The Effect of Ligand Environment on the Mechanism of Substitution at Chromium(III)

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Summary Kinetic and thermodynamic data for the formation and aquation of acidopenta-amminechromium(III) complexes provide strong evidence for a dissociative mechanism.

RATE constants and equilibrium constants as defined in equations (1) and (2), with $K_{IS} = k_{an}/k_{aq}$ and $k_f = K_{OS}k_{an}$, have been determined by conventional spectrophotometric techniques for $X^- = NCS^-$, $CCl_3CO_2^-$, $CF_3CO_2^-$, Cl^-, Br^-, and I^-, at 50 °C, $I = 1{\cdot}00$M ($LiClO_4$). Values obtained are compared (Table) with data for $X^- = C_2O_4H^-$, $C_2O_4^{2-}$,[1] and $^+NH_3CH_2CO_2^-$,[2] as well as H_2O exchange studies.[3] The rate constants k_{aq} were determined directly by studying the aquation of the complexes $[Cr(NH_3)_5X]^{2+}$.

$$[Cr(NH_3)_5H_2O]^{3+} + X^- \overset{K_{OS}}{\rightleftharpoons} [Cr(NH_3)_5H_2O]^{3+}, X^- \qquad (1)$$

$$[Cr(NH_3)_5H_2O]^{3+}, X^- \underset{k_{aq}}{\overset{k_{an}}{\rightleftharpoons}} [Cr(NH_3)_5X]^{2+} + H_2O \qquad (2)$$

Rate constants k_f for the formation of $[Cr(NH_3)_5X]^{2+}$ were obtained under conditions in which there was no contribution from k_{aq} ($X^- = NCS^-$, $CCl_3CO_2^-$), and in other cases from equilibration rate constants after allowing for k_{aq}. With iodide, too high a concentration of I^- is required to allow precise values of k_f to be determined. It was possible with NCS^- (as with $C_2O_4H^-$, $C_2O_4^{2-}$, and $^+NH_3CH_2CO_2^-$) to obtain K_{OS} from the kinetic treatment.

The data as summarised show that rate constants k_f vary by only one order of magnitude for eight ions with 1− charge. The value for $C_2O_4^{2-}$ is understandably larger and is outside this range because K_{OS} is larger for a 2− charged species. Comparable k_f values for the anation of $[Cr(H_2O)_6]^{3+}$ give a range of values varying by at least three orders of magnitude.[4] The choice of anions is limited in the case of the penta-ammine series owing to interference from subsequent reactions involving loss of ammonia.[5] It has been suggested previously[6] that the ratio of anation (k_f) rate constants for the reactions of NCS^- and Cl^- is diagnostic of the mechanism. The value of this ratio for $[Cr(H_2O)_6]^{3+}$ is

TABLE

Summary of kinetic and thermodynamic data for the formation and aquation of $[Cr(NH_3)_5X]^{2+}$ complexes at 50 °C, $[H^+] = 0{\cdot}1$—$0{\cdot}5$M (except as stated),[a] $I = 1{\cdot}00$M ($LiClO_4$).

Ligand X^-	$10^4\,k_f$/ l mol^{-1} s^{-1}	$10^4\,k_{an}$[b]/ s^{-1}	$10^4\,k_{aq}$/ s^{-1}	$K_{OS}K_{IS}$[c]/ l mol^{-1}	$K_{OS}K_{IS}$[d]/ l mol^{-1}	K_{OS}[e]/ l mol^{-1}	References
NCS^-	4·16	6·12	0·011	310	380	0·68	This work
$CCl_3CO_2^-$[f]	1·81	—	0·37	5·3	4·9	—	This work
$CF_3CO_2^-$[f]	1·37	—	0·50	2·4	2·7	—	This work
Cl^-	0·69	—	1·75	0·48	0·4	—	This work
Br^-	3·71	—	12·5	0·21	0·3	—	This work
I^-	—	—	102	0·022)[g]	—	—	This work
$^+NH_3CH_2CO_2^-$	7·82	14·2	—	—	—	0·55	2
$HC_2CO_4^-$	6·45	5·86	—	—	—	1·16	1
$C_2O_4^{2-}$	29·1	6·46	—	—	—	4·5	1
H_2O	—	13·7	—	—	—	—	3

