with the expectations that the binuclear complexes of type $M(C_2O_4)_3{}^{3-}$–Ce(IV) will be of similar stability that the remaining details of coordination about the cerium(IV) will be similar for such complexes and for the transition state and that the rhodium and cobalt centers will influence similarly the capacity of oxalate to transfer an electron to cerium(IV).

Acknowledgment.—We wish to thank Mrs. Nancy S. Rowan for helpful discussions on this work.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CANTERBURY, CHRISTCHURCH, NEW ZEALAND

Enthalpy Data as Evidence for a Dissociative Mechanism in the Base Hydrolysis of Some Acidopentaamminecobalt(III) Complexes

BY D. A. HOUSE AND H. K. J. POWELL*

Received November 20, 1970

The enthalpy changes for the reactions $Co(NH_3)_5X^{2+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^-$ (X = Cl, Br, I, NO_3) have been measured in 0.097 *F* NaOH at 25° as -6.1 ± 0.25, -5.7 ± 0.15, -3.65 ± 0.05, and -3.85 ± 0.05 kcal mol^{-1}, respectively. These numerical data, when subtracted from the enthalpies of activation for these reactions, give a constant value of 32.0 ± 0.9 kcal mol^{-1} for the "transition enthalpy." This experimental result and other calculated data are discussed in support of a transition state in which the leaving group is essentially dissociated. The heats of formation of the complexes $Co(NH_3)_5X^{n+}$ ($X = OH^-$, H_2O, I^-) were determined as -172.0 ± 0.8, -180.8 ± 0.9, and -126.6 ± 1.0 kcal mol^{-1}, respectively.

Introduction

The mechanism of the base hydrolysis of octahedral cobalt(III) complexes has been the subject of much discussion.[1] Both bimolecular (associative) (SN2,[2] SN2IP,[3] and SN2CB[4]) and unimolecular (dissociative) (SN1CB[1,5] and SN1IP[3]) displacement mechanisms (CB, conjugate base; IP, ion pair) have been proposed and recently Gillard[6] has postulated a bimolecular mechanism involving electron transfer.

For the reaction

$$Co(NH_3)_5X^{2+} + OH^- \longrightarrow Co(NH_3)_5OH^{2+} + X^- \qquad (1)$$

the rate law rate = k_2[complex][OH^-] indicates that the nucleophile is involved in the approach to the transition state. However, the nucleophile may or may not be a part of the metal coordination sphere in the transition state. By considering the involvement of OH^- in the rate expression alone, it is not possible to distinguish between the associative or dissociative mechanisms.[7]

To focus attention on the leaving group in the transition state, we have measured the enthalpy changes for the base hydrolysis reactions $Co(NH_3)_5X^{2+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^-$ (X = Cl, Br, I, NO_3). We find that the heat content of the transition state species, with respect to the products X^- and $Co(NH_3)_5OH^{2+}$, is essentially constant and independent of the leaving group. These results are discussed in support of a dissociative[7] mechanism for this type of reaction.

Experimental Section

Complex Salts and Analyses.—The perchlorate salts of the acidopentaamminecobalt(III) cations were prepared from solutions of the halide or nitrate salts in 0.1 *F* $HClO_4$ by the addition of excess $NaClO_4 \cdot H_2O$. These salts were recrystallized twice from 0.1 *F* $HClO_4$ by the addition of $NaClO_4 \cdot H_2O$. $[Co(NH_3)_5NO_3](NO_3)_2$ was prepared using the method of Schlessinger.[8] Ammonia was determined using a micro Kjeldahl apparatus. The complexes were decomposed with hot NaOH solution (7 *F*) and the released NH_3 was steam distilled into 2% boric acid and titrated with standard HCl solution. *Anal.* Calcd for $[Co(NH_3)_5Cl](ClO_4)_2$:[8] NH_3, 22.5. Found: NH_3, 22.3. Calcd for $[Co(NH_3)_5Br](ClO_4)_2$:[8] NH_3, 20.1. Found: NH_3, 20.0. Calcd for $[Co(NH_3)_5I](ClO_4)_2$:[9] NH_3, 18.1. Found: NH_3, 18.3. Calcd for $[Co(NH_3)_5OH_2](ClO_4)_3$:[8] NH_3, 18.5. Found: NH_3, 18.5. Calcd for $[Co(NH_3)_5NO_3](NO_3)_2$: NH_3, 25.8. Found: NH_3, 26.0.

