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Kinetics and Mechanism of the Anation Reaction of the Aquapentaamminechromium(III) Ion with the Hexacyanocobaltate(III) Ion

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The anation reaction of $Co(CN)_6^{3-}$ with $Cr(NH_3)_5H_2O^{3+}$ yields the neutral, binuclear complex $Cr(NH_3)_5$–NC–$Co(CN)_5$, which was isolated and characterized. The value of the overall equilibrium constant, K_T, for its formation, is 110 ± 2 M^{-1} at 50.0 °C with values of 11.2 ± 0.6 kJ mol^{-1} and 74 ± 2 J K^{-1} mol^{-1} for $\Delta H°$ and $\Delta S°$, respectively. The rate law for the equilibration reaction is $-d[Co(CN)_6^{3-}]/dt = \{k_{aq} + (k_sK_{os}[Cr(III)])/(1 + K_{os}[Cr(III)])\}[Co(CN)_6^{3-}]$. The value of the outer-sphere association constant, K_{os}, is 15 ± 4 M^{-1} and is independent of temperature over the range from 43.8 to 63.7 °C. The values for the activation parameters for k_s, the rate constant for the substitution within the outer-sphere complex, are 95 ± 8 kJ mol^{-1} and −22 ± 25 J mol^{-1} K^{-1} for ΔH^* and ΔS^*, respectively. The value of k_s is 2.5×10^{-4} s^{-1} at 50 °C. The rate of reaction is independent of $[H^+]$ from 1.0 to 0.10 M H^+. The value of k_s for this reaction falls in the middle of the narrow range of k_s values found for other entering ligands, and this lack of dependence of k_s on the entering ligand is consistent with a dissociative or an I_d mechanism for substitutions on $Cr(NH_3)_5(H_2O)^{3+}$.

Introduction

There is general agreement that substitution reactions of pentaammine–Co(III) complexes follow an I_d mechanism, but there is not the same agreement on the intimate mechanism for substitution reactions of $Cr(NH_3)_5H_2O^{3+}$. Monsted, in his review,[1] lists the experiments, years, and mechanistic assignments (as I_a, borderline line I_a/I_d, or I_d) that the various investigators have ascribed to the substitution on pentaammine–Cr(III) complexes on the basis of the results of their experiments. All possible assignments of the I mechanism have been made more than once, and there is no correlation between the mechanistic assignment and the year. The assignment of the I_a mechanism is mainly based upon the negative volume of activation for the aquation rates and for the water exchange.[2] In recent studies, the rate constant, k_s, for the substitution within the outer-sphere complex has been determined for several entering ligands, and there appears to be little variation in the value of k_s with the entering ligand. This observation has been used to support the I_d (and the borderline I_a/I_d) mechanism.[3-9] However, all but one (i.e., the SCN^- study) of these studies involve ligands with oxygen as the entering atom, and the ligands are either mononegative or neutral (the exception here is the dinegative oxalate ion). While there is not a large spread in the reported rate constants for substitution, there is likewise not a large variation in the types of entering ligands. Support for the I_d or even the borderline I_a/I_d mechanism would be stronger if a larger variety of ligands are shown to have similar values for k_s. Additional support for the I_d mechanism for the pentaammine–Cr(III) complex has been offered by Lay.[10]

The product of the anation of the $Cr(NH_3)_5H_2O^{3+}$ by $Co(CN)_6^{3-}$ is the neutral, binuclear complex $Cr(NH_3)_5$–NC–$Co(CN)_5$, and so in this reaction $Co(CN)_6^{3-}$ is the entering ligand replacing the H_2O ligand on the Cr(III) center. The nature of this entering ligand is very different from the oxoanions and halide ligands that have previously been studied. If the substitution on $Cr(NH_3)_5H_2O^{3+}$ proceeds by an I_a mechanism, there should be a sizable difference between the rate of substitution for this cyano–Co complex and the rates of substitution for the previously reported ligands. Of course, it is the value of the rate constant k_s (for the substitution within the outer-sphere complex) that must be compared for these entering ligands. In this system the formation constant for the outer-sphere complex, K_{os}, is favored by the high ionic charge on both reactants, and its value, as well as the value for k_s, can be determined from the kinetic study.

