Solvent Effects on Solvolysis of Transition Metal Complexes: Part III†—Kinetics of Aquation of Chloropentaamminecobalt(III) in Aquo-Organic Solvent Media

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Received 24 February 1987; accepted 6 July 1987

The kinetics of aquation of chloropentaamminecobalt(III) ion has been investigated in aquo-organic solvent media in the temperature range of 40-55°C and in 0-60 wt% organic cosolvent such as MeOH, EtOH, isopropanol and t-butanol. Activation parameters are interpreted in terms of initial state and transition state solvation effects. It appears that the transition state is solvent-stabilised to a greater extent than the initial state. The rate data in isodielectric solvent media involving MeOH, EtOH, isopropanol, t-butanol, ethyleneglycol and dioxan (D = 50 at 40°C) interestingly point out the differential solvation interaction of these solvents with the substrate, the individuality of the monohydroxylic alcohols being completely lost in the correlation of aquation rate constant (log kaq) with the mol fraction of the organic solvent component.

It has now been realised that solvent structure plays important role in controlling the rate and activation parameters of solvolysis of haloamminecobalt(III) complexes. The interaction of ionic substrates with aquo-organic solvent media is likely to be influenced by the potential H-bonding sites available in the substrate and the solvent. The chloropentaamminecobalt(III) ion [([NH3]5)CoCl2+] is an ideally suited substrate in this regard as it possesses potential hydrophilic NH-centres for H-bonding with aqueous-alcoholic solvent systems. Earlier studies on solvolytic aquation of this substrate have been concerned with the correlation of aquation rate constant with 1/D (D = bulk dielectric constant) or Grunwald-Winstein's Y' parameters of the solvent to provide evidence in favour of the dissociative interchange mode (L) of activation. We present in this paper the results of a detailed investigation of the energetics of aquation of this substrate in different aquo-organic solvent media with a view to throwing light on the solvation of its initial state and transition state and explore the role, if any, of the structure of the solvent medium in modulating its reactivity.

Materials and Methods
Chloropentaamminecobalt(III) diperoxochlorate, prepared as mentioned earlier, analysed satisfactorily and its spectral parameters were in excellent agreement with those reported in the literature: \( \lambda_{\text{max}} = 532 \text{ nm} \) (e, dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)), 532 (50.5) lit \( \lambda_{\text{max}} = 532 \) (50.5)\(^4\) and 532 (50.8 \( \pm 0.4\)\(^5\)).

Absorption spectra were recorded on a Beckman DU\(_2\) spectrophotometer. Methanol and isopropanol (AR, BDH) were distilled before use. Absolute ethanol was prepared from rectified spirit. Dioxan (AR, BDH) was refluxed for 48 hr over solid caustic soda and distilled. It was again treated with sodium wire, kept overnight and redistilled. t-Butanol (AR, BDH) and ethyleneglycol (LR, BDH) were dried over anhydrous potassium carbonate before fractional distillation. All solvents were kept out of contact with atmospheric moisture. Solvent mixtures of desired compositions (weight %) were prepared using measured densities of the organic solvent and water.

The kinetics of aquation were followed by potentiometric titration of the liberated chloride against standard AgNO\(_3\) (N/100) and the pseudo-first order rate constant (k\(_{aq}\)) was calculated from the gradient of the plots of log (V\(_m\) - V) against time. V\(_m\) was determined by subjecting the mixture (5 cm\(^3\)) to base hydrolysis in the presence of alkali and then working up in the usual way.

For most of the solvent systems used and at > 40 Wt % organic cosolvent, the reverse reaction shown in Eq. (1), interfered with the aquation process. Under such condition the equilibrium point was established and the titration data were treated in terms of a first order reaction opposed by a second order reaction.

\[
\text{[NH}_3\text{]}_5\text{CoCl}_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{[NH}_3\text{]}_5\text{CoOH}_2^+ + \text{Cl}^-
\]

... (1)
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Table 1—Rate Data for Aquation of \((\text{NH}_3)_5\text{CoCl}^{2+}\) in Aquo-Organic Solvent Mixtures

<table>
<thead>
<tr>
<th>Wt % of organic cosolvent</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Isopropanol</th>
<th>t-Butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40°</td>
<td>45°</td>
<td>50°</td>
<td>40°</td>
</tr>
<tr>
<td>10.0</td>
<td>8.11</td>
<td>16.7</td>
<td>28.5</td>
<td>8.11</td>
</tr>
<tr>
<td>20.0</td>
<td>6.63</td>
<td>11.8</td>
<td>24.0</td>
<td>6.92</td>
</tr>
<tr>
<td>30.0</td>
<td>5.65</td>
<td>10.4</td>
<td>19.3</td>
<td>6.19</td>
</tr>
<tr>
<td>40.0</td>
<td>4.20</td>
<td>7.72</td>
<td>14.2</td>
<td>5.46</td>
</tr>
<tr>
<td>50.0</td>
<td>3.26</td>
<td>6.55</td>
<td>10.8</td>
<td>4.86</td>
</tr>
<tr>
<td>60.0</td>
<td>—</td>
<td>5.46</td>
<td>7.31</td>
<td>3.83</td>
</tr>
</tbody>
</table>

(a) \([\text{H}^+]_0 = 0.01, [\text{Complex}]_0 = 0.005 \text{ mol dm}^{-3}\)

\(10^6 k_{aq} (\text{s}^{-1})\) = 10.2 (40°C), 18.7 (45°C) and 33.7 (50°C) in the absence of organic cosolvent.