The Calorimeter.—The calorimeter and circuits were essentially the same as described previously.[10] The solid sample container was similar to that described by Arnett, *et al.*[11] Solutions were added as weighed samples from thin-walled glass bulbs. The heat changes associated with container opening or bulb breaking were not detectable (<0.009 cal).

The accuracy and reliability of the calorimeter were tested by measuring the heat of solution of potassium chloride. Analar KCl was recrystallized from hot water, oven dried, ground, and sieved to 100 mesh. For the solution of KCl (1:500), ΔH was determined as 4179 ± 11 cal mol^{-1} (mean of four measurements; ± value is the standard deviation), in satisfactory agreement with the literature value[12] of 4200 cal mol^{-1}.

Enthalpy Changes.—For the complexes $Co(NH_3)_5X^{2+}$ (X = I, NO_3), the enthalpy of base hydrolysis (ΔH_R, reaction 1) was determined by addition of a small sample of concentrated alkali (*ca.* 2 ml of 1 *F* NaOH) to a solution (95 or 100 ml) of $Co(NH_3)_5X^{2+}$ (*ca.* 6×10^{-3} *F*) in $NaClO_4$ (0.08 *F*) and $HClO_4$ (*ca.* 5×10^{-3}

---

[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

[2] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956).

[3] S. C. Chan, *J. Chem. Soc. A*, 1124 (1966).

[4] M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).

[5] F. J. Garrick, *Nature (London)*, **139**, 507 (1937).

[6] R. D. Gillard, *J. Chem. Soc. A*, 917 (1967).

[7] Here we define an associative mechanism as one involving a seven-coordinate transition state with the OH^- and X^- groups associated with the metal ion. Conversely, a dissociative mechanism is one involving a six-coordinate transition state with the X^- group substantially dissociated and the OH^- not directly involved in the coordination sphere. This six-coordinate transition state could subsequently form a five-coordinate intermediate with the X^- group completely dissociated (see Figure 1).

[8] G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., New York, N. Y., 1962.

[9] R. G. Yalman, *J. Amer. Chem. Soc.*, **77**, 3219 (1955).

[10] H. K. J. Powell and N. F. Curtis, *J. Chem. Soc. B*, 1205 (1966).

[11] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).

[12] *Nat. Bur. Stand. (U. S), Circ.*, **No. 500** (1950).

TABLE I

ENTHALPY DATA FOR BASE HYDROLYSIS (REACTION 1) AND DISSOLUTION (REACTIONS 3 AND 4) OF COMPLEXES $Co(NH_3)_5X^{n+}$ ($X^- = Cl^-, Br^-, I^-, NO_3^-$)

