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Activation Volumes for Aquation of a Neutral Ligand from Ionic or Neutral Octahedral Complexes: Ureapentaamminecobalt(III) Dithionate and Chlorobis(dimethylglyoximato)ureacobalt(III)

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It has become common practice in both organic and inorganic reactions studied at elevated pressures to divide the experimental activation volume ($\Delta V^{\neq}_{exp}$) into two components [1, 2]. This separates intrinsic contributions resulting from nuclear displacements at the reaction centre ($\Delta V^{\neq}_{intr}$) from rearrangement of solvent molecules about the reactants ($\Delta V^{\neq}_{solv}$) which occur in forming the transition state. When dealing with dissociative reactions of charged ligands in the activation step, $\Delta V^{\neq}_{solv}$ is dominated by volume changes resulting from changes in electrostriction ($\Delta V^{\neq}_{el}$).

It has generally been assumed that the $\Delta V^{\neq}_{intr}$ term is the dominant component of $\Delta V^{\neq}_{exp}$ when displacement of neutral ligands is involved. Solvation changes between the ground and transition state should be minor in this case, hence $\Delta V^{\neq}_{solv}$ will be small. To date, this assumption has not been firmly tested for aquation reactions of octahedral complex ions. We have now approached this problem by determining $\Delta V^{\neq}_{exp}$ for aquation of cobalt(III) complexes of different formal charge but with the same unidentate leaving group, and present the results in this report. Results for a neutral leaving group are also contrasted with results for a charged leaving group.

For complex ions with anionic leaving groups, $\Delta V^{\neq}_{el}$ has been shown to be strongly negative and to dominate $\Delta V^{\neq}_{exp}$. For example, the complexes $Co(NH_3)_5(SO_4)^+$, $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5(Me_2SO)^{3+}$ exhibit $\Delta V^{\neq}_{exp}$ values of −18.5, −10.6 and −1.7 cm^3 mol^{-1} respectively for aquation as the charge on the leaving group falls from 2− to 1− to 0 [3, 4]. A dissociative mechanism applies in each case. The charge separation of, for example, $Co(NH_3)_5Cl^{2+}$ into $Co(NH_3)_5^{3+}$ and Cl^- in the dissociative limit leads to greater electrostriction of the transition state. Since the partial molar volume of bulk solvent water ($\bar{V}$ = 18 cm^3 mol^{-1}) and electrostricted water ($\bar{V} \approx 15$ cm^3 mol^{-1}) differ, increased electrostriction of the transition state demands a strongly negative $\Delta V^{\neq}_{el}$ when an anionic ligand is dissociated from a cationic complex. A range of reactions involving dissociation of charged ligands in the transition state have $\Delta V^{\neq}_{exp}$ which reflect the dominance of $\Delta V^{\neq}_{el}$ [2, 3, 5].

For complex ions with neutral leaving groups, observed $\Delta V^{\neq}_{exp}$ have been assumed to reflect mainly the $\Delta V^{\neq}_{intr}$ contribution. For example, aquo ligand exchange in $Co(NH_3)_5(OH_2)^{3+}$ ($\Delta V^{\neq}_{exp}$ = +1.2 cm^3 mol^{-1}) [6] and $Cr(NH_3)_5(OH_2)^{3+}$ ($\Delta V^{\neq}_{exp}$ = −5.8 cm^3 mol^{-1}) [7] can be interpreted in terms of dissociative and associative character arising from partial release or entry of a water molecule respectively in the transition state. While solvation changes in the transition state are assumed to be minor for neutral leaving groups, this has not been explicitly probed. We have chosen for study the strongly solvated 3+ ion $Co(NH_3)_5(urea)^{3+}$ and the formally neutral molecule $Co(dmg)_2Cl(urea)$ (dmg^- = dimethylglyoximato), both of which aquate spontaneously with loss of neutral O-bound urea and without any stereochemical change. Analytically pure samples of complexes studied were prepared using previously described methods [8–10].

Complex cations of 3+ charge possess several solvation layers of significantly electrostricted water molecules of lower molar volume than bulk water [5], while the relatively insoluble neutral molecule presents a system about which electrostricted solvation layers should be minimal. If $\Delta V^{\neq}_{solv}$ is not minor in these aquation reactions, the expectation is that the difference in this term and hence in $\Delta V^{\neq}_{exp}$ should be marked for these differently solvated complexes.

Determined $\Delta V^{\neq}_{exp}$ for the spontaneous aquation of $Co(NH_3)_5(urea)^{3+}$ and $Co(dmg)_2Cl(urea)$ in water (no added electrolyte) at elevated pressures are both small and positive (Table I). The similarity is sufficient to indicate that $\Delta V^{\neq}_{solv}$ is minor and that $\Delta V^{\neq}_{exp}$ hence reflects changes in the intrinsic volume of reactants on forming the transition state. Subsequently, the concept of a positive activation volume indicating a dissociative mechanism and a negative activation volume suggesting an associative mechanism has validity for reactions of complexes with neutral leaving groups. $\Delta V^{\neq}_{exp}$ is a more effective mechanistic guide than $\Delta S^{\neq}$ in these systems, since the latter varies markedly for the two complexes (Table) even though the expectation is for a dissociative mechanism in each case.

While it is not possible to maintain the same non-leaving groups in the above experiment, we may contrast the above results with $\Delta V^{\neq}_{exp}$ for aquation

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TABLE. Activation Volumes and Activation Entropies for Aquation Reactions.

Complex	$\Delta V^{\neq}$ ($cm^3\ mol^{-1}$)	$\Delta S^{\neq}$ ($J\ K^{-1}\ mol^{-1}$)	Reference
$Co(NH_3)_5(urea)^{3+}$	+1.3 (±0.5)	−10 (±4)	[a]
$Co(dmg)_2Cl(urea)^0$	+3.5 (±0.3)	−108	[a], 9
$Co(NH_3)_5Cl^{2+}$	−10.6	−44	3
$Co(dtcd)(N_3)Cl^+$	+8.3	−51	11

[a] This work.

of an anionic leaving group (Cl^-) from the complexes $Co(NH_3)_5Cl^{2+}$ and $Co(dtcd)(N_3)Cl^+$ (dtcd = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), where again both charge and non-leaving groups have been altered. The previously reported negative $\Delta V^{\neq}_{exp}$ for the $Co(NH_3)_5Cl^{2+}$ ion [3] contrasts markedly with the positive value for the macrocyclic $Co(dtcd)(N_3)Cl^+$ ion [11] (Table).

The substantial variation of $\Delta V^{\neq}_{exp}$ in the case of aquation of a charged ligand (dominant $\Delta V^{\neq}_{solv}$) from complexes with different charge and non-leaving groups contrasts sharply with the essentially similar $\Delta V^{\neq}_{exp}$ when aquation of a neutral ligand (dominant $\Delta V^{\neq}_{intr}$) is involved. One implication of this study is that activation volume alone may be a less successful indicator of mechanism when dealing with aquation of charged ligands than is the case for aquation of neutral ligands.

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