Effect of ion-pairing on the kinetics of aquation of bromopentamminecobalt(III) perchlorate in dicarboxylate-acetate media

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Kinetics of aquation of [Co(NH$_3$)$_5$Br]$^2^+$ in different types of dicarboxylate solutions containing acetone (10%, v/v), at different temperatures have been investigated in the light of the effects of ion-pairing on reaction rates and mechanism. A new empirical correlation between the rate coefficient and the stoichiometric concentration of the ion-pairing dicarboxylate ligand (C$_L$) has been established and a reaction mechanism is proposed.

Aquation of [Co(NH$_3$)$_5$Cl]$^2^+$ is increased by the presence of monovalent like chloride, nitrate, chlorate, formate and acetate since the rate depended on the concentration of these ions. Jones et al. found that the correlation of the rate coefficient, $k_{o_b_s}$, with the stoichiometric concentration of the univalent ligand is linear for the aquation of [Cr(NH$_3$)$_5$Cl]$^2^+$ while that of the divalent dicarboxylate ligands is a non linear one. Amira et al. proposed a new empirical equation correlating $k_{o_b_s}$ and the stoichiometric concentration of the ion-pairing ligand, $C_L$, in the form

$$k_{o_b_s} = k_1 + C \cdot K_{a_s_s} C_L$$

where $C$ is an empirical constant and $K_{a_s_s}$ is the thermodynamic association constant.

The present work is a new application of the aquation of [Co(NH$_3$)$_5$Br]$^2^+$ in 10% (v/v) acetonediacarboxylate solutions at six different temperatures in an attempt to correlate the rate coefficient with the stoichiometric concentration of the dicarboxylate ligand and to discuss the effect of temperature on ion-pair formation.

Experimental

Succinic, malic, tartaric, malonic, maleic acids and sodium carbonate used were of Analar grade. Bromopentamminecobalt(III) bromide was prepared by literature method and converted to the perchlorate salt [Co(NH$_3$)$_5$Br][ClO$_4$]$_2$ by precipitation from a hot concentrated solution of acidified LiClO$_4$ by cooling in ice-water.

The rate of aquation was followed by potentiometric titration of the released bromide ions at regular time intervals using cooled samples in a bath containing ice-water. This method of analysis was found to be in a good agreement with both spectrophotometric and potentiometric methods.

Results and discussion

The kinetics of aquation of [Co(NH$_3$)$_5$Br]$^2^+$ was performed at six different temperatures in the range 30-60°C using succinate, malate, tartrate, malonate and maleate containing 10% (v/v) acetone. For each dicarboxylate system (80% neutralized dicarboxylic acid by Na$_2$CO$_3$) a set of kinetic runs were conducted for different stoichiometric concentrations of the dicarboxylate ligand $C_L$. The values of the observed first order rate constant, $k_{o_b_s}$, were calculated from the potentiometric titration readings by the linear least squares analysis of

$$\ln V_w / V_\infty - V_t = k_{o_b_s} t \quad (V_t = \text{titre at time } t \text{ and } V_\infty = \text{infinity titre})$$

Empirical correlation of $k_{o_b_s}$ with $C_L$

Figure 1 shows that plot of $k_{o_b_s}$ versus $C_L$ for three temperatures. It is obvious from Fig. 1 that for a given temperature a group of linear plots originating from $k_1$ (the first order rate coefficient in the absence of dicarboxylate ligand) are obtained while $k_{o_b_s}$ attains a maximum value called $k_s$ at higher $C_L$ value. This linear correlation takes the form

$$k_{o_b_s} = k_1 + bC_L \quad \ldots (1)$$

The order of increase in slope $b$ is succinate < malate < tartrate < malonate < maleate. A linear correlation of $b$ with the ion-pair association constant ($K_{a_s_s}$) ($K_{a_s_s}$ values are taken from ref. 4) for different buffers is found and Fig. 2 represents this correlation at 50°C and 55°C. This correlation takes the form

$$b = C K_{a_s_s} \quad \ldots (2)$$

from Eqs 1 and 2

$$k_{o_b_s} = k_1 + C K_{a_s_s} C_L \quad \ldots (3)$$

The plot of $k_s$ versus $K_{a_s_s}$ for a given temperature (Fig. 3), is linear with a positive slope and a posi-
rivative intercept (equal to $k_1$) which can be represented as,

$$k_s = k_1 + d K_{\text{ass}}$$  \hspace{1cm} (4)

from Eqs 1, 3 and 4 one can obtain

$$k_{\text{obs}} = k_1 + C/d (k_s - k_1) C_L$$  \hspace{1cm} (5)