Run no.	X^-	Reaction type	[Complex], mmol	Q, cal	Q_{cor}, cal ($=Q + A^a + B^b + C^c$)	ΔH, kcal mol^{-1}	
1	Cl^-	3	0.7436	11.89	11.9 ± 0.1	16.0	16.0 ± 0.15[e]
2	Cl^-	3	0.7436	11.85	11.85 ± 0.05	15.95	
3	Cl^-	3	0.7436	11.79	11.79 ± 0.05	15.85	
4	Cl^-	3	0.7436	12.01	12.01 ± 0.05	16.15	
5	Cl^-	4	0.7436	7.46	7.46 ± 0.07	9.9	9.9 ± 0.1[e]
6	Cl^-	4	0.7436	7.26	7.26 ± 0.07	9.8	
7	Cl^-	4	0.7436	7.37	7.37 ± 0.07	9.9	
8	Cl^-	4	0.7443	7.30	7.30 ± 0.07	9.8	
9	Cl^-	4	0.7443	7.47	7.47 ± 0.04	10.0	
10	Br^-	3	0.7315	11.75	11.75 ± 0.05	16.07	16.15 ± 0.1[e]
11	Br^-	3	0.7285	11.80	11.80 ± 0.05	16.20	
12	Br^-	3	0.7308	11.74	11.74 ± 0.05	16.07	
13	Br^-	4	0.7290	7.61	7.61 ± 0.07	10.45	10.40 ± 0.05[e]
14	Br^-	4	0.7290	7.57	7.57 ± 0.07	10.4	
15	Br^-	4	0.7303	7.61	7.61 ± 0.07	10.4	
16	I^-	1	0.5220	−6.33	−1.80 ± 0.02	−3.63[d]	−3.65 ± 0.05[e]
17	I^-	1	0.6060	−8.78	−2.20 ± 0.02	−3.73[d]	
18	I^-	1	0.5875	−8.69	−2.10 ± 0.02	−3.67[d]	
19	NO_3^-	1	0.5190	−8.56	−1.85 ± 0.02	−3.85[d]	−3.85 ± 0.05[e]
20	NO_3^-	1	0.5190	−8.56	−1.85 ± 0.02	−3.85[d]	

[a] Correction for heat of dilution of NaOH: runs 17 and 18, *ca.* 1.2 ml of 1.2 *M* NaOH, 0.04 cal; runs 16, 19, and 20, *ca.* 2.0 ml of 1.0 *M* NaOH, 0.05 cal. [b] Correction for neutralization of $HClO_4$ present: run 16, 4.05×10^{-4} mol, 4.37 cal; runs 17 and 18, 4.805×10^{-4} mol, 6.47 cal; runs 19 and 20, 4.812×10^{-4} mol, 6.50 cal. [c] Correction for neutralization of aquopentaamminecobalt(III) ion, reaction 2: 0.11, 0.07, 0.16, and 0.16 cal for runs 16–20, respectively: A. J. Cunningham, D. A. House, and H. K. J. Powell, *Aust. J. Chem.*, **23,** 2375 (1970). [d] Calculation of these molar quantities involved allowance for the aquation of the reactant $Co(NH_3)_5X^{2+}$. [e] Mean value ± standard deviation from the mean.

F) solution. Data are given in Table I. The observed heat change was corrected for (a) the heat of dilution of NaOH(aq),[12] (b) the heat of neutralization of the $HClO_4$ present ($\Delta H = -13.5$ kcal mol^{-1} at $\mu = 0.10$, extrapolated from data in ref 13), and (c) the heat of neutralization of the aquo complex (eq 2) which forms

$$Co(NH_3)_5OH_2^{3+} + OH^- \longrightarrow Co(NH_3)_5OH^{2+} + H_2O \quad (2)$$

from the aquation of $Co(NH_3)_5X^{2+}$ during the equilibration of the acid solution of complex in the calorimeter. The amount of aquation was calculated using the rate constants 1.64×10^{-3} min^{-1} (NO_3^-) and 5×10^{-4} min^{-1} (I^-) and for example amounted to 7.1% (NO_3^-, 45-min equilibration, runs 19 and 20) and 4.1% (I^-, 80-min equilibration, run 16). In Table I, $Q_{cor} = Q + A + B + C$. The heat change for reaction 2 was determined as for reaction 1 with corrections (a) and (b) above being applied.

