$  is defined as  $\Delta H_{\rm a} - \Delta H_{\rm R}$  where  $\Delta H_{\rm a}$  is the activation enthalpy and  $\Delta H_{\rm R}$  is the enthalpy change for the reaction.<sup>5,6</sup>  $\Delta H_{\rm T}$  measures the heat content of the transition state species relative to the enthalpy of formation of the reaction products. For an associative mechanism  $\Delta H_{\rm T}$  will vary with the leaving group X whereas for a dissociative mechanism<sup>†</sup>  $\Delta H_{\rm T}$  will be independent of X.<sup>6</sup> For the base hydrolysis<sup>6</sup> and the aquation<sup>7</sup> reaction of complexes Co(NH<sub>3</sub>)<sub>5</sub>X<sup>2+</sup> an observed constant value of  $\Delta H_{\rm T}$  suggests a dissociative mechanism with the leaving group substantially dissociated and solvated in the transition state.

Table 1 presents values of  $\Delta H_a$ ,  $\Delta H_R$ , and  $\Delta H_T$  for reaction (1). The observed spread of values for  $\Delta H_T$  ( $6 \cdot 4 \pm 1 \cdot 3$  kcal mol<sup>-1</sup>) is larger than for the base hydrolysis<sup>6</sup> ( $2 \cdot 0$  kcal mol<sup>-1</sup>, six compounds) or the aquation<sup>7</sup> ( $2 \cdot 9 \pm 1 \cdot 3$  kcal mol<sup>-1</sup>, four compounds) of Co(NH<sub>3</sub>)<sub>5</sub>X<sup>2+</sup>. The enthalpy of hydration of the leaving group X is increasingly exothermic in the sequence H<sub>2</sub>O, NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-8,9</sup> and the data in

<sup>4</sup> Postmus, C., and King, E. L., J. phys. Chem., 1955, 59, 1216.

<sup>5</sup> House, D. A., and Powell, H. K. J., Chem. Commun., 1969, 383.

- <sup>6</sup> House, D. A., and Powell, H. K. J., Inorg. Chem., 1971, 10, 1583.
- 7 Powell, H. K. J., Inorg. nucl. Chem. Lett., in press.
- <sup>8</sup> U.S. National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties." U.S. natn. Bur. Stand. Tech. Note 270-3.

<sup>9</sup> Dasent, W. E., "Inorganic Energetics." (Penguin: London 1970.)

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<sup>†</sup> The terms "associative" and "dissociative" are defined in ref. 6.

<sup>&</sup>lt;sup>1</sup> Swaddle, T. W., J. Am. chem. Soc., 1967, 89, 4338.

<sup>&</sup>lt;sup>2</sup> Swaddle, T. W., and King, E. L., Inorg. Chem., 1965, 4, 532.

<sup>&</sup>lt;sup>8</sup> Guthrie, F. A., and King, E. L., Inorg. Chem., 1964, 3, 916.

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Table 1 show that the instability of the transition state species relative to the reaction products (i.e.  $\Delta H_{\rm T}$ ) increases in this order. These results suggest<sup>6</sup> that in the transition state the leaving group X is less strongly dissociated and solvated in the reaction of the chromium compounds than in the reaction of the analogous cobalt compounds.

TABLE 1							
ENTHALPY DATA	$(\text{kcal mol}^{-1})$ for the reaction, in aqueous solution						
$\mathrm{Cr}(\mathrm{H}_{2}\mathrm{O})_{5}\mathrm{X}^{2+} + \mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{Cr}(\mathrm{H}_{2}\mathrm{O})_{6}{}^{3+} + \mathrm{X}$							

	$X = H_2O$	$X = Cl^-$	X == Br-	$X = SCN^{-}$	$X = NO_3^-$
$\Delta H_{\rm R}$	0.0	$-6.6+0.5^{a}$	$-5.1 \pm 0.2^{b}$	$1 \cdot 4 + 0 \cdot 2^{\circ}$	$-4.5 \pm 0.2^{d}$
$\Delta H_{a}$	$26 \cdot 1 \pm 1 \cdot 0^{ ext{e}}$	$24 \cdot 3 \pm 0 \cdot 2^{\mathrm{f}}$	$23 \cdot 8 \pm 0 \cdot 3^{\mathrm{g}}$	$27 \cdot 5h$	$21 \cdot 6 \pm 0 \cdot 1^{i}$
$\Delta H_{\mathrm{T}}$	$26 \cdot 1 \pm 1 \cdot 0$	$30.9 \pm 0.7$	$28 \cdot 9 \pm 0 \cdot 5$	$25 \cdot 9 \pm 0 \cdot 4^{0,11}$ 26 · 1	$26 \cdot 1 \pm 0 \cdot 3$
				$24\cdot5\pm0\cdot6$	

<sup>a</sup> Schug, K., and King, E. L., J. Am. chem. Soc., 1958, 80, 1089.

<sup>b</sup> Espensen, J. H., and King, E. L., J. phys. Chem., 1960, 64, 380.

<sup>c</sup> Poulsen, K. G., Bjerrum, J., and Poulsen, I., Acta chem. scand., 1954, 8, 921.

<sup>d</sup> Ardon, M., and Sutin, N., Inorg. Chem., 1967, 6, 2268.

° Hunt, J. P., and Plane, R. A., J. Am. chem. Soc., 1954, 76, 5960 ( $\Delta H_a = E_{-1}^{\circ} - RT$  assuming a unimolecular reaction).

<sup>f</sup> Ref. 2.

<sup>g</sup> Ref. 3.

<sup>h</sup> Ref. 4;  $\Delta H_a = E_a - RT$ .

<sup>i</sup> Ref. 1.

This deduction is consistent with the observed<sup>1,2</sup> correlation between  $S_{\mathbf{x}}^{\circ}$  (corrected for rotation of X<sup>-</sup>) and  $\Delta S^{\ddagger}$  for reaction (1):

 $\Delta S^{\ddagger} = pS_{\mathbf{x}}^{\circ} + C$  (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>)

where p = 0.53. In contrast  $p \approx 1.0$  for  $Co(NH_3)_5 X^{2+}$  aquation, and for this reaction linear free energy<sup>10</sup> and transition enthalpy<sup>7</sup> correlations indicate that the leaving group X is substantially dissociated and solvated in the transition state.

<sup>10</sup> Langford, C. H., Inorg. Chem., 1965, 4, 265.