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Kinetic Studies of the Aquopentaamminecobalt(III)/- and Aquopentaamminechromium(III)/ Hydrogen Chromate Complexation Reaction[1]

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The kinetics of the complexation reaction between $M(NH_3)_5OH_2^{3+}$ (M = Co, Cr) and $HCrO_4^-$ have been determined by stopped-flow measurements in acidic aqueous solution ($\mu = 0.50$ M). A new mechanism is proposed to account for the nonlinear acid dependence of the reaction rate at low pH. Aquation of the complex occurs almost exclusively via the protonated species, $M(NH_3)_5HCrO_4^{2+}$. Activation parameters for the Cr(III) complexation with $HCrO_4^-$ have been measured and are discussed in relation to other oxo anion substitution reactions.

Introduction

Substitution mechanisms of oxo anion species have been the focus of recent attention.[3-7] Reactions between Co(III) or Cr(III) cations and oxo anions can be divided into four major categories: (i) "slow" processes involving fission of the M(III)–O bond in the cation, (ii) ligand linkage isomerization of a coordinated oxo anion, (iii) oxo anion addition to the aquo ligand of the cation, and (iv) "fast" reactions involving cleavage of the X–O bond in the oxo anion.

Our interest in the type iv complexation reaction between aquo pentaammine species and $HCrO_4^-$ was prompted by conflicting rate expressions proposed for the formation of chromatopentaamminecobalt(III) (eq 1) in acidic solution.[8,9]

$$\mathrm{Co(NH_3)_5OH_2^{3+} + HCrO_4^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} complex + H_2O} \qquad (1)$$

Woods and Sullivan[8] used the stopped-flow technique to monitor the absorbance change at 255 nm resulting from mixing $Co(NH_3)_5OH_2^{3+}$ and $HCrO_4^-$ over the pH range 2.3–4, while Okumura and co-workers[9] investigated both the hydrolysis of $[Co(NH_3)_5CrO_4]Cl{\cdot}H_2O$ (pH 6.0–8.5) and the anation of $Co(NH_3)_5OH_2^{3+}$ by $HCrO_4^-$ (pH 3.5–7.5). The major difference between the studies was the acid-catalysis term found for the forward reaction by Okumura et al.[9]

Our preliminary results showed that neither reaction scheme adequately described the complexation kinetics at higher acidities. We have therefore reinvestigated the $Co(NH_3)_5OH_2^{3+}/HCrO_4^-$ complexation at 25 °C in order to identify the major species in solution, resolve the reaction scheme, and determine the dominant mechanisms. Reaction with $Cr(NH_3)_5OH_2^{3+}$ was used to assess the effect of the entering "ligand" upon the kinetics of Cr(VI) substitution. Activation parameters were evaluated for this reaction and are discussed in relation to other oxo anion substitution processes.

Experimental Section

Materials and Solution Preparation. The synthesis and characterization of $[Co(NH_3)_5OH_2](ClO_4)_3$ and $[Cr(NH_3)_5OH_2](ClO_4)_3$ have been described previously.[3] Stock solutions of $Cr(NH_3)_5OH_2^{3+}$ were prepared daily to avoid hydrolysis and polymerization. Chromium(VI) solutions were prepared from $Na_2CrO_4{\cdot}4H_2O$ and standardized spectrophotometrically.[3]

Solutions, prepared from twice-distilled, once-deionized water, were maintained at 0.50 M ionic strength by addition of a standardized $NaClO_4$ solution.

Preliminary results showed that the observed reaction rate was extremely sensitive to acid concentration, and consequently both reactant solutions were adjusted to the same pH (within ±0.002 unit) prior to mixing in the stopped-flow apparatus. It was also noted that $[H^+]$ increased during reaction; thus equal aliquots of each reactant were mixed and allowed to reach equilibrium, and the pH was remeasured. In all cases, this final pH agreed with the stopped-flow effluent value within 0.05 pH unit.

Physical Methods. A full description of the stopped-flow apparatus and the kinetic procedure is given elsewhere.[6] Reaction traces were recorded at 380 nm corresponding to the wavelength of maximum absorbance enhancement.[3] Usually 12 runs were recorded for each solution and signal-averaged.

The measurement of solution pH was performed using a Radiometer GK2401C combined glass electrode, in which the saturated KCl reference solution was replaced with 0.50 M NaCl to prevent the precipitation of $KClO_4$ at the liquid junction. The electrode was calibrated daily with $[H^+]$ standards at $\mu = 0.50$ M.