Results and Discussion

Table 1 presents the \(k_{aq}^+\) values, corresponding to the forward reaction in Eq (1), in various solvent systems at different temperatures. The plots of \(\log k_{aq}^+\) against \(D_s^{-1}\) (\(D_s = \text{bulk dielectric constant of the medium}\)) and \(X_{org}\) (\(X_{org} = \text{mol fraction of the organic solvent component}\)) at 40-45°C were linear in the MeOH-, EtOH- and isopropanol-water systems. However, deviations from linearity in the plots were distinct in t-butanol-water system beyond 30 wt%.

Linearity in the correlation of \(\log k_{aq}^+\) with \(Y_-\)-parameter was good in MeOH-water and EtOH-water systems but was poor in isopropanol and t-butanol-water systems (using the data of Robertson and Sugamori7 for the values of \(Y\)) (see Fig. 1). Hence individuality of solvent system is evident. Nevertheless, the electrostatic effect mediated by the solvent interaction with substrate appears to be the dominant factor in Co-Cl bond heterolysis. It is interesting to note that the individuality of the monohydroxylic alcohols is completely lost in the plot of \(\log k_{aq}^+\) versus \(X_{org}\) under isodielectric condition (Fig. 2). The data points in ethyleneglycol and dioxan clearly deviate significantly from linearity in opposite direction, indicating the rate- accelerating effect of the former and the rate- retardation of the latter (relative to monohydroxylic alcohols). It is in line with the fact that between ethyleneglycol and dioxan, the former acts as a better solvating agent than the monohydroxylic alcohols.

It has been suggested that aquation of \((\text{NH}_3)_5\text{CoCl}^{2+}\) in fully aqueous and mixed solvent media involves \(I_4\) mode of activation in which \(\text{Cl}^-\) at best is very weakly bound to the cobalt(III) centre in the transition state8. Recently volume profile calculations for aquation of \((\text{NH}_3)_5\text{CoX}^{n+}\) \((X = \text{Cl}^-, \text{Br}^-, \text{SO}_4^{2-}, \text{NO}_3^-, \text{Me}_2\text{SO} \text{ and } \text{H}_2\text{O})\) by Palmer and Kelm9 agree with the fact that the charges of the departing groups are fully developed in the transition state. Their calculations, based upon the additivity principle for the molar volume of the transition state, indicate that the transition state is a D-type one which leads to the formation of the intermediate \((\text{NH}_3)_5\text{Co}^3+\). It then seems reasonable to represent the general scheme of activation as shown in Scheme 1.

In accord with Scheme 1, and assuming that the additivity principle is valid for the transfer free energy of the transition state,

\[\Delta G_i(t.s.)_{(s-w)} = [\Delta G_i(\text{C}^+)_{(s-w)} + [\Delta G_i(\text{Cl}^-)]_{(s-w)} + [\Delta G_i(\text{Cl}^-)]_{(s-w)}\]

All runs were made at least in duplicate. The mean deviation of \(k_{aq}^+\) in most cases was <2%.
from water to mixed solvent, \([\Delta G^e_i (C_{3+})_{I_s-w} - \Delta G^e_{(I_s.)_{I_s-w}}]\). It may be noted, however, that the disagreement in two sets of values of \(\Delta G^e_{(I_s.)_{I_s-w}}\) is relatively more stabilised than the dipo­site initial state when transfer occurs from water to the mixed solvent (s). The free energy of activation in mixed solvent and in water respectively; \([\Delta G^e_i (C_{3+})_{I_s-w}\) is the transfer free energy of the species i when transferred from water (w) to the mixed solvent (s).