For the chloro and bromo complexes, ΔH_R was determined from the difference between the heat of solution of the solid (a) in dilute acid (0.097 *F* $NaClO_4$; *ca.* pH 3, $HClO_4$), ΔH_s, and (b) in 0.097 *F* NaOH, ΔH_B.

$$[Co(NH_3)_5X](ClO_4)_2(s) + xH_2O \longrightarrow Co(NH_3)_5X^{2+}(aq) + 2ClO_4^-(aq) \quad \Delta H_s \quad (3)$$

$$[Co(NH_3)_5X](ClO_4)_2(s) + xH_2O + OH^- \longrightarrow Co(NH_3)_5OH^{2+}(aq) + 2ClO_4^-(aq) + X^-(aq) \quad \Delta H_B \quad (4)$$

I.e., $\Delta H_R = \Delta H_B - \Delta H_s$. Solution of solid samples was complete in 1–6 min.

Results and Discussion

Results for reactions 1, 3, and 4 are given in Table I. The base hydrolysis reaction

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

is one example of a cobalt(III) ligand substitution in aqueous solution where a nucleophile, other than water, appears to react directly with the cobalt complex. Rates for hydroxide ion substitution are six to eight orders of magnitude greater than those for other base nucleophiles (*e.g.*, N_3^-) upon cobalt(III) complexes.

A simplified reaction coordinate profile, illustrating the two types of mechanism, is given in Figure 1.

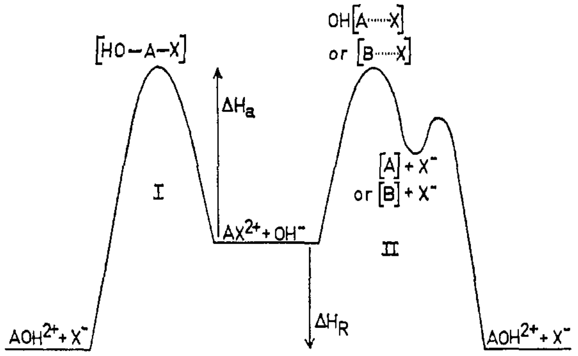


Figure 1.—A simplified reaction coordinate profile for the base hydrolysis $AX^{2+} + OH^- \rightarrow AOH^{2+} + X^-$ [$A = Co(NH_3)_5$; $B = Co(NH_3)_4NH_2$; X = Cl, Br, I, NO_3] assuming an associative transition state (I) or a dissociative transition state (II) with a five-coordinate intermediate.

(This is simplified to the extent that ion-pair ($Co(NH_3)_5X,OH^+$) or amido complex ($Co(NH_3)_4(NH_2)X^+$) formation may give rise to low-energy transition states before the formation of the rate determining transition state.) In consideration of the thermodynamics of the systems presented in Figure 1, we define a quantity, the transition enthalpy (ΔH_T) such that $\Delta H_T = \Delta H_a - \Delta H_R$, where ΔH_a is the activation enthalpy and ΔH_R is the enthalpy change for the base hydrolysis reaction. ΔH_a values are available from the literature and ΔH_R values have been measured calorimetrically at 25°.

The transition enthalpy permits the calculation of the heat content of the transition state species with respect to the enthalpy of formation of the reaction products, $Co(NH_3)_5OH^{2+}$ and X^-. For a substitution reaction proceeding *via* a strictly five-coordinate transition state, the leaving group will be independent of the complex species in the transition state. The transition enthalpy will thus be independent of the leaving group which appears in the same form (X^-(aq)) in both the

---

(13) J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, **67,** 2605 (1963).