Iterative nonlinear least-squares analyses were performed using the ITERAT routine.[10]

Results

The transient generated by the mixing of $Co(NH_3)_5OH_2^{3+}$ and $HCrO_4^-$ in acidic solution was a combination of two reactions, as shown in Figure 1. The initial decrease in absorbance was due to the response of the $HCrO_4^-/Cr_2O_7^{2-}$ equilibrium to the 2-fold dilution involved in the stopped-flow experiment. The increase in absorbance during the slower second process agreed with the absorbance enhancement upon formation of $Co(NH_3)_5HCrO_4^{2+}$.[3]

Determination of the complexation kinetics necessitated resolution of these two processes, requiring accurate rate constants for the chromium(VI) dimerization. This reaction has been well characterized at 25 °C and a range of ionic strengths, including $\mu = 0.1$ M,[11] $\mu = 0.2$ M,[12] and $\mu = 1.0$ M.[13] A brief reinvestigation

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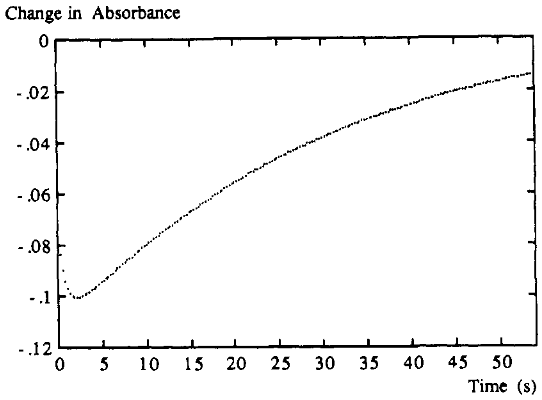

Figure 1. Preliminary stopped-flow reaction transient for $Co(NH_3)_5OH_2^{3+}/HCrO_4^-$ complexation illustrating the two different absorbance changes.

of this process was conducted at 0.50 M ionic strength, over the temperature range 10–30 °C.

Kinetics of the Chromium(VI) Dimerization Reaction. The dimerization equilibrium was perturbed by mixing the Cr(VI) solution with water at the same pH and ionic strength. Reaction transients were recorded at 380 nm for solutions ranging in total chromium(VI) concentration from 1×10^{-3} to 5×10^{-3} M and in pH from 3.3 to 4.4.

Data analysis was performed according to Pladziewicz and Espenson, and the kinetics conformed to their rate law:[13]

$$-d[Cr_2O_7^{2-}]/dt = k_1[Cr_2O_7^{2-}][H^+] - k_2[HCrO_4^-]^2[H^+]$$

Values for k_1, k_2, and the dimerization constant, K_D, are presented in Table I. There is excellent agreement between the kinetically determined value for K_D (77 ± 3 M^{-1}) and the independent spectrophotometric value of 74 ± 3 M^{-1}.[3] At other temperatures, first-order rate constants needed for the resolution of the complexation reaction transients were interpolated from plots of k_{obs} versus $[H^+]$. Equilibrium concentrations of $HCrO_4^-$ at each temperature were calculated using K_D values determined previously.[3]

Kinetics of the $M(NH_3)_5OH_2^{3+}/HCrO_4^-$ Complexation Reaction. Reaction transients were recorded for the complexation process between $M(NH_3)_5OH_2^{3+}$ and $HCrO_4^-$ over the pH ranges 2–6 for M = Co and 2–4 for M = Cr. The $M(NH_3)_5OH_2^{3+}$ concentrations were varied between 3.125×10^{-3} M and the solubility limit of 2.50×10^{-2} M.[14] The chromium(VI) concentration was held fixed at 1.00×10^{-3} M for all kinetic measurements. The equilibria describing solution speciation are illustrated in Scheme I.

(a) Complexation Reaction between $Co(NH_3)_5OH_2^{3+}$ and $HCrO_4^-$ at 25.0 °C. Rate constants were determined from a Guggenheim analysis of the deconvoluted reaction transients.[15] All reactions were found to be first-order for at least 5 half-lives. The rate of complexation was found to depend upon both pH and cation concentration.

Figure 2 illustrates the dependence of the observed rate constant upon $[H^+]$ for [Co(III)] = 0.0125 M. Similar behavior was observed for all cation concentrations. The acid dependence can be nominally divided into three separate regions: At the lowest acid concentrations studied, an inverse relationship is apparent. In the middle acid range (0.0005–0.003 M), the rate constant appears directly proportional to $[H^+]$, while at high $[H^+]$ (>0.01 M), the rate constant is tending toward a constant value. The linear dependence and the reciprocal acid term are consistent with the reaction schemes proposed both by Haight[16] (based on the data of Woods and Sullivan[8]) and by Okumura and co-workers.[9] However, our kinetic measurements at acid concentrations higher than those used in either of the previous studies have revealed that these schemes do not fully describe the complexation process. The results of both Woods and Sullivan and Okumura et al. would suggest that, even at very low pH, the linear dependence upon $[H^+]$ would continue, in contradiction to the experimentally determined behavior depicted in Figure 2.

(b) Development of the Rate Expression. The concentration excess of Co(III) over Cr(VI) was limited to a range of 3:1 up to a maximum of 25:1 by solubility and the necessity of a detectable absorbance change during reaction. Consequently, an expression for k_{obs} was developed which incorporated changes to both reactant concentrations during complexation:[17]

$$k_{obs} = k_f([CoOH_2^{3+}]_0 + [HCrO_4^-]_0 - 1.5a_2[CoHCrO_4^{2+}]_e) + k_r \quad (2)$$

where $[CoOH_2^{3+}]_0$ and $[HCrO_4^-]_0$ are the concentrations at the "instant of mixing", a_2 (=1 + $K_{CH}[H^+]^{-1}$) describes the mass balance between protonated and deprotonated product, and $[CoHCrO_4^{2+}]_e$ is the concentration at equilibrium.

