Inorganica Chimica Acta, 45 (1980) L275–L276
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Activation Volumes for Aquation of *cis*-Dichlorotetraaminecobalt(III) Ions: a View on the Molar Volume Difference between the Transition Intermediate and Precursor Complex

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Received September 3, 1980

The importance of volumes of activation ($\Delta V^{\neq}$) as a mechanistic guide in reactions of octahedral complexes has been established and reviewed previously [1–5]. It has become clear that in mechanistic elucidation based on $\Delta V^{\neq}$ data, some assumptions regarding the apparent molar volume (ϕ_V) of the transition intermediate ion need to be made. While molar volumes of reactants and products can be determined experimentally in most cases, affording the overall reaction volume (ΔV°) for a particular substitution process, no separate measure of the molar volume of the complex ion in the activated state is available. Consequently, conjecture about the molar volume of the complex intermediate is central to any mechanistic argument based on $\Delta V^{\neq}$ data.

From experimental data for a wide range of $Co(NH_3)_5X^{n+}$ ions, Palmer and Kelm have estimated a molar volume of 55 cm^3 mol^{-1} for the presumed $Co(NH_3)_5^{3+}$ intermediate [6]. This calculated volume is usually appreciably lower than partial molar volumes measured for a range of $Co(NH_3)_5X^{n+}$ ions, and implies that generally $\phi_V(ML_5^{n+}) < \phi_V(ML_5X^{n+})$. Stranks has argued earlier that the molar volumes of ML_6^{n+} and ML_5^{n+} will be essentially identical [2]; this analysis was developed specifically for the case of an ion with six identical ligands, as exemplified by $Ni(NH_3)_6^{2+}$ and the hypothetical $Ni(NH_3)_5^{2+}$ ion. Langford's recent analysis [7] of $Ni(OH_2)_6^{2+}$ and $Ni(OH_2)_5^{2+}$ predicts a volume difference of the order of only –4 cm^3 mol^{-1}, essentially in accord with Stranks' concept. Further, the observation [6] that $\phi_V(Co(NH_3)_6^{3+}) \cong \phi_V(Co(NH_3)_5^{3+})$ is consistent with their analyses. Nevertheless, for a dissociative mechanism, it is implied that ML_5^{n+} will be of a lower molar volume than the precursor ML_5X^{m+} ion as a result of (i) bond compression in the primary coordination sphere in the intermediate, and (ii) collapse of solvent onto the contracted ion [7]. A question of obvious significance is whether the molar volume of the pentacoordinate intermediate can approach that of its octahedral precursor under any circumstances other than the special and established case where all ligands are identical.

In the dissociative limit for the general reaction

$$ML_5X^{n+} \xrightarrow{\text{slow}} \{ML_5^{m+}\}^{\neq} + X^{q-} \xrightarrow[OH_2]{\text{fast}} \text{products}$$

one can write an expression for $\Delta V^{\neq}$ in terms of the apparent molar volumes (or, effectively, the partial molar volumes, $\bar{V}$):

$$\Delta V^{\neq} = \{\bar{V}(ML_5^{m+}) + \bar{V}(X^{q-})\} - \bar{V}(ML_5X^{n+}) \qquad (1)$$

$$= \{\bar{V}(ML_5^{m+}) - \bar{V}(ML_5X^{n+})\} + \bar{V}(X^{q-}) \qquad (2)$$

Since $\bar{V}(X^{q-})$ is usually positive, even for anionic leaving groups, a near-zero $\Delta V^{\neq}$ (*e.g.* $\Delta V^{\neq} = 1.7$ cm^3 mol^{-1} for Me_2SO aquation in $Co(NH_3)_5Me_2SO^{3+}$) or negative $\Delta V^{\neq}$ (*e.g.* $\Delta V^{\neq} = -9.9$ cm^3 mol^{-1} for halide aquation in $Co(NH_3)_5Cl^{2+}$) demands that $\bar{V}(ML_5^{m+})$ be smaller than $\bar{V}(ML_5X^{n+})$, at least for the pentaamminecobalt(III) system exemplified. However, there is no firm evidence supporting the universality of this behaviour; the possible role of the non-labile ligands has been mentioned but not analyzed in detail previously [5, 7].