[a] No dependence on $[H^+]$ observed. [b] $k_{an} = k_f/K_{OS}$. [c] Obtained following ion-exchange separation (and determination) of components in equilibrated solutions. [d] From rate constants k_f/k_{aq}. [e] From kinetic treatment. [f] $[H^+]$ range 0·005—0·02M to avoid protonation of $CCl_3CO_2^-$ (pK_a 0·66) and $CF_3CO_2^-$ (pK_a 0·23). [g] Not included in log k_{aq} *vs.* log $K_{OS}K_{IS}$ plot since the small amount of the 2+ eluant was not positively identified as $[Cr(NH_3)_5I]^{2+}$ in ion exchange separation. The value here is consistent however with a log k_{aq} *vs.* log $K_{OS}K_{IS}$ plot of slope 0·91.

60 and is believed to support an associative mechanism, whereas values < 10 are believed to be more in keeping with a dissociative process. The value for $[Cr(NH_3)_5H_2O]^{3+}$ is 6.

It is possible to obtain values of k_{an} in those cases in which K_{OS} has been determined, $X^- = NCS^-$, $HC_2O_4^-$, $C_2O_4^{2-}$, and $^+NH_3CH_2CO_2^-$. Values lie in a narrow range, $(5$—$14) \times 10^{-4}$ s^{-1} at 50 °C, and are comparable to the rate constant for H_2O exchange ($13{\cdot}7 \times 10^{-4}$ s^{-1}). From the data reported a linear relation of log k_{aq} against − log $K_{OS}K_{IS}$ of slope $0{\cdot}91 \pm 0{\cdot}05$ is observed. A much smaller slope of 0·56 is observed for the corresponding plot for the $[Cr(H_2O)_5X]^{2+}$ series of reactions.[7] These observations strongly suggest that breaking of the $Cr–OH_2$ bond is the dominant factor.

The assignment of a dissociative I_d process for $[Cr(NH_3)_5H_2O]^{3+}$ and an associative I_a mechanism for $[Cr(H_2O)_6]^{3+}$ lends support to the hypothesis that a metal ion may not be associated with a single type of mechanism in all ligand environments. With Co^{III} it is now established that $[Co(NH_3)_5H_2O]^{3+}$ and $[Co(CN)_5H_2O]^{2-}$ undergo I_d and D substitutions, respectively.[8] Rate constants for the anation of $[Co(H_2O)_6]^{3+}$ with NCS^- (86·5 l mol^{-1} s^{-1})[9] and Cl^- ($\leqslant 2{\cdot}0$ l mol^{-1} s^{-1})[10] differ by a factor of $\geqslant 43$ suggesting some associative character.

The present study indicates that $[Cr(H_2O)_6]^{3+}$ and $[Cr(NH_3)_5H_2O]^{3+}$ differ in their substitution properties. From a consideration of $Cr–NH_3$ and $Cr–OH_2$ bonds it might be expected that since oxygen is more electronegative than nitrogen the donation of electron density to the metal will be more favourable in the $Cr–NH_3$ bond as compared to $Cr–OH_2$. As π back-bonding is impossible in the two cases, the net electron density on Cr^{III} should be higher for a penta-ammine than for a penta-aquo environment. This is likely to reduce the susceptibility to an associative attack and will tend to favour dissociative processes. Langford and Sastri[11] have estimated that five NH_3 groups would be expected to labilise one H_2O ligand by a factor of 10^3 as compared to an environment of five H_2O ligands. It is not surprising that for such drastic labilizing effects, a change in mechanism is sometimes observed.

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