\[
\frac{\Delta G^e_i (C_{3+}) - \Delta G^e_i (I_s.)}{\Delta G^e_i (I_s. - w)} = \Delta G^e - \Delta G^e_{(I_s.)_{I_s-w}} - \Delta G^e_{(I_s.)_{I_s-w}} = \Delta G^e_{(I_s.)_{I_s-w}} < \Delta G^e_{(I_s.)_{I_s-w}}
\]

where \(C^e_{3+} = [(NH_3)_5Co^3+]\), \(\Delta G^e_{(I_s.)_{I_s-w}}\) and \(\Delta G^e_{(I_s.)_{I_s-w}}\) denote the free energy of activation in mixed solvent and in water respectively; \([\Delta G^e_i (I_s.)_{I_s-w}\) is the transfer free energy of the species i when transferred from water (w) to the mixed solvent (s). The values of \(\Delta G^e_i (Cl^-)\) at 298.2 K for the solvent systems were taken from literature, (directly or by extrapolation/interpolation to the desired solvent composition), were converted into the mol fraction scale and the values of the relative transfer free energy term at all solvent compositions \([\Delta G^e_i (C_{3+}) - \Delta G^e_i (I_s.)(I_s.-w)\) were calculated at 25°C. These were plotted as a function of \(X_{org}\) (Fig. 3). It is interesting to note that the relative transfer free energy term is strongly negative at all solvent compositions except in MeOH-water system for which it is less convincing due to the larger disagreement in the data for \(\Delta G^e_i (Cl^-)\) reported by Abraham et al., Kundu et al., and Wells. Nevertheless it is worth noting that tripositive cobalt(III) centre in the transition state is relatively more stabilised than the dipositive initial state when transfer occurs from water to mixed solvent, \([\Delta G^e_i (C_{3+})]_{I_s.-w} < [\Delta G^e_i (I_s.)(I_s.-w)\) in MeOH-water system is perhaps due to different extra thermodynamic assumptions used as pointed out by Blandamer et al. Also it is important to note that different experimental methods of evaluation of \([\Delta G^e_i (Cl^-)(I_s.-w)\) yield slightly different results for isopropanol-water and t-butanol-water solvent systems (see Fig. 3). Nevertheless the nonlinear variation of \([\Delta G^e_i (C_{3+}) - \Delta G^e_i (I_s.)_{I_s.-w}\) with \(X_{org}\) exhibiting minima in the plots (Fig. 3) depict the solvent structural reorganisation in the cospheres of the initial state and transition state of the substrate. The activation parameters are given in Table 2.

The solvent structural changes in the cospheres of the initial state and the transition state are also evident in the activation enthalpy and activation entropy versus \(X_{org}\) plots (Fig. 4, curves a and b). The solvent cosphere effects on \(\Delta H^*$ and \(\Delta S^*$ seem to vary with the nature of the organic solvent component in the order: t-butanol > isopropanol > EtOH > MeOH. It is worthwhile to note that there exists

![Diagram](image)

**Table 2—Activation Parameters* for Aquation of (NH$_3$)$_5$CoCl$_2$ in Aquo-Organic Solvent Mixtures**

<table>
<thead>
<tr>
<th>% of organic cosolvent</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Isopropanol</th>
<th>t-Butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Delta H^*)</td>
<td>(\Delta S^*)</td>
<td>(\Delta H^*)</td>
<td>(\Delta S^*)</td>
</tr>
<tr>
<td>10.0</td>
<td>103 ± 1</td>
<td>-15 ± 5</td>
<td>108 ± 1</td>
<td>+25 ± 2</td>
</tr>
<tr>
<td>20.0</td>
<td>100 ± 2</td>
<td>-23 ± 7</td>
<td>108 ± 2</td>
<td>+2 ± 5</td>
</tr>
<tr>
<td>30.0</td>
<td>102 ± 2</td>
<td>-20 ± 5</td>
<td>103 ± 1</td>
<td>-17 ± 2</td>
</tr>
<tr>
<td>40.0</td>
<td>101 ± 2</td>
<td>-25 ± 5</td>
<td>102 ± 2</td>
<td>-21 ± 7</td>
</tr>
<tr>
<td>50.0</td>
<td>105.9 ± 0.4</td>
<td>-11 ± 2</td>
<td>99.1 ± 0.4</td>
<td>-29 ± 1</td>
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<tr>
<td>60.0</td>
<td></td>
<td></td>
<td>106.2 ± 0.4</td>
<td>-10 ± 1</td>
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</table>

*Units: kJ mol$^{-1}$ for \(\Delta H^*\) and JK mol$^{-1}$ for \(\Delta S^*\); \(\Delta H^* = 97.9 ± 0.8$ kJ mol$^{-1}$ and \(\Delta S^* = -28 ± 2.5$ JK mol$^{-1}$ in aqueous medium.
ensatory. It is reasonably to think that variation in enthalpy and entropy values are associated with the enthalpy and entropy changes, due to H-bond breaking and reformation in the Gurney-cosphere\textsuperscript{14} of the initial state and the transition state of the substrate.

**Acknowledgement**

One of the authors (ACD) is thankful to the CSIR, New Delhi for financial support. This work forms a part of the Ph.D thesis of NCN who is thankful to the UGC, New Delhi for the award of Junior Research Fellowship.

**References**