Under the conditions used here, the ratio of $([CoOH_2^{3+}]_0 + [HCrO_4^-]_0)$ to $(1.5a_2[CoHCrO_4^{2+}]_e)$ was normally in excess of 20 (and often much larger),[18] so that the sum of the initial reactant concentrations dominates the term in eq 2.

At all Co(III) concentrations, the acid dependencies of k_f and k_r conformed to

$$k_f = k_a + k_b[H^+]^{-1} \qquad k_r = k_c(x + y[H^+]^{-1})^{-1}$$

The acid dependence of k_r is consistent with the reverse aquation reaction proceeding solely via the protonated $Co(NH_3)_5HCrO_4^{2+}$ species, where x and y are 1 and K_{CH}, respectively, so that eq 2 becomes

$$k_{obs} = (k_a + k_b[H^+]^{-1})f + k_c(1 + K_{CH}[H^+]^{-1})^{-1} \quad (3)$$

where

$$f = [CoOH_2^{3+}]_0 + [HCrO_4^-]_0 - 1.5[CoHCrO_4^{2+}]_e(1 + K_{CH}[H^+]^{-1})$$

Equation 3 was solved simultaneously for k_a, k_b, and k_c using ITERAT. Values of K_C and K_{CH} have been obtained previously.[3] A weighting scheme involving the inverse square of the proportional error for each rate constant as suggested by Nielsen[19] was applied.

The derived rate constants were evaluated as $k_a = 2.53 \pm 0.13$ $M^{-1}\,s^{-1}$, $k_b = (1.16 \pm 0.2) \times 10^{-4}$ $M^{-1}\,s^{-1}$, and $k_c = 0.493 \pm 0.009$ s^{-1}. Okumura and co-workers reported a value for k_a of 2.30 ± 0.09 $M^{-1}\,s^{-1}$, while Woods and Sullivan found values of 0.80 ± 0.20 $M^{-1}\,s^{-1}$ for k_a and (1.68 ± 0.38) × 10^{-4} $M^{-1}\,s^{-1}$ for k_b. At low acid concentrations, $[H^+] \ll K_{CH}$; consequently the reverse term may be approximated by $k_c[H^+]K_{CH}$ to allow comparison with the corresponding values obtained in the other studies. The value of 111 ± 4 $M^{-1}\,s^{-1}$ determined in this manner lies between the (k_r) value of 64 ± 4 $M^{-1}\,s^{-1}$ found by Woods and Sullivan and the value of 151 ± 5 $M^{-1}\,s^{-1}$ reported by Okumura et al.

Incorporation of an ion-pairing term into the rate expression improved the calculated fit to the experimental data. The concentration term, f, in eq 3 was modified according to eq 4, where K_{os} is the outer-sphere ion-pairing constant between

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[14] All reactant concentrations quoted in the stopped-flow studies are at the "instant of mixing" and are thus half the analyte concentration.

[15] Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; John Wiley and Sons: New York, 1961.

[16] Haight, G. P., Jr. *Inorg. Chem.* **1973**, *12*, 1461.

[17] A brief derivation of this expression is given in the supplementary material.

[18] Values for $[CoOH_2^{3+}]_0$, $[HCrO_4^-]_0$, and the equilibrium concentration of $CoHCrO_4^{2+}$ were calculated using the expressions developed in ref 3.

[19] Nielsen, K. L. *Methods in Numerical Analysis*; Macmillan: New York, 1956.

Table I. Rate Constants for the Chromium(VI) Dimerization Reaction at 25 °C

μ (M)	k_1 (M^{-1} s^{-1})	k_2 (M^{-2} s^{-1})	K_D (M^{-1})	ref
0.20 (NaNO$_3$)	1.05×10^4	4.20×10^5 [a]	40	12
0.50 (NaClO$_4$)	$(6.86 \pm 0.09) \times 10^3$	$(5.29 \pm 0.01) \times 10^5$	77 ± 3	this work
1.00 (NaClO$_4$)	$(6.08 \pm 0.16) \times 10^3$	$(6.48 \pm 0.21) \times 10^5$	107 ± 6	13

[a] Calculated as k_1K_D.

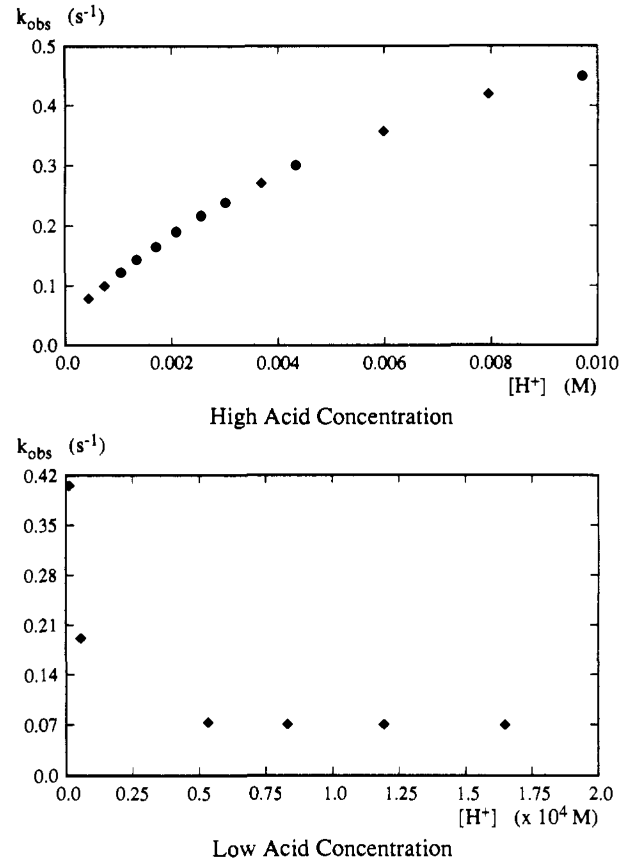
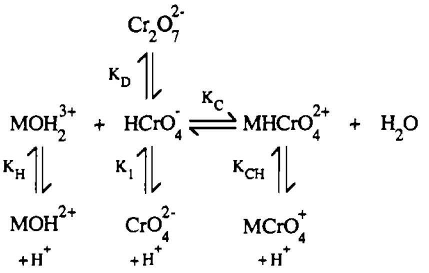