Experimental Section

Materials. $[Cr(NH_3)_5H_2O](ClO_4)_3$ was prepared by a literature procedure.[6,11] $K_3Co(CN)_6$ was purchased from Aldrich. Stock solutions of $HClO_4$ and $LiClO_4$ were prepared and standardized by standard procedures.

Kinetics. The ionic medium was kept at 1.0 M ClO_4^- using $LiClO_4$. The kinetics were measured with $Co(CN)_6^{3-}$ as limiting reagent at low concentrations, since this complex is isolated as the K^+ salt and $KClO_4$ is only slightly soluble in 1.0 M ClO_4^-. The concentration range for the Cr(III) complex was also limited because of the solubility of the Cr(III) complex in 1.0 M ClO_4^-. In an initial experiment, the spectrum of a reaction solution was recorded at regular time intervals, and isosbestic points at 494 and 374 nm were maintained for more than 5 half-lives. For the kinetic studies, the solutions were placed in cuvettes that were then placed in the thermostated cell holder of a Perkin-Elmer Lambda 4B UV–vis spectrophotometer. A MGU Lauda M3 circulating water bath was used to maintain the temperature in the cell holder. The temperature was measured within a cell in the cell holder. The absorbance of each cell was monitored at 240 nm. The values of k_{obs} and A_∞ were obtained from a nonlinear least-squares fit of the first-order equation $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obs}t)$. In cases where A_∞ was experimentally determined, the difference between the calculated and the experimental values for A_∞ was less than 5%. For runs with long half-lives, it was not practical to obtain an experimental value for A_∞, and so only calculated values were used. Runs were followed from 2 to 10 half-lives; the standard deviations for k_{obs} were always less than 1%; values for k_{obs} in duplicate runs were within 5% of each other.

Equilibrium Measurement. The procedures described by Ramasami and Sykes were followed.[5] The range of concentrations of $Cr(NH_3)_5H_2O^{3+}$ and $Co(CN)_6^{3-}$ was 0.008–0.006 M in each reactant with $[HClO_4]$ = 0.10 M and $[LiClO_4]$ = 0.90 M. Dowex 50W-X4 (50–100 mesh) was used as the cation-exchange column, and since the product in this study is neutral, the column was rinsed with 0.10 M $HClO_4$. In each case, more than 97% of the total Cr(III) was recovered.

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Table I. Values of k_{obs} for the Anation of $Cr(NH_3)_5H_2O^{3+}$ by $Co(CN)_6^{3-}$ (I = 1.0 M ($LiClO_4$); $[H^+]$ = 0.100 M; $[Co(CN)_6^{3-}]$ = 5.1 × 10^{-4} M[a])

T, °C	$[Cr(NH_3)_5H_2O^{3+}]$, M	10^5k_{obs}, s^{-1}	T, °C	$[Cr(NH_3)_5H_2O^{3+}]$, M	10^5k_{obs}, s^{-1}
43.8	0.0400	5.45	58.3	0.0400	26.7
	0.0300	3.88		0.0300	23.1
	0.0200	3.56		0.0200	17.8
	0.0100	2.20		0.0100	11.5
	0.00700	1.76		0.00700	9.42
53.6	0.0400	15.5	63.7	0.0400	46.8
	0.0300	13.7		0.0300	41.1
	0.0200	10.6		0.0200	32.8
	0.0100	6.90		0.0100	20.6
	0.00700	5.66		0.00700	16.6

[a] $[Co(CN)_6^{3-}]$ = 2.5 × 10^{-4} M when $[Cr(NH_3)_5H_2O^{3+}]$ = 0.0400 M (to prevent precipitation).