TABLE II

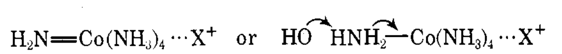
ENTHALPY DATA (KCAL MOL^{-1}) FOR THE REACTION $Co(NH_3)_5X^{2+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^-$ IN AQUEOUS SOLUTION

	X			
	Cl	Br	I	NO_3
ΔH_R[a]	-6.1 ± 0.25	-5.7 ± 0.15	-3.65 ± 0.05[b]	-3.85 ± 0.05
E_a	27.2[c]	27.6[d]	27.8[e]	28.8[f]
ΔH_a[g]	26.6	27.0	27.2	28.2
$\Delta H_T = \Delta H_a - \Delta H_R$	32.7	32.7	30.85	32.05

[a] At 298°K, ionic strength *ca.* 0.1 *F*. [b] A different value reported earlier (−4.4 kcal mol^{-1}) (D. A. House and H. K. J. Powell, *Chem. Commun.*, 383 (1969)) resulted from the use of an incorrect value for the heat of dilution of NaOH solution. [c] G. C. Lalor and W. Bushnell, *J. Inorg. Nucl. Chem.*, **30**, 219 (1968). [d] M. B. Davies and G. C. Lalor, *ibid.*, **31**, 799 (1969). [e] M. B. Davies and G. C. Lalor, *ibid.*, **31**, 2189 (1969); A. J. Cunningham, D. A. House, and H. K. J. Powell, *ibid.*, **33,** 572 (1971). [f] W. E. Jones, R. B. Jordan, and T. W. Swaddle, *Inorg. Chem.*, **8,** 2504 (1969). [g] $\Delta H_a = E_a - RT = E_a - 0.59$ at 298°K, where E_a is the activation energy.

product and transition states. However, for a reaction proceeding *via* an associative mechanism and a seven-coordinate transition state, the transition enthalpy will vary with the nature of the leaving group X, that is, unless the algebraic sum of the heats of formation of $Co(NH_3)_5X(OH)^+$ and X^- is invariant with X. This latter possibility is considered to be unlikely as the $\Delta H_f(X^-(aq))$ values are −49.6, −40.0, −29.0, and −13.2 kcal mol^{-1} for NO_3^-, Cl^-, Br^-, and I^-, respectively,[14] whereas the $\Delta H_f(Co(NH_3)_5X(OH)^+(aq))$ values may be more similar because of the uniform large size of the complex ions and therefore similar hydration enthalpies. For comparison, using NBS data[14] for the heats of formation of acidopentaamminecobalt(III) complexes, the differences $\Delta H_f(X^-(aq)) - \Delta H_f(Co(NH_3)_5X^{2+}(aq))$ are 110.2, 110.1, 112.1, 113.2, and 121.6 kcal mol^{-1} for X = SO_4^{2-}, Cl^-, Br^-, NO_3^-, and NO_2^-, respectively, a spread of 11.4 kcal mol^{-1}.

The resultant thermodynamic data are shown in Table II. The ΔH_T values vary only slightly with the leaving group X and the uncertainties in the ΔH_a data may well account for the observed spread of 1.9 kcal mol^{-1}. We consider that this observation supports a dissociative mechanism which may involve transition state species such as



$$H_2N{=}Co(NH_3)_4\cdots X^+ \quad \text{or} \quad HO\ HNH_2{-}Co(NH_3)_4\cdots X^+$$

where the leaving group X is substantially dissociated and solvated.

Complexes containing acido groups other than Cl^-, Br^-, I^-, and NO_3^- react too slowly with OH^- to permit accurate calorimetric studies at 25°. At higher temperatures (50°), extensive deamminolysis occurs in the basic solution to yield cobalt oxides. We note that ΔH_R is given by the algebraic sum of four terms

$$\Delta H_R = \Delta H_f(Co(NH_3)_5OH^{2+}(aq)) - \Delta H_f(OH^-(aq)) + \Delta H_f(X^-(aq)) - \Delta H_f(Co(NH_3)_5X^{2+}(aq))$$

and of these, the first two are common for different substrates, and $\Delta H_f(X^-(aq))$ is known for many anions.[14] This equation can be used to extend the series of ΔH_R values.