Figure 2. Acid dependence of the observed rate constant for complexation of Co(NH$_3$)$_5$OH$_2$$^{3+}$ (0.0125 M) and HCrO$_4$$^-$ (1×10^{-3} M) at 25 °C and 0.50 M ionic strength.

Scheme I. Equilibria Involved in Metal–Chromate Complex Formation in Acidic, Aqueous Solution



Co(NH$_3$)$_5$OH$_2$$^{3+}$ and HCrO$_4$$^-$. A value of 7.62 was calculated for K_{os} from the Fuoss equation[20] using a separation of 5 Å at 25 °C. The resulting rate constants were then $k_a = 0.393 \pm 0.019$ M^{-1} s^{-1}, $k_b = (1.77 \pm 0.03) \times 10^{-5}$ M^{-1} s^{-1}, and $k_c = 0.489 \pm 0.009$ s^{-1}. Attempts to resolve an independent K_{os} from the kinetic data were unsuccessful due to the high degree of correlation among k_a, k_b, and K_{os}.

$$f' = K_{os}f/(1 + K_{os}f) \qquad (4)$$

Table II. Derived Rate Constants for the Cr(NH$_3$)$_5$OH$_2$$^{3+}$/HCrO$_4$$^-$ Complexation Reaction

T (°C)	K_{os} (M^{-1})	k_a (M^{-1} s^{-1})	k_b (M^{-1} s^{-1})	k_c (s^{-1})	Σd^2
10		2.35 ± 0.20 [a]	$(4.9 \pm 0.8) \times 10^{-4}$	0.574 ± 0.021	4.41×10^{-3}
	8.50 [b]	0.343 ± 0.023	$(6.2 \pm 0.9) \times 10^{-5}$	0.559 ± 0.018	3.12×10^{-3}
15		3.52 ± 0.17	$(4.3 \pm 0.5) \times 10^{-4}$	1.164 ± 0.028	1.35×10^{-2}
	8.19	0.518 ± 0.024	$(5.4 \pm 0.7) \times 10^{-5}$	1.144 ± 0.028	1.25×10^{-2}
20		5.70 ± 0.28	$(3.0 \pm 0.8) \times 10^{-4}$	2.113 ± 0.042	0.146
	7.89	0.846 ± 0.037	$(4.4 \pm 1.0) \times 10^{-5}$	2.098 ± 0.037	0.135
25		9.28 ± 0.36	$(3.0 \pm 1.0) \times 10^{-4}$	3.594 ± 0.069	0.319
	7.62	1.434 ± 0.044	$(3.6 \pm 1.2) \times 10^{-5}$	3.554 ± 0.056	0.209
30		10.21 ± 0.57	$(1.9 \pm 0.3) \times 10^{-3}$	6.13 ± 0.11	0.698
	7.36	1.674 ± 0.079	$(2.6 \pm 0.4) \times 10^{-4}$	6.05 ± 0.10	0.553

[a] Quoted errors are 1 standard deviation. [b] Calculated using the Fuoss equation[20] at an ionic strength of 0.50 M and an interionic separation of 5 Å.

Table III. Comparison of Equilibrium Constants Derived from Kinetic and Equilibrium Measurements of the Cr(NH$_3$)$_5$OH$_2$$^{3+}$/HCrO$_4$$^-$ Complexation Reaction

T (°C)	K_{os} [a] (M^{-1})	K_C(kinetics) [b,c] (M^{-1})	K_C(equilibria) [c,d] (M^{-1})
10	8.50	5.1 ± 0.5	5.22 ± 0.09
15	8.19	3.7 ± 0.3	4.27 ± 0.06
20	7.89	3.2 ± 0.2	4.06 ± 0.07
25	7.62	3.1 ± 0.1	3.80 ± 0.09
30	7.36	2.0 ± 0.1	1.98 ± 0.03

[a] Calculated using the Fuoss equation[20] at an ionic strength of 0.50 M and an interionic separation of 5 Å. [b] Calculated as the ratio $K_{os}k_a/k_c$. [c] Quoted errors are 1 standard deviation. [d] Reference 3.