Preparation of $Cr(NH_3)_5$–NC–$Co(CN)_5·H_2O$. A solution of 0.70 g of $[Cr(NH_3)_5H_2O](ClO_4)_3$ in 50 mL of 0.1 M HCF_3SO_3 and a solution of 0.5 g of $K_3Co(CN)_6$ in a 50 mL of water were heated to 70 °C. The two solutions were mixed, and the mixture was kept at 70 °C for 2 h. Crystals of $[Cr(NH_3)_5H_2O][Co(CN)_6]$, if present, were removed by filtration. To the solution was added 0.50 g of $Zn(NO_3)_2$ to precipitate excess $Co(CN)_6^{3-}$ as $Zn_3[Co(CN)_6]_2$, and this solid was removed by filtration. The filtrate was passed through a cation-exchange column (Dowex 50-X8, 50–100 mesh) to remove any unreacted $Cr(NH_3)_5H_2O^{3+}$ and Zn^{2+}. The column was rinsed with dilute HCF_3SO_3, and the resulting solution was concentrated using a rotary evaporator (bath temperature was 40 °C). When the volume of the solution was about 5 mL, the solution was cooled in ice. Five volumes of ethanol were added, and the solution was left in the ice bath for 1 h. An orange solid formed and was collected on a glass frit. A recrystallization (water/ethanol) was necessary to obtain a pure product; yield 0.20 g. Anal. Calcd for $CrCoN_{11}C_6H_{17}O$: Cr, 14.0; Co, 15.9; C, 19.47; N, 41.62; H, 4.65. Found: Cr, 13.6; Co, 15.9; C, 20.61; N, 40.12; H, 4.58.

Results

The synthesis and properties of (μ-cyano)[pentacyanocobaltato(III)]pentaamminechromium(III), $Cr(NH_3)_5NCCo(CN)_5$, have been previously reported by Kane-Maguire et al.[12] The synthesis described in this paper reflects the procedure used in the kinetic runs. Excess $Co(CN)_6^{3-}$ is removed by precipitating it with Zn^{2+} rather than by anion exchange, since these neutral, binuclear compounds are absorbed by the anion-exchange resin.[13] The properties found for the binuclear complex isolated by this method are essentially the same as those reported previously. The analysis requires a water of crystallization, and so the solid isolated is $[Cr(NH_3)_5NCCo(CN)_5]·H_2O$, which makes it a coordination isomer of the ion-pair product, $[Cr(NH_3)_5H_2O^{3+}][Co(CN)_6^{3-}]$. However, the properties of the two isomers are quite different. The ion-pair product precipitates as a crystalline product from an aqueous solution, is very insoluble, and appears to be quite stable in air. The bridged product can only be isolated by the addition of alcohol or ether to the aqueous solution, and the bridged complex is thermally unstable in air. The freshly isolated product is very soluble in water, but if air-dried, the resulting solid is no longer soluble. Kane-Maguire et al. reported that the binuclear complex can be stored in a freezer for 3–4 weeks. The bridged complex has four bands in the IR spectrum (2159, 2139, 2127, and 2118 cm^{-1}) with the 2159-cm^{-1} band being assigned to the bridging cyanide ligand. The UV–vis spectrum of the binuclear complex has absorbance maxima at 468 and 310 nm (compared to 480 nm for $Cr(NH_3)_5H_2O^{3+}$ and 311 nm for $Co(CN)_6^{3-}$). The positions of these peaks are consistent with the cyano bridge being attached to the Cr(III) center through the nitrogen atom.[13]

The kinetic studies were carried out with $Cr(NH_3)_5H_2O^{3+}$ in excess. The values of k_{obs} at different concentrations of $Cr(NH_3)_5H_2O^{3+}$ at four different temperatures (from 43.8 to 63.7 °C) are listed in Table I. The values of k_{obs} at different $[H^+]$'s are listed in Table II. A plot of k_{obs} versus $[Cr(NH_3)_5H_2O^{3+}]$ is curved, indicating that the reaction order is less than first order in Cr(III). A plot of $1/k_{obs}$ vs 1/[Cr(III)] is linear (see Figure 1A), which is consistent with the mechanism represented by eqs 1 and 2.