Recently, $\Delta V^{\neq}$ values for chloride aquation from complexes with multidentate amine ligands have been reported [8, 9] and are positive. No dramatic mechanistic change is expected or has been implied for these aquation processes, although the molecules involved are apparently larger than $Co(NH_3)_5X^{n+}$ species previously studied. It has been suggested [8] that as the size of the precursor ion increases, the difference between the molar volumes of the precursor and intermediate ion diminishes, leading to more positive $\Delta V^{\neq}$ values, in accord with eqn. 2. To further assess this proposal, two other complexes with multidentate amine ligands and a chloride leaving group have been studied. The complexes *cis*-$Co(N_4)Cl_2^+$ (N_4 = tren = tris(aminoethyl)amine or N_4 = β-trien = triethylenetetramine) were selected since their aquation reactions to $Co(N_4)(OH_2)Cl^{2+}$ proceed with retention of configuration [10]; aquation of the previously studied *cis*-$Co(en)_2Cl_2^+$ [9] is complicated by isomerization [11].

Data for $Co(tren)Cl_2^+$ ($10^4 \cdot k_{obs}$ (s^{-1}), P (bar): 7.25, 1; 6.54, 345; 5.76, 690; 5.22, 1035; 4.76, 1380) and $Co(trien)Cl_2^+$ ($10^3 \cdot k_{obs}$ (s^{-1}), P(bar): 1.46, 1; 1.40, 345; 1.33, 690; 1.27, 1035; 1.24, 1380) collected at 13.8 °C and 25.0 °C respectively were treated as previously described [5], yielding positive and pressure-independent $\Delta V^{\neq}$ values (Table I) similar to data for previously studied systems with multidentate amine ligands. The distinctly different value obtained previously for $Co(NH_3)_5Cl^{2+}$ is

TABLE I. Activation Volumes for Aquation of Chloroaminecobalt(III) Complexes.

Complex	$\Delta V^{\neq}$ (cm^3 mol^{-1})	Ref.
$Co(NH_3)_5Cl^{2+}$	−9.9	6
trans-$Co(en)_2Cl_2^+$	+11.0	9
cis-$Co(tren)Cl_2^+$	+7.3 (±0.4)	a
cis-β-$Co(trien)Cl_2^+$	+3.0 (±0.6)	a
trans-$Co(dtcd)(N_3)Cl^{+}$ [b]	+8.3	8

[a] This work. [b] dtcd = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

remarkable, although it is obvious that the chromophore and charge has been altered.

Evidently, the data for the *cis*-$Co(N_4)Cl_2^+$ complexes can be interpreted in terms of similar molar volumes for precursor and intermediate ions for these larger molecules. Assuming in the limit that the precursor and intermediate ions are equivalent in molar volume, $\Delta V^{\neq}$ would approximate $\bar{V}(X^{q-})$ from eqn. 2, and $\bar{V}(X^{q-})$ is usually positive [12]. This analysis must be treated cautiously at present, since available data is limited. A possible alternative analysis of the data is that motion of the chelate rings in forming the activated intermediate may cause "squeezing out" of water molecules in their vicinity; this enforced motion of solvent away from the ion may counter other effects partially or completely. A recent study of isomerization reactions *trans* → *cis*-$Co(en)_2X(OH_2)^{n+}$ in D_2O suggests [13] that an appreciable positive contribution to $\Delta V^{\neq}$ from solvation changes exists at least in that system. The validity of the former analysis is being probed more fully by a systematic study of aquation reactions of alkyl-substituted pentaamminecobalt(III) complexes, where increasing $\bar{V}$ is not complicated by introducing chelation, and the same chromophore as in $Co(NH_3)_5Cl^{2+}$ is preserved.

It is apparent that the arguments applied to the interpretation of $\Delta V^{\neq}$ in the well-studied pentaamminecobalt(III) system are not readily extended to other amine systems where dissociative mechanisms apparently apply. Obviously, further study of systems with a variety of non-leaving groups is warranted. At present, it appears that measurement of an isolated $\Delta V^{\neq}$ value may not provide definitive mechanistic information, although useful evidence is usually forthcoming.

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