Activation Volumes for Aquation of Alcoholpentaamminecobalt(III) Ions

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Application of activation volume ($\Delta V^{\neq}$) as a mechanistic guide in inorganic reaction kinetics has attracted considerable attention in recent years [1–4], and the utility of the method has been demonstrated. In particular, pentaamminecobalt(III) complexes have been well studied, mainly with anionic leaving groups [5–10]. Negative $\Delta V^{\neq}$ values generally observed for anionic leaving groups suggest that solvent electrostriction changes in forming the activated state contribute significantly to $\Delta V^{\neq}$ [5]. Where the leaving group is not charged, such electrostrictive effects are apparently minor [9]; the limited data available for aquation reactions of cationic complexes involving neutral leaving groups indicates near-zero $\Delta V^{\neq}$ values in each case, contrasting with negative values for charged leaving groups.

Recent preparative advances have allowed ready access to a range of pentaamminecobalt(III) complexes with neutral ligands [11]. Consequently, it has been possible to complete a systematic study of the series of complexes $Co(NH_3)_5(OHR)^{3+}$ where R = H, CH_3, CH_2CH_3 or $CH(CH_3)_2$. The aquation rates of this series in aqueous acid have been compared at 25 °C, and vary as 1:11:14:57 for H:CH_3:CH_2CH_3: $CH(CH_3)_2$ [11]. Examination of Dreiding models revealed that there is little steric interaction between coordinated ammonias and the alcohols. The pressure-dependent aquation of the aqua complex alone has been reported previously [10]. In this study, the pressure dependence (to 1650 bar) of the aqua-

tion rate in dilute (0.01 *M*) CF_3SO_3H for each alcohol complex was determined, and $\Delta V^{\neq}$ values calculated as described previously [4]. Further, partial molar volumes ($\bar{V}$) of the complex $CF_3SO_3^-$ salts were determined in the usual manner [12], using a precision digital density apparatus. Results are presented in Table 1, together with literature values of $\bar{V}$ for the free alcohols in aqueous solution [13–15].

While $\bar{V}$ (alcohol) increases four-fold through the series studied, $\Delta V^{\neq}$ is essentially unchanged (differences < 3 cm³ mol⁻¹). The activation volumes are small and positive, although a small increase with increasing bulk of the leaving group is apparent. Together with $\Delta V^{\neq}$ values previously reported for the pentaamminecobalt(III) complexes of dimethylsulfoxide (−1.7 cm³ mol⁻¹) [5] and urea (+1.3 cm³ mol⁻¹) [9], all aquation reactions with neutral leaving groups exhibit near-zero $\Delta V^{\neq}$ values. In contrast, the anionic leaving groups Cl^- and SO_4^{2-} exhibit $\Delta V^{\neq}$ values of −10.6 cm³ mol⁻¹ and −18.5 cm³ mol⁻¹ respectively [6], presumably due to increasing and negative electrostrictive contributions. The small range of $\Delta V^{\neq}$ values observed with various neutral leaving groups supports the view that electrostrictive effects or solvation changes in forming the activated state are minor in this particular case.

For the overall reaction

$$Co(NH_3)_5(OHR)^{3+} + OH_2 \rightarrow$$
$$Co(NH_3)_5(OH_2)^{3+} + OHR \qquad (1)$$
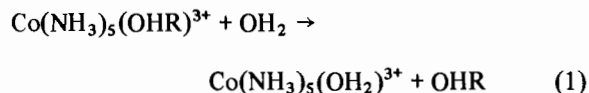
the reaction volume ($\Delta\bar{V}$) is defined as

$$\Delta\bar{V} = \{\bar{V}[Co(NH_3)_5(OH_2)^{3+}] + \bar{V}(OHR)\} -$$
$$- \{\bar{V}[Co(NH_3)_5(OHR)^{3+}] + \bar{V}(OH_2)\} \qquad (2)$$

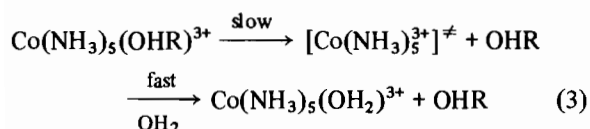The $\Delta\bar{V}$ values calculated from eqn. (2) are included in Table I, and closely approximate determined $\Delta V^{\neq}$

TABLE 1. Activation Volumes and Calculated Reaction Volumes for Aquation of $Co(NH_3)_5(OHR)^{3+}$ Complexes, and Partial Molar Volumes of Complex Ions and Ligands in Aqueous Solution at 25 °C.[a]

Ligand	$\Delta V^{\neq}$	$\Delta\bar{V}$[b]	$\bar{V}$(complex ion)	$\bar{V}$(ligand)[c]
OH_2	+1.2[d]	0.0	60.3	18.0
$OHCH_3$	+2.2	+1.6	78.8	38.1
$OHCH_2CH_3$	+2.9	+2.2	95.2	55.1
$OHCH(CH_3)_2$	+3.8	+2.9	111.3	71.9

[a]Units of cm³ mol⁻¹. [b]Calculated from eqn. (2). [c]Refs. 13–15. [d]Ref. 10.

values. This is also the case for anionic leaving groups, and a common mechanism is presumably operating, with electrostrictive effects contributing to both $\Delta V^{\neq}$ and $\Delta \bar{V}$ when the leaving group is charged.

The mechanism for aquation of aminecobalt(III) complexes has been established as dissociative in nature. Competition experiments have yielded evidence for a short-lived pentacoordinate intermediate in several cases [16]. In the dissociative limit, it is possible to express the aquation reaction as

$$Co(NH_3)_5(OHR)^{3+} \xrightarrow{\text{slow}} [Co(NH_3)_5^{3+}]^{\neq} + OHR$$

$$\xrightarrow[OH_2]{\text{fast}} Co(NH_3)_5(OH_2)^{3+} + OHR \qquad (3)$$

whence

$$\Delta V^{\neq} = \{\bar{V}[Co(NH_3)_5^{3+}] + \bar{V}(OHR)\} -$$

$$- \bar{V}[Co(NH_3)_5(OHR)^{3+}], \qquad (4)$$

exact only when complete bond-breaking occurs in the activated state. Substitution of experimental data yields an average $\bar{V}(Co(NH_3)_5^{3+})$ of 43 (±0.4) cm^3 mol^{-1} for the OHR series. This estimate for the pentacoordinate intermediate volume differs from the value of 55 cm^3 mol^{-1} estimated previously [5], from data for mainly anionic (1−) leaving groups.

The physical significance of these estimated $\bar{V}$ for the putative pentacoordinate intermediate is questionable, however, since the activated state may not contain the leaving group fully dissociated. There is evidence that competition for the intermediate is mediated somewhat by the type of leaving group [17]. The implication is that the lifetime of $Co(NH_3)_5^{3+}$ would be insufficient for the pentacoordinate species to adopt a common solvent environment in each case [18].

Subsequently, departure of a 1− ligand probably leaves the intermediate with the approximate solvation environment of the 2+ precursor, while a neutral leaving group yields an intermediate with the approximate solvation environment of the 3+ precursor; these intermediates react to yield products before they rearrange their solvent sheaths. The disparate

estimated $\bar{V}(Co(NH_3)_5^{3+})$ for the 3+ (OHR) and mainly 2+ precursors may reflect this phenomenon. A more extensive study with a variety of neutral leaving groups will probe this prospect further.

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