Table II. Dependence of k_{obs} on Acid Concentration in the Anation of $Cr(NH_3)_5H_2O^{3+}$ by $Co(CN)_6^{3-}$ (I = 1.0 M ($LiClO_4$); $[Cr(NH_3)_5H_2O^{3+}]$ = 0.0100 M; $[Co(CN)_6^{3-}]$ = 5.1 × 10^{-4} M; T = 58.3 °C)

$[H^+]$, M	10^4k_{obs}, s^{-1}	$[H^+]$, M	10^4k_{obs}, s^{-1}
0.100	1.12	0.700	1.19
0.200	1.14	1.00	1.08
0.500	1.14		

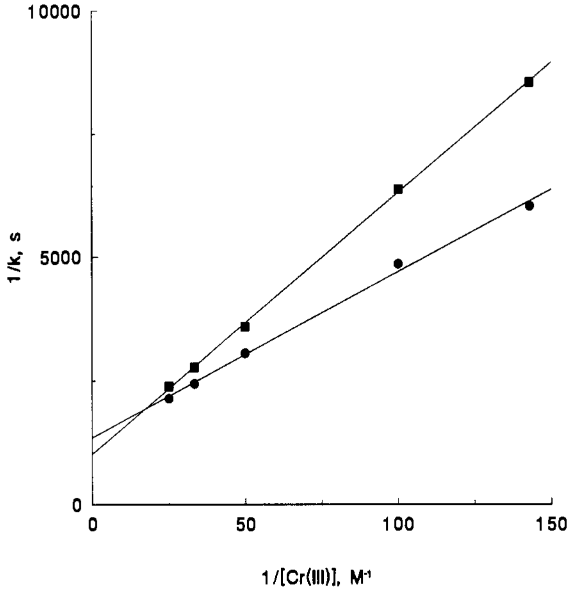

Figure 1. $1/k$ vs 1/[Cr(III)] for the runs at 63.7 °C with $[H^+]$ = 0.100 M and I = 1.0 M ($LiClO_4$): (A) circles, $1/k = 1/k_{obs}$; (B) squares, $1/k = 1/(k_{obs} - k_{aq})$ with k_{aq} = 4.9 × 10^{-5} s^{-1}. The lines are the linear regression fits to the points.

The values of the overall equilibrium constant, K_T (temperature in parentheses, °C) are 94 ± 4 (40.0), 103 ± 2 (45.0), 110 ± 2 (50.0), 115 ± 3 (55.0), and 125 ± 4 (60.0). The analysis for Cr in the eluent and on the column accounted for more than 97% of the total chromium in the reaction mixtures. $\Delta H°$ and $\Delta S°$ for K_T are 11.2 ± 0.6 kJ mol^{-1} and 73.5 ± 2 J K^{-1} mol^{-1}.

Discussion

The step mechanism for the substitution of $Co(CN)_6^{3-}$ on $Cr(NH_3)_5H_2O^{3+}$ can be represented by the following:

$$Cr(NH_3)_5H_2O^{3+} + Co(CN)_6^{3-} \overset{K_{os}}{\rightleftharpoons} \underset{\text{outer-sphere complex}}{Cr(NH_3)_5H_2O\cdot Co(CN)_6} \quad (1)$$

$$Cr(NH_3)_5H_2O\cdot Co(CN)_6 \underset{k_{aq}}{\overset{k_s}{\rightleftharpoons}} Cr(NH_3)_5\text{–NC–}Co(CN)_5 + H_2O \quad (2)$$

where K_{os} is the constant for the association of the outer-sphere complex, k_s is the rate constant for the substitution of the ligand within the outer-sphere complex, and k_{aq} is the rate constant for the aquation of the ligand. The constant for the association of the inner-sphere complex, K_{is}, is equal to k_s/k_{aq}. The overall equilibrium constant, K_T, is represented by $K_{os}K_{is}$. In cases where K_{os} is too small, separate values of k_s and K_{os} cannot be determined, and the rate constant for the forward reaction, $k_f = K_{os}k_s$, is obtained.[5]

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Table III. Values of k_s, K_{os}, and k_{aq} for the Anation of $Cr(NH_3)_5H_2O^{3+}$ by $Co(CN)_6^{3-}$ (I = 1.0 M ($LiClO_4$); $[H^+]$ = 0.100 M) and the Activation Parameters for k_s and k_f