(c) Temperature Dependence of the Complexation Reaction between Cr(NH$_3$)$_5$OH$_2$$^{3+}$ and HCrO$_4$$^-$. The temperature dependence of the reaction between HCrO$_4$$^-$ and Cr(NH$_3$)$_5$OH$_2$$^{3+}$ (used in preference to the Co(III) analogue due to the larger absorbance change) was evaluated over five temperatures from 10 to 30 °C. In all cases, the kinetics conformed to the rate expression developed in section b). Table II lists the derived rate constants calculated with and without the ion-pairing term and the "sum of the squares of the residuals" (Σd^2) for each data-fitting process. There is a consistent and significant improvement in Σd^2 upon allowance for ion-pairing.

A value for the equilibrium constant for the complexation reaction between Cr(NH$_3$)$_5$OH$_2$$^{3+}$ and HCrO$_4$$^-$ (K_C) may be estimated from the ratio $K_{os}k_a/k_c$. Table III lists K$_C$ and includes the spectrophotometric values from ref 3. The very good agreement between the equilibrium constants at each temperature highlights the self-consistency between the equilibrium scheme and the rate expression and provides justification for using calculated K_{os} values.

A maximum pH of 4 was used to avoid possible hydrolysis and polymerization of the Cr(NH$_3$)$_5$OH$_2$$^{3+}$. As a result, the reciprocal acid term in the forward reaction is poorly resolved.

Activation parameters were calculated for the acid-independent forward path, k_a, and for the reverse reaction, k_c, from ln (k/T) versus $1/T$ plots. The resultant ΔH^* and ΔS^* values are 59.2 ± 2.4 kJ mol^{-1} and −44 ± 8 J K^{-1} mol^{-1} for k_a and 80.1 ± 1.0 kJ mol^{-1} and 34.2 ± 3.5 J K^{-1} mol^{-1} for k_c.

Discussion

Implications of the Rate Expression. The most striking feature of these results is the absence of the linear acid dependence in either the forward or reverse reaction paths reported in the earlier studies of the Co(NH$_3$)$_5$OH$_2$$^{3+}$/HCrO$_4$$^-$ complexation.[8,9] These rate laws suggest that the reverse term is linearly dependent upon acid concentration. The extension of the acid range in this work

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(20) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

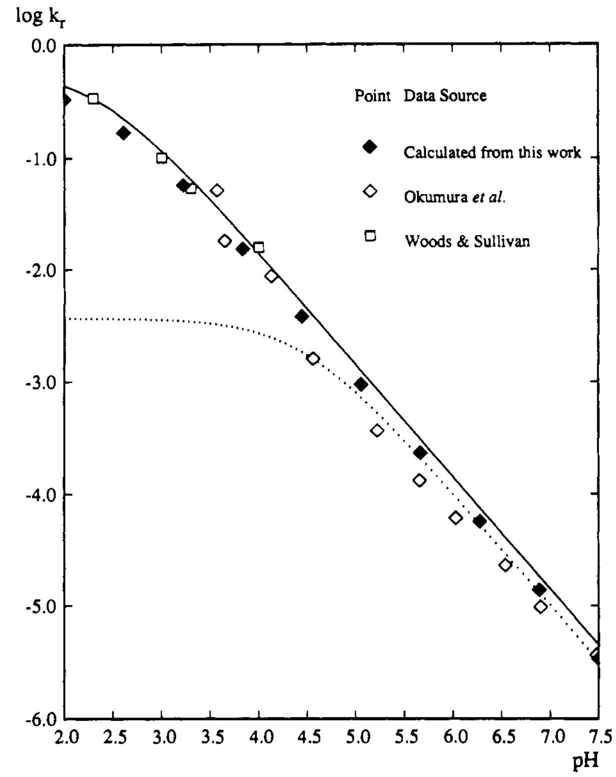

Figure 3. Comparison of the reverse rate constants, k_r, for the $Cr(NH_3)_5OH_2^{3+}/HCrO_4^-$ complexation and the calculated fit to this data using $k_r = k_c(1 + K_{CH}[H^+]^{-1})^{-1}$ where $K_{CH} = 3.63 \times 10^{-5}$ M (···) and 4.43×10^{-3} M (—) at 25 °C.

to pH 2 revealed that the apparent linear dependence of k_r upon $[H^+]$ observed by the other workers at pH's greater than 2.5 resulted from the approximation that k_r $(=k_c/(1 + K_{CH}/[H^+]))$ $\approx k_c[H^+]/K_{CH}$. However, as the acid concentration is further increased, the approximation is no longer valid and a curvature of the k_{obs} versus $[H^+]$ plots is observed.

Okumura and co-workers[9] proposed that the reverse (aquation) path is acid-catalyzed because plots of k_r versus $(1 + K_{CH}/[H^+])^{-1}$ had a significant positive deviation with increasing acid concentration. However, as can be seen in Figure 3, this is caused by using an incorrect value for K_{CH} in the analysis of their kinetic data. The dotted line in the figure represents the acid-independent reverse term calculated from the data[21] of Okumura et al. and using their value for K_{CH} of 3.63×10^{-5} M. The full line represents the calculated fit of eq 3 to the full k_r data of both Okumura et al. and Woods and Sullivan[8] using our K_{CH} value of 4.43×10^{-3} M.[3] The resultant value for k_c is 0.63 ± 0.02 s^{-1}, in good agreement with the value of 0.493 ± 0.009 s^{-1} determined here. Figure 3 includes k_r values from this work and highlights the excellent concordancy in determining this parameter over a very wide pH range in all three studies when a consistent analysis is applied.