The different values of $b$, $C$ and $d$ are given in Table 1. The parallelism between either the catalytic constant $b$ or $k_1$ and $K_{\text{ass}}$ for all studied dicarboxylate ligands is a strong evidence for the fact that the dicarboxylate anions form an electrostatic ion-pair in which the anion is localized in its interaction with the complex cation. The position taken up by the anion is across the back edge of the octahedron in such a way that $\pi$-bonding with $t_{2g}$ orbital is possible. Equation (5) can explain the Garrie equation

$$k_{\text{obs}} = k_1 + K_L C_L$$

where $K_L$ is the catalytic coefficient which can be compared with $C/d (k_s - k_1)$.

The catalytic coefficient $b$ is temperature dependent, and $\log b$ is linearly correlated with the reciprocal of the absolute temperature. This correlation takes the form $b = m e^{-n/T}$ and the constants $m$ and $n$ are given in Table 1. This final correlation reflects the dependence of ion-pair formation on the temperature.

**Proposed reaction mechanism**

The following proposed reaction mechanism can explain the empirical Eq. (3)

$$[\text{Co(NH}_3\text{)}_5\text{Br}]^2+ + \text{H}_2\text{O} \xrightarrow{k_0} [\text{Co(NH}_3\text{)}_5\text{H}_2\text{O}]^3+ + \text{Br}^-$$

$$\text{CpBr}^2+ + \text{L}^2- \xrightarrow{K_{\text{ass}}} \text{CpBrL} \text{ (ion pair)}$$

($\text{L}^2-$ is the dicarboxylate anion, $K_{\text{ass}}$ is the association concentration constant and $[\text{Co(NH}_3\text{)}_5\text{Br}]^2+$ = $\text{CpBr}^2+$).
Table 1—Values of $10^4 (b)$, $10^5 (k_1)$, $10^6 (C)$, $10^4 d$, $10^{-3} (n)$ and $10^{-5} (m)$ for the aquation of $\text{[Co(NH}_3\text{)}_s\text{Br}_2]^2^+$

<table>
<thead>
<tr>
<th>Buffer</th>
<th>$30^\circ$</th>
<th>$40^\circ$</th>
<th>$45^\circ$</th>
<th>$50^\circ$</th>
<th>$55^\circ$</th>
<th>$60^\circ$</th>
<th>$10^{-3} (n)$</th>
<th>$10^{-5} (m)$</th>
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<tbody>
<tr>
<td>Succinate</td>
<td>0.50</td>
<td>8.10</td>
<td>18.00</td>
<td>28.00</td>
<td>28.00</td>
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<tr>
<td>($10^3 k_1$)</td>
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<td>(17.50)</td>
<td>(24.20)</td>
<td>(42.20)</td>
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<tr>
<td>Malate</td>
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<td>8.50</td>
<td>21.50</td>
<td>32.00</td>
<td>37.00</td>
<td>94.00</td>
<td>5.10</td>
<td>16.45</td>
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<tr>
<td>($10^5 k_1$)</td>
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<td>(18.60)</td>
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<td>60.00</td>
<td>105.00</td>
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<tr>
<td>($10^6 k_1$)</td>
<td>(2.10)</td>
<td>(3.70)</td>
<td>(11.20)</td>
<td>(21.80)</td>
<td>(32.80)</td>
<td>(47.70)</td>
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<td>Malonate</td>
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<td>(12.47)</td>
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<td>$10^4 (d)$</td>
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<td>40.00</td>
<td>73.60</td>
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</table>

\[\text{CpBrL} + \text{H}_2\text{O} \xrightarrow{k} \text{[Co(NH}_3\text{)}_s\text{H}_2\text{O}^2^+] + \text{Br}^- + \text{L}^2^-\]

The overall rate equation

\[k_{obs}C = k_0C + kK_{ass}C\text{C}_L\]  \hspace{1cm} ... (6)

or

\[k_{obs} = k_0 + kK_{ass}\text{C}_L\] \hspace{1cm} ... (7)

Equation (7) discusses the effect of \(C\_L\) on \(k_{obs}\) which is identical to the empirical Eq. (3) which is in good agreement with other similar complexes.

References