T, °C	10^4k_s, s^{-1}	K_{os},[a] M^{-1}	10^6k_{aq}, s^{-1}
43.8	1.2 ± 0.3	14 ± 3	6.5
53.6	3.8 ± 0.2	14 ± 1	23
58.3	7.3 ± 0.4	12 ± 1	39
63.7	9.9 ± 0.6	19 ± 1	49

activation parameters	k_s	k_sK_{os}
$\Delta H^\ddagger$, kJ mol^{-1}	95 ± 8	103 ± 8
$\Delta S^\ddagger$, J K^{-1} mol^{-1}	−22 ± 25	+26 ± 17
k(at 50 °C), s^{-1}	2.5×10^{-4}	3.5×10^{-3}

[a] Average value of K_{os} is 15 M^{-1} with $\Delta H^\circ = 0$ and $\Delta S^\circ = 22 \pm 2$ J K^{-1} mol^{-1}.

The expression for k_{obs} derived from this mechanism[5,14] is

$$k_{obs} = k_{aq} + (K_{os}k_s[Cr(NH_3)_5H_2O^{3+}])/(1 + K_{os}[Cr(NH_3)_5H_2O^{3+}]) \quad (3)$$

Initially, the value of k_{aq} was believed to be sufficiently small to be ignored and values for k_s and K_{os} were determined from plots of $1/k_{obs}$ vs 1/[Cr(III)] (Figure 1A). When the experimental value of 110 M^{-1} at 50 °C was obtained for K_T, it was apparent that k_{aq} was too large to be neglected. The equation can be rearranged to

$$1/(k_{obs} - k_{aq}) = 1/(K_{os}k_s[Cr(III)]) + 1/(k_s) \quad (4)$$

and a plot of $1/(k_{obs} - k_{aq})$ versus 1/[Cr(III)] should be linear. A linear least-squares program was used to fit the data to this equation, and the value of k_{aq} was varied to maximize the correlation coefficient, R. A plot of $1/(k_{obs} - k_{aq})$ versus 1/[Cr(III)] at 63.7 °C is illustrated with $k_{aq} = 0$ (with R = 0.996 39) in Figure 1A and $k_{aq} = 4.9 \times 10^{-5}$ s^{-1} (with R = 0.999 53) in Figure 1B. The resulting values for K_{os}, k_s, and k_a are listed in Table III. This method produced consistent, reasonable results for these parameters. However, five data points are being used to fit three variables, and so the results must be viewed with some caution (other methods for solving for the three variables in eq 4 did not produce consistent values at the four temperatures). In order to obtain better values, the range of [Cr(III)] must be increased; however, higher concentration of Cr(III) results in the precipitation of the Cr(III) complex as the perchlorate salt, and changes in absorption are too small at lower concentrations of Cr(III).

The value of K_{os} is essentially independent of temperature, which is consistent with the temperature independence of K_{os} that has been found in previous studies of different entering ligands.[6,7,9] If the four values at the different temperatures are averaged, the value for K_{os} is 15 ± 4 M^{-1}, and if K is assumed to be independent of temperature (i.e., ΔH° = 0 kJ mol^{-1}), then ΔS° = 22 ± 2 J K^{-1} mol^{-1}. The activation parameters for k_s are listed in Table III along with the activation parameters for k_sK_{os}.

The value for k_{aq} can also be calculated using the values for k_s, K_{os}, and K_T. The values of k_{aq} from this calculation are 18×10^{-6}, 47×10^{-6}, 90×10^{-6}, and 110×10^{-6} s^{-1} at each respective temperature. In general, they are within a factor of 2 of those determined from the least-squares fit of eq 4 and are within the precision of the data. A value of K_{os} can be calculated using the Fuoss equation.[14] If a distance of 6.68 Å between the metal centers is used,[15] the calculated value of K_{os} is 12.6 M^{-1}. The experimental value of 15 M^{-1} is therefore reasonable.