The rate law for the reverse path is consistent with the aquation process occurring solely via the protonated $M(NH_3)_5HCrO_4^{2+}$ product. This phenomenon has also been observed with a number of other oxo anions. The carbonato complex, $Co(NH_3)_5CO_3^+$, only undergoes aquation after protonation of the carbonate ligand[22] according to

$$k_{aq} = k_1(1 + K_{CH}[H^+]^{-1})^{-1}$$

where K_{CH} is the deprotonation constant of $Co(NH_3)_5HCO_3^{2+}$.

A number of reports on the formation of M(III) sulfito-*O* complexes[23] propose rate laws that include a term for SO_2 elimination identical in form to the reverse term in eq 3, which are interpreted as aquation only occurring via the protonated sulfite ligand.

The acid independence of the forward rate constant, k_a, is consistent with reaction involving direct complexation between $Co(NH_3)_5OH_2^{3+}$ and $HCrO_4^-$. No evidence of acid catalysis of this path as suggested by Okumura et al. was found. Haight[16] proposed that k_a is an acid-catalyzed anation between $Co(NH_3)_5OH^{2+}$ and $HCrO_4^-$. In this instance, the resultant value of $k_f^{H^+}$ would be 5.3×10^6 M^{-2} s^{-1}, an order of magnitude larger than other values for acid-catalyzed substitution into $HCrO_4^-$.[24,25]

The reciprocal acid dependence of k_b may be attributed to either of the reactions

$$CoOH_2^{3+} + CrO_4^{2-} \rightleftharpoons CoCrO_4^+ + H_2O$$

$$CoOH^{2+} + HCrO_4^- \rightleftharpoons CoCrO_4^+ + H_2O$$

where $k_b/[H^+]$ can be rewritten as k_b'/K_5 or k_b'/K_H (depending on whether the deprotonated species is CrO_4^{2-} or $CoOH^{2+}$). The inherent proton ambiguity precludes assignment of either as the correct path. As the principle of microscopic reversibility requires that the reverse paths should include a term proportional to $[H^+]^{-1}$, corresponding to direct aquation of $Co(NH_3)_5CrO_4^+$, eq 3 was modified appropriately. The rate constant calculated for this reverse path was effectively 0. In their study covering a pH range up to 8.5, Okumura and co-workers[9] estimated a maximum value for this rate constant of 3.6×10^{-7} s^{-1}. Therefore, this process made no discernible contribution to the total reverse rate in the pH range studied here and was omitted from subsequent analysis.

The rate of uncatalyzed oxygen exchange on $HCrO_4^-$ is almost 10^4 times faster than that on CrO_4^{2-}.[26] This increased reactivity of $HCrO_4^-$ toward an oxygen nucleophile suggests that the reciprocal acid term of the complexation reaction probably involves $HCrO_4^-$ and the $Co(NH_3)_5OH^{2+}$ cation, even though electrostatic arguments would favor a $Co(NH_3)_5OH_2^{3+}/CrO_4^{2-}$ pathway. Ignoring outer-sphere contributions, this results in a value for k_b' of 242 M^{-1} s^{-1} (where $k_b' = k_b/K_H$). Hence the complexation reaction of $HCrO_4^-$ with the hydroxy cation occurs almost 100 times more rapidly than that with $Co(NH_3)_5OH_2^{3+}$ ($k_a = 2.53$ M^{-1} s^{-1}). A similar reactivity increase was observed in the limited data of Woods and Sullivan ($k_a = 0.80$, $k_b' = 350$[27]). This effect may be attributed to the greater nucleophilicity of the OH^- group toward the chromium(VI) ion. The inclusion of appropriate K_{os} terms makes this reactivity enhancement slightly greater.

Hydrogen-bonded transition states, as shown for a generalized oxo anion, HXO_4^-, in Figure 4, have been proposed for a wide variety of oxo anion complexation reactions, including $Co(NH_3)_5OH_2^{3+}/AsO_4^{3-}$,[28] $Co(tn)_2(OH_2)_2^{3+}/SeO_3^{2-}$,[29] $Co(NH_3)_5OH_2^{3+}$/malonate$^-$,[30] $Cr(H_2O)_6^{3+}/H_3AsO_4$,[5] Co-

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[21] Seven values for k_r over the pH range 4.5–7.5 were interpolated from Figure 5 of ref 9.

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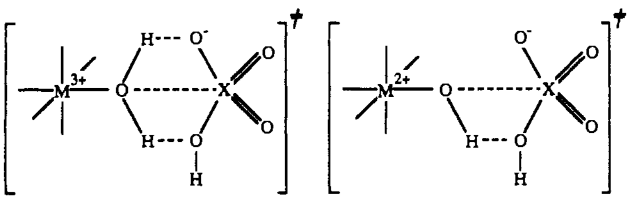

Figure 4. Hydrogen-bonding interactions in the postulated transition states for the reaction of HXO_4^- with aquo and hydroxo Co(III) complexes.

