Aquation of Neutral Ligands from Penta-ammine-cobalt(III) and -chromium(III) Ions: Mechanistic Differentiation

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Volumes of activation for the aquation of a series of $Cr(NH_3)_5L^{3+}$ ions are all negative with an average value of *ca.* -6 cm^3 mol^{-1}, contrasting with an average positive value of *ca.* $+2$ cm^3 mol^{-1} for the Cobalt(III) analogues, and supporting disparate associative (I_a) and dissociative (I_d) mechanisms, respectively.

Over a period of several decades, various studies have supported a mechanistic differentiation between the aquation reactions of cobalt(III) and chromium(III) complexes. Reactions of cobalt(III) are apparently dominated by bond-breaking (dissociative) processes, while those of chromium(III) appear to be characterized by bond-making (associative) processes.[1] All examples for aquation of penta-ammine and pentakis(methylamine) complexes of cobalt(III), with either ionic or neutral leaving groups, show a significant rate enhancement for the methylamine systems, consistent with steric relief in forming a dissociated transition state, while halide loss from the alkylamine chromium(III) complexes is actually retarded, thought to be appropriate for steric congestion of an associated transition state.[2—6] However, several recent studies have placed doubt on the general validity of these divisions. Our earlier paper[4] dealing with aquation reactions of $M(NH_2R)_5Cl^{2+}$ (M = Co, Cr; R = H, Me) indicated that the importance of bond-breaking processes may change significantly from the penta-ammine to the pentakis(methylamine) complexes of chromium(III), permitting the mechanism in the latter case to be even described as I_d. Recently, Lay[7] has suggested that an I_d mechanism may generally apply to the aquation reactions of $M(NH_2R)_5Cl^{2+}$ (M = Co, Cr; R = H, Me), and based his arguments on the shorter Cr–Cl bond in $[Cr(NH_2Me)_5Cl]Cl_2$ than in $[Cr(NH_3)_5Cl]Cl_2$. Here, we present new evidence to suggest that mechanistic differentiation in aquation reactions of penta-ammine complexes of cobalt(III) and chromium(III) does exist.

When charged leaving groups are involved in aquation reactions, solvent electrostriction changes in forming the transition state contribute significantly to both the activation volume ($\Delta V^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$), and complicate the elucidation of the intimate nature of the reaction mechanism.[8] In this respect it is important to note that an I_a mechanism was suggested for the aquation of $Cr(NH_3)_5Cl^{2+}$ and an I_d mechanism for the aquation of $Co(NH_3)_5Cl^{2+}$ although $\Delta V^{\ddagger}$ is practically identical for both reactions, *viz.* -10.6 ± 0.3 and -9.9 ± 0.5 cm^3 mol^{-1}, respectively.[9,10] Such a negative $\Delta V^{\ddagger}$ can either be ascribed to bond formation with the entering water molecule (I_a), or increasing electrostriction during breakage of the metal–chloride bond (I_d). It is understandable that the unequivocal assignment of a mechanism is rather difficult under such conditions. Consequently, we have been investigating compounds with neutral leaving groups, where activation parameters more closely define intrinsic volume and entropy changes.[11] An earlier study of aquation reactions of complexes of the type $Co(NH_3)_5L^{3+}$ identified an essentially ligand-independent $\Delta V^{\ddagger}$ of *ca.* $+2$ cm^3 mol^{-1}, which was asserted to be consistent with the favoured I_d mechanism.[11] This study of an analogous series of chromium(III) complexes yielded $\Delta V^{\ddagger}$ values that are significantly negative with an average value of *ca.* -6 cm^3 mol^{-1} (see Table 1 for a few typical examples).