Table IV. Summary of Rate Constants and Activation Parameters for the Substitution of $Cr(NH_3)_5H_2O^{3+}$ by Different Entering Ligands at 50 °C and I = 1.0 M ($LiClO_4$)

ligand	10^4k_s, s^{-1}	$10^4K_{os}k_s$, M^{-1} s^{-1}	ΔH_a, kJ mol^{-1}	ΔS_a, J K^{-1} mol^{-1}	ref
Cl^-		0.69	107	8	5
Br^-		3.71	91.5	−17	5
$Cl_3CO_2^-$		1.81	105	9.2	5
$CF_3CO_2^-$		1.37			5
NCS^-	6.12	4.16	102	12	5
$HC_2O_4^-$	6.2	6.45	112	39	4
$C_2O_4^{2-}$	6.2	29.1	104	33	4
H_3PO_4	1.45	0.46			6
$H_2PO_4^-$	1.45	2.59			6
H_3PO_3	1.5	0.47			9
$H_2PO_3^-$	1.5	2.37			9
H_3PO_2	3.44	0.45			7
$H_2PO_2^-$	3.44	1.14			7
$Co(CN)_6^{3-}$	2.5	35	103 ± 8	26 ± 17	this work
H_2O	13.7		97.0	0	a

[a] Swaddle, T. W.; Stranks, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 8357–8359.

Substitutions on $Cr(NH_3)_5H_2O^{3+}$ are generally independent of the $[H^+]$ at pH <4, but there is a possibility that $Co(CN)_6^{3-}$ can be protonated at higher $[H^+]$. However, the value of k_{obs} is constant (see Table II) as $[H^+]$ is varied from 0.10 to 1.0 M. $Co(CN)_6^{3-}$ apparently remains unprotonated up to 1.0 M H^+.

In Table IV the values of k_s for the substitution on $Cr(NH_3)_5H_2O^{3+}$ by several ligands are listed. The variation in k_s for all of the listed ligands is only a factor of 4, and k_s for $Co(CN)_6^{3-}$ falls in the middle of these values. If bond formation in the activated complex is important, then there should a sizable difference in rate for the substitution of $Co(CN)_6^{3-}$ compared to these other ligands. Since there is not, bond breaking between the Cr and the leaving H_2O must be the important factor. In some systems, individual values for K_{os} and k_s cannot be determined, and so only the rate constant and activation parameters for the forward reaction, k_f ($=K_{os}k_s$), are measured (Table IV). Since the enthalpy for K_{os} is approximately 0 in the cases where this value has been determined,[6,7,9] $\Delta H^\ddagger$ for k_s will be approximately the same as $\Delta H^\ddagger$ for k_f. There is little variation in the values of $\Delta H^\ddagger$ for the various entering ligands, which means that a similar pathway must be present for all of these substitutions and that there is little bond formation between the Cr(III) center and the entering ligand in the activated complex. There is little evidence of association between the entering ligands and the Cr(III) center, and the I_d mechanism best describes the substitutions on $Cr(NH_3)_5H_2O^{3+}$.

The thiocyanate ligand is the other non-oxygen ligand in Table IV for which a value of k_s is given. The greater affinity of Cr(III) for SCN^- than for $Co(CN)_6^{3-}$ is evident in the greater value of K_T for SCN^- (350 M^{-1}, which is the average value[5] for the two different methods of measuring K_T for SCN^-, versus 110 M^{-1} for $Co(CN)_6^{3-}$). However, the values of K_{is} ($=K_T/K_{os}$) provide an even better measure of this affinity, since it eliminates the attraction due to the charge difference of these two anions. The value of K_{is} for SCN^- is 500 (if K_{os} is taken to be 0.7 M^{-1}),[5] and for $Co(CN)_6^{3-}$ it is 7. Therefore, one would expect a sizable difference in the values of k_s for these two systems if bond making is important in the activated complex. The k_s value for SCN^- given in Table IV is about 2.4 times that for $Co(CN)_6^{3-}$, which is probably within the experimental errors of these numbers. If bond formation between the entering ligand and the central chromium ion is important in the transition state, the differences in k_s in these two systems should be greater. Again, the I_d mechanism is consistent with the similar rates of substitution for these two ligands within the outer-sphere complex.

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