$(NH_3)_5OH_2^{3+}/MoO_4^{2-}$,[6] and $Cr(NH_3)_5OH_2^{3+}/IO_3^-$.[31] The relative reactivities of the coordinated H_2O and OH^- species arise from an interplay of hydrogen-bonding effects (favoring H_2O) and intrinsic nucleophilicity (favoring OH^-). The establishment of strong hydrogen-bonding in the transition state facilitates an associative reaction mechanism. For the larger oxo anions (MoO_4^{2-}, WO_4^{2-}, SeO_3^{2-}, IO_3^-, AsO_4^{3-}) associative modes of complex formation have been postulated, which correlate well with the observed enhanced reactivity of the entering coordinated aquo ligand. However, it has been proposed by Haim[32] that reactions of Cr(VI) are more dissociative in nature, thereby diminishing the importance of the hydrogen-bonded intermediate and favoring the stronger nucleophile. This is in good agreement with the observed 100-fold greater reactivity of the $Co(NH_3)_5OH^{2+}$ cation with $HCrO_4^-$ observed here and also observed by Lin and Beattie.[24] However, the activation parameters discussed in the next section strongly suggest that hydrogen-bonding is still extremely important in complex formation.

Various studies have also found that the rate of $M(NH_3)_5XO_n^{z+}$ (X = As, Se, Cr, I, Mo, W) formation is similar to the rate of oxygen exchange on the oxo anion. Wharton and co-workers[33] suggest that to explain this observation using the proposed hydrogen-bonded transition state (Figure 4 (left)) requires that the weaker nucleophilicity of the aquo ligand (compared to solvent water) is balanced out by more facile proton transfer due to its enhanced acidity. An alternative explanation is that, in both complexation and oxygen-exchange reactions, the rate-determining step is the elimination of the water ligand, rather than the formation of the transition state of increased coordination number.

The Intimate Reaction Mechanism. The excellent concordancy of reaction enthalpy, entropy, and free energy values (at 298 K) determined from this kinetic study and the same parameters measured during equilibrium investigations[3] is illustrated in Figure 5. ΔH and ΔS for ion-pair formation were determined from a van't Hoff plot for K_{os} values determined at each temperature and $\mu = 0.50$ M using the Fuoss Equation.[20]

Activation enthalpies for anation reactions of $Cr(NH_3)_5OH_2^{3+}$ almost exclusively fall within the narrow range 96–112 kJ mol^{-1}.[34] ΔH^* for water exchange has been measured as 97.1 kJ mol^{-1}.[35] A similar value of 96.4 kJ mol^{-1} has also been reported for uncatalyzed oxygen exchange on CrO_4^{2-}.[26] However, acid-catalyzed exchange results in more favorable activation enthalpies. For example, the acid-catalyzed formation of $Cr_2O_7^{2-}$ from $HCrO_4^-$ has a ΔH^* of only 24 ± 3 kJ mol^{-1}.[13] The value observed for the complexation reaction in this study, 59.2 ± 2.4 kJ mol^{-1}, strongly suggests that reaction proceeds via proton-assisted rupture of the labile Cr(VI)–oxygen bond in the hydrogen-bonded transition state rather than by Cr(III)–O bond fission.

The activation enthalpy for the reverse (aquation) reaction is 21 kJ mol^{-1} larger than that for the forward process. By analogy with the crystal structure of $Co(NH_3)_5CrO_4^+$,[4] it would be expected that the aquation of $Cr(NH_3)_5HCrO_4^{2+}$ requires disturbing the significant intramolecular hydrogen-bonding regime between the ammine hydrogen atoms on the Cr(III) and two of the terminal oxygens attached to the Cr(VI) center.

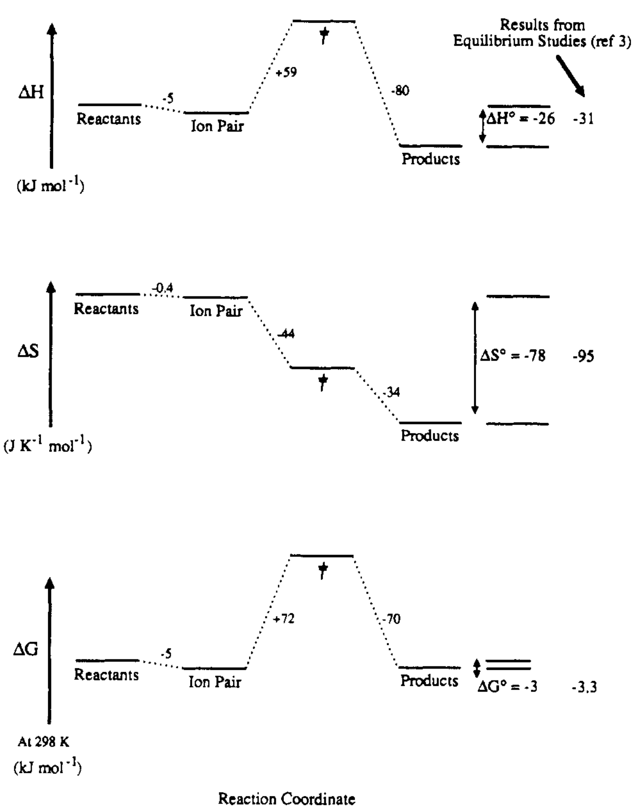

Figure 5. Energy profiles for the $Cr(NH_3)_5OH_2^{3+}/HCrO_4^-$ complexation.