Notably, activation enthalpies for aquation of cobalt(III) complexes (average 102 kJ mol^{-1} for the series) and chromium(III) complexes (average 94 kJ mol^{-1} for the series) differ. Since M–Cl in $Cr(NH_3)_5Cl^{2+}$ is larger (2.327 Å)[7] than in $Co(NH_3)_5Cl^{2+}$ (2.286 Å),[12] this may reflect less bond extension to the transition state for chromium(III) in a common mechanism, assuming that data in the crystal lattice are directly transferable to the situation in the solvated ion, which need not be strictly correct. However, it is evident from our data (Table 1) that there is a volume contraction in

Table 1. Rate and activation parameters for reactions of the type $M(NH_3)_5L^{3+} + H_2O \longrightarrow M(NH_3)_5H_2O^{3+} + L$.

M = Co^{III}

Ligand (L)	$10^5 k$ at 25 °C/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}
OH_2	0.59	111	+28	+1.2
$OSMe_2$	1.8	103	+10	+2.0
$OCH{\cdot}NH_2$	0.58	107	+12	+1.1
$OCH{\cdot}NMe_2$	0.16	111	+16	+2.6
$OC(NH_2)_2$	5.5	94	−10	+1.3
$OC(NHMe)_2$	5.1	102	+17	+1.5

M = Cr^{III}

Ligand (L)	$10^5 k$ at 25 °C/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}
OH_2	5.2	97	0	−5.8
$OSMe_2$	1.9	95	−15	−3.2
$OCH{\cdot}NH_2$	5.1	94	−12	−4.8
$OCH{\cdot}NMe_2$	1.4	93	−25	−7.4
$OC(NH_2)_2$	2.0	93	−22	−8.2
$OC(NHMe)_2$	1.0	97	−14	−3.8

forming the transition state for the chromium(III) complexes. In terms of the simplest picture of a 'special' solvent molecule approaching the metal ion for eventual co-ordination, this can best be taken to imply some close approach by this solvent molecule in the transition state. The compressed transition state, occurring in a system where solvation phenomena beyond the site of exchange are as non-intrusive as practicable, clearly supports the definition of the mechanism for aquation of $Cr(NH_3)_5L^{3+}$, at least in terms of the conventional nomenclature, as I_a rather than the I_d mechanism appropriate for the aquation of $Co(NH_3)_5L^{3+}$. Furthermore, the data for the series of aquation reactions (Table 1) are in close agreement with the earlier reported data for the solvent exchange reactions of the aqua complexes[8,13] and underline the similarity in the ligand substitution process. The data do not exhibit a specific trend with the nature of the leaving group, only with the nature of the central metal ion.

Mechanistic differentiation on the basis of the sign and magnitude of $\Delta V^‡$ has been demonstrated with remarkable success especially for solvent exchange reactions of octahedral complexes.[13] This also holds for complex formation reactions involving neutral ligands,[14] and the presented data demonstrate how this can be extended to aquation reactions of complexes of the type $M(NH_3)_5L^{3+}$ ($M = Co^{III}, Cr^{III}$; L = neutral ligand). Such mechanistic differences are not inviolable, however, and steric crowding by alkylamine non-leaving ligands may lead to a common dissociative (I_d) process for the $Co(NH_2Me)_5Cl^{2+}$ and $Cr(NH_2Me)_5Cl^{2+}$ systems.[4,7] In the case of the cobalt(III) complexes, the increase in steric hindrance from ammine to alkylamine is accompanied by an increase in aquation rate constant and a more positive $\Delta V^‡$, *i.e.* a more dissociative process.[5] For the chromium(III) complexes, however, the retardation of the rate of aquation on increasing the steric hindrance is mainly due to a decrease in the Cr–Cl bond length,[7] which in turn may account for the changeover from an I_a to an I_d mechanism. This changeover is accompanied by an increase in $\Delta V^‡$ of 11.1 $cm^3 mol^{-1}$ (from -10.6 to $+0.5$ $cm^3 mol^{-1}$ for the aquation of $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_2Me)_5Cl^{2+}$, respectively).[4] Nevertheless, owing to the difficulties encountered in the interpretation of activation parameters for reactions in which major changes in electrostriction occur (see earlier discussion), the unequivocal assignment of a mechanistic changeover will have to await the corresponding activation parameters for the aquation reactions of sterically hindered chromium(III) complexes involving neutral leaving groups.

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