From the $\Delta H_f(Co(NH_3)_5X^{2+}(aq))$ data[14] for X^- = Cl^-, Br^-, and NO_3^- (−150.1, −141.1, and −162.8 kcal mol^{-1}, respectively) and our ΔH_R values for these ions, the constant $\Delta H_f(Co(NH_3)_5OH^{2+}(aq)) - \Delta H_f(OH^-(aq))$ is calculated to be -117.0 ± 0.8 kcal mol^{-1} Using this value and NBS data[14] for $\Delta H_f(Co(NH_3)_5X^{n+}(aq))$ where X = NO_2^- and SO_4^{2-} (−146.6 and −327.5 kcal mol^{-1}, respectively), we calculate ΔH_R as 4.6 and −6.8 kcal mol^{-1}. From the ΔH_a data (37.4[1] and 25.7[15] kcal mol^{-1}, respectively) we calculate ΔH_T as 32.8 and 32.5 kcal mol^{-1} for X = NO_2^- and SO_4^{2-}. These data are in good agreement with the values in Table II and further support a dissociative mechanism.

Support for a dissociative mechanism for the base hydrolysis of these complexes also comes from other experiments which investigate the role of the leaving group in the transition state, *e.g.*, nucleophile competition reactions,[16] $Co(NH_3)_5X^{2+}$ + 0.01 *F* NaOH + 0.5 *F* NaY (Y^- = N_3^-, NCS^-, NO_2^-), in which the uptake of nucleophile Y (2–10%) is independent of the leaving group X and of the $[OH^-]$ but dependent on Y. This requires that the OH^- generates a common intermediate (shown in the right-hand reaction profile of Figure 1) which reacts with either water (or OH^-) or Y.

The heats of formation of the $Co(NH_3)_5OH^{2+}$ and $Co(NH_3)_5OH_2^{3+}$ ions are also obtained from our data. Using the relationship $\Delta H_f(Co(NH_3)_5OH^{2+}(aq)) - \Delta H_f(OH^-(aq)) = -117.0 \pm 0.8$ kcal mol^{-1} and $\Delta H_f(OH^-(aq)) = -55.0$ kcal mol^{-1},[14] we calculate $\Delta H_f(Co(NH_3)_5OH^{2+}(aq)) = -172.0 \pm 0.8$ kcal mol^{-1}. The enthalpy change for the deprotonation of $Co(NH_3)_5OH_2^{3+}$ is given by[17]

$$\Delta H = -4.5 \pm 0.1 \text{ kcal mol}^{-1} = \Delta H_f(Co(NH_3)_5OH^{2+}(aq)) + \Delta H_f(H_2O(l)) - \Delta H_f(OH^-(aq)) - \Delta H_f(Co(NH_3)_5OH_2^{3+}(aq))$$

Taking $\Delta H_f(H_2O(l)) = -68.3$ kcal mol^{-1}, the above data give $\Delta H_f(Co(NH_3)_5OH_2^{3+}(aq))$ as -180.8 ± 0.9 kcal mol^{-1}, compared with the NBS value[14] of −181.7 kcal mol^{-1}.

A similar calculation using

$$\Delta H_R(I^-) = \Delta H_f(Co(NH_3)_5OH^{2+}(aq)) + \Delta H_f(I^-(aq)) - \Delta H_f(OH^-(aq)) - \Delta H_f(Co(NH_3)_5I^{2+}(aq))$$

yields the heat of formation of the iodo complex as -126.6 ± 1.0 kcal mol^{-1}.

Acknowledgments.—The Research Grants Committee of the New Zealand Universities Grants Committee is thanked for financial assistance toward components for the calorimeter.

---

(14) *Nat. Bur. Stand. (U. S.), Tech. Note,* **No. 270-3, 270-4** (1970).

(15) L. L. Po and R. B. Jordan, *Inorg. Chem.*, **7**, 526 (1968).

(16) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **88,** 5443 (1966).

(17) A. J. Cunningham, D. A. House, and H. K. J. Powell, *Aust. J. Chem.*, **23,** 2375 (1971).