

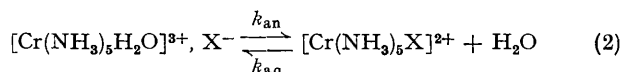
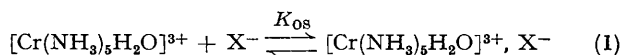
The Effect of Ligand Environment on the Mechanism of Substitution at Chromium(III)

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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 $k_f = K_{OS} \cdot k_{an}$, have been determined by conventional spectrophotometric techniques for $X^- = NCS^-$, $CCl_3CO_2^-$, $CF_3CO_2^-$, Cl^- , Br^- , and I^- , at 50 °C, $I = 1.00M$ ($LiClO_4$). 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 $[Cr(NH_3)_5X]^{2+}$.



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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 aquation 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 previously⁶ that the ratio of aquation (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 $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+}$ complexes at 50 °C, $[\text{H}^+] = 0.1\text{--}0.5\text{M}$ (except as stated),^a $I = 1.00\text{M}$ (LiClO_4).

Ligand X^-	$10^4 k_t /$ $1 \text{ mol}^{-1} \text{ s}^{-1}$	$10^4 k_{an}^b /$ s^{-1}	$10^4 k_{aq} /$ s^{-1}	$K_{os}K_{18}^c /$ 1 mol^{-1}	$K_{os}K_{18}^d /$ 1 mol^{-1}	$K_{os}^e /$ 1 mol^{-1}	References
NCS^-	4.16	6.12	0.011	310	380	0.68	This work
$\text{CCl}_3\text{CO}_2^-$ ^t	1.81	—	0.37	5.3	4.9	—	This work
CF_3CO_2^- ^t	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
$^+\text{NH}_3\text{CH}_2\text{CO}_2^-$	7.82	14.2	—	—	—	0.55	2
HC_2O_4^-	6.45	5.86	—	—	—	1.16	1
$\text{C}_2\text{O}_4^{2-}$	29.1	6.46	—	—	—	4.5	1
H_2O	—	13.7	—	—	—	—	3

^a No dependence on $[\text{H}^+]$ observed. ^b $k_{an} = k_t/K_{os}$. ^c Obtained following ion-exchange separation (and determination) of components in equilibrated solutions. ^d From rate constants k_t/k_{aq} . ^e From kinetic treatment. ^f $[\text{H}^+]$ range 0.005—0.02M to avoid protonation of $\text{CCl}_3\text{CO}_2^-$ (pK_a 0.66) and CF_3CO_2^- (pK_a 0.23). ^g Not included in $\log k_{aq}$ vs. $\log K_{os}K_{18}$ plot since the small amount of the 2+ eluant was not positively identified as $[\text{Cr}(\text{NH}_3)_5\text{I}]^{2+}$ in ion exchange separation. The value here is consistent however with a $\log k_{aq}$ vs. $\log K_{os}K_{18}$ 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 $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ is 6.

It is possible to obtain values of k_{an} in those cases in which K_{os} has been determined, $\text{X}^- = \text{NCS}^-$, HC_2O_4^- , $\text{C}_2\text{O}_4^{2-}$, and $^+\text{NH}_3\text{CH}_2\text{CO}_2^-$. Values lie in a narrow range, $(5\text{--}14) \times 10^{-4} \text{ s}^{-1}$ at 50 °C, and are comparable to the rate constant for H_2O exchange ($13.7 \times 10^{-4} \text{ s}^{-1}$). From the data reported a linear relation of $\log k_{aq}$ against $-\log K_{os}K_{18}$ of slope 0.91 ± 0.05 is observed. A much smaller slope of 0.56 is observed for the corresponding plot for the $[\text{Cr}(\text{H}_2\text{O})_6\text{X}]^{2+}$ series of reactions.⁷ These observations strongly suggest that breaking of the $\text{Cr}\text{--}\text{OH}_2$ bond is the dominant factor.

The assignment of a dissociative I_d process for $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and an associative I_a mechanism for $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ 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 $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ undergo I_d and D substitutions, respectively.⁸ Rate constants for the anation

of $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ with NCS^- ($86.5 \text{ l mol}^{-1} \text{ s}^{-1}$)⁹ and Cl^- ($\leq 2.0 \text{ l mol}^{-1} \text{ s}^{-1}$)¹⁰ differ by a factor of ≥ 43 suggesting some associative character.

The present study indicates that $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ differ in their substitution properties. From a consideration of $\text{Cr}\text{--}\text{NH}_3$ and $\text{Cr}\text{--}\text{OH}_2$ 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 $\text{Cr}\text{--}\text{NH}_3$ bond as compared to $\text{Cr}\text{--}\text{OH}_2$. 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 Sastri¹¹ 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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