There is also a large difference between the activation entropies for the forward and reverse reaction paths; $\Delta S^*_a = -44$ J K^{-1} mol^{-1}, $\Delta S^*_c = +34$ J K^{-1} mol^{-1}. The positive value of ΔS^*_c is consistent with the importance of hydrogen-bonding in the $Cr(NH_3)_5HCrO_4^{2+}$ product, which is diminished upon formation of the transition state.

These findings are in conflict with the activation entropy for the aquation of $Co(NH_3)_5HSeO_3^{2+}$,[29] where $\Delta S^*_{aq} = -79 \pm 10$ J K^{-1} mol^{-1} at pH 1.0. A strong intramolecular hydrogen bond between an ammine hydrogen and a terminal selenite oxygen was reported by Elder and Ellis for the crystal structure of $[Co(NH_3)_5OSeO_2]Cl \cdot 2.5H_2O$.[36] The origin of the large difference in entropy terms remains unclear. A dissociative interchange mechanism for the chromato reaction can be discounted by the negative activation entropy for the forward reaction and the dependence of k_a upon the nature of the aquo pentaammine substrate.

The rate of $M(NH_3)_5OH_2^{3+}/HCrO_4^-$ complexation is certainly influenced by the interaction between the Cr(VI) ion and the entering ligand. This view is supported by considering the effect of the acidity of the entering aquo group upon the rate of the forward reaction (k_a). At 25 °C, k_a for the reaction with $Cr(NH_3)_5OH_2^{3+}$ is ca. 3 times greater than for the Co(III) analogue. This may be attributed to the lower pK_H for the chromium cation, resulting in the aquo protons being more easily transferred to the Cr(VI) hydroxo group. A much larger rate constant of 2.0×10^4 M^{-1} s^{-1} was observed for $HCrO_4^-$ complexation with the more acidic $HS_2O_3^-$ ($pK_H = 1.2$).[24] This dependence of reaction rate upon substrate acidity is complicated by the nucleophilicity of the entering oxygen. The greater the degree of nucleophilicity, the stronger will be the bridging oxygen to Cr(VI) bonding interaction. This also has the effect of increasing the apparent acidity of the proton(s) coordinated to the bridging oxygen. In a study of the complexation between

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$H_3AsO_4/H_2AsO_4^-$ and $Cr(L)_5OH_2^{3+}$ ($L = H_2O, NH_3$), Ferrer et al.[5] attributed the much faster reaction of the pentaammine species with the As(V) center to the greater nucleophilicity of the Cr(III) oxygen (shown by the higher pK_a of 5.0 compared with 4.1 for $Cr(H_2O)_6^{3+}$).

Using a K_{os} value of 0.1 M^{-1} for the Cr(VI) dimerization reaction, the forward rate constant of 2 M^{-1} s^{-1} [11] becomes 20 s^{-1}. Although the pK_a of $HCrO_4^-$ is similar to that for $Co(NH_3)_5OH_2^{3+}$, the 40-fold increase in the rate of substitution into $HCrO_4^-$ is due to the greater strength of the bridging O–Cr(VI) bond in the transition state during the dimerization process. This is supported by the much lower activation enthalpy for the dimerization process (24 kJ mol^{-1} compared to 59 kJ mol^{-1} for the $Cr(NH_3)_5OH_2^{3+}$ complexation).

Unfortunately, there is still no direct evidence to distinguish between the reaction of $M(NH_3)_5OH_2^{3+}$ and $HCrO_4^-$ and the acid-catalyzed reaction of $M(NH_3)_5OH^{2+}$ and $HCrO_4^-$ (or $M(NH_3)_5OH_2^{3+}$ and CrO_4^{2-}) for the rate path described by k_a. Values for $k_f^{H^+}$ of $(7.37 \pm 0.29) \times 10^5$ M^{-2} s^{-1} (M = Cr) and $(5.3 \pm 0.3) \times 10^6$ M^{-2} s^{-1} (M = Co) are respectively equal to and much higher than the general-acid-catalyzed substitution of negatively charged ligands into $HCrO_4^-$,[24] but no account has been taken of ion-pairing in any of the $k_f^{H^+}$ values. The larger value of $k_f^{H^+}$ for the cobalt reaction may possibly be attributed to the greater nucleophilicity of its hydroxo group.

Haight[16] inferred that the mechanism for the reciprocal acid term of the forward path did not involve proton transfer from $CoOH^{2+}$ to $HCrO_4^-$ due to the negligible acidity of the hydroxo proton, although no other possibility was suggested. But, as is seen with the dimerization process, the formation of a strong bridging O–Cr(VI) bond would greatly enhance the $CoOH^{2+}$ acidity. The high nucleophilicity of the hydroxo species would also facilitate such bond making.

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Supplementary Material Available: Tables of solution parameters and observed rate constants and the derivation of the expression for k_{obs} (11 pages). Ordering information is given on any current masthead page.