Kinetics & Mechanism of Oxidation of Coordinated Formate by Chlorine

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The kinetics of chlorine oxidation of formatopentamminecobalt(III) perchlorate has been investigated in the temperature range 45 to 60°C. The reaction is first order each in the reactants. The reaction rate is enhanced by increasing pH and increasing [chloride]. Assuming Cl₂ and OCl⁻ to be the active oxidising species a probable mechanism has been proposed.

Though kinetics of chlorine oxidation of a number of substrates have been studied, similar studies on coordinated substrate species are lacking. Presently we have investigated the kinetics and mechanism of oxidation of coordinated formate in a substitution-inert complex like formatopentamminecobalt(III) perchlorate by chlorine.

Formatopentamminecobalt(III) perchlorate was prepared by following published method. The compound was characterised by estimating cobalt and formate. All solutions were prepared from reagent grade chemicals. Sodium perchlorate and sodium chloride solutions, standardised by ion exchange method using Dowex 50 WX-8 cation exchange resin, were used to maintain ionic strength and chloride concentration respectively. Acetic acid-sodium acetate buffer was used for adjusting pH.

A standard solution of chlorine in water was used as oxidant. It was standardised iodometrically.

The course of the reaction, which was conducted in dark-coloured bottles, was followed by estimating unreacted chlorine iodometrically. Iodine did not react with formato complex under these conditions. Blank experiments indicated that the loss of chlorine under the present experimental conditions was only 3% and hence was neglected. The results of stoichiometric runs with five-fold excess of chlorine indicated that one mol of substrate consumes one mol of oxidant.

The reaction between chlorine and formato complex was studied under second order conditions and the kinetic results fitted best the second order rate equation. The observed second order rate constant, \( k_{obs} \), was independent of both the [substrate] and [oxidant] (Table I) indicating that the reaction is first order in each reactant. The second order rate constant did not vary with change in ionic strength. The reaction rate was enhanced by increasing [chloride] and increasing pH. For example, increasing [chloride] from 0.05 to 0.4 mol dm⁻³ at 45°C when [complex] = [chlorine] = 3 × 10⁻³ mol dm⁻³ and pH = 4.4 increased \( 10^2 k_{obs} \) (dm² mol⁻¹ s⁻¹) from 0.79 to 2.02 while the increase was from 0.87 to 7.71 when pH was increased from 4 to 5.6 at [Cl⁻] = 0.1 mol dm⁻³ all other conditions remaining the same.

Chlorine in aqueous solution exists as Cl₂, HOCI and OCl⁻ as per the following equilibria 1 and 2.

\[
\begin{align*}
\text{Cl}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{HOCI} + \text{H}^+ + \text{Cl}^- \\
\text{HOCI} & \rightleftharpoons \text{OCl}^- + \text{H}^+ 
\end{align*}
\]

The values of \( K_1 \) and \( K_2 \) at 25°C have been reported to be \( 4.2 \times 10^{-4} \) and \( 3.4 \times 10^{-8} \) respectively. Since water is present in large excess its concentration is constant; the value of \( K = K_1 [\text{H}_2\text{O}] \) was calculated to be \( 2.34 \times 10^{-2} \).

Using Eqs 1 and 2 it is possible to deduce Eqs 3 and 4 under the conditions pH = 4 to 5.6 and [Cl⁻] = 0.05-0.4 mol dm⁻³.

\[
\frac{[\text{Cl}_2]}{[\text{Cl}^-]} = \frac{[\text{H}^+]}{[\text{Cl}_2][\text{H}_2\text{O}]} \\
\text{and} \quad \frac{[\text{OCl}^-]}{[\text{Cl}_2]} = \frac{K_2}{[\text{H}^+]}
\]

(Where [Cl₂]ₜ and [Cl⁻]ₜ are free and total chlorine concentrations respectively). The observed variation of the second order rate constant with [Cl⁻] and [H⁺] can be explained by assuming Cl₂ and OCl⁻ to be the oxidant species and the following mechanism (Scheme I) for the reaction may be proposed:

Table I — Effect of Varying Reactant Concentration on Rate

<table>
<thead>
<tr>
<th>Temp. = 50±0.1°C, pH = 4.4, [Cl⁻] = 0.1 mol dm⁻³</th>
<th>10⁻²[Complex], mol dm⁻³</th>
<th>3.0</th>
<th>4.0</th>
<th>6.0</th>
<th>8.0</th>
<th>10.0</th>
<th>3.0</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻²[Chlorine], mol dm⁻³</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>4.0</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>10⁻²k_{obs}, dm² mol⁻¹ s⁻¹</td>
<td>1.94</td>
<td>1.76</td>
<td>1.74</td>
<td>1.89</td>
<td>1.88</td>
<td>2.04</td>
<td>2.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(±0.02)</td>
<td>(±0.24)</td>
<td>(±0.20)</td>
<td>(±0.30)</td>
<td>(±0.31)</td>
<td>(±0.28)</td>
<td>(±0.06)</td>
<td></td>
</tr>
</tbody>
</table>
The rate of the reaction is given by Eq. (5),

\[
\text{Rate} = k_1^{'} [\text{Cl}_2]_T [\text{S}] + k_2^{'} [\text{OCI}^-] [\text{S}] \quad \ldots (5)
\]

where \([\text{S}]\) stands for the substrate concentration. Substituting the values of \([\text{Cl}_2]_T\) and \([\text{OCI}^-]\) from Eqs (3) and (4) in Eq. (5) one obtains Eq. (6).

\[
\text{Rate} = [\text{S}] [\text{Cl}_2]_T \left( \frac{k_1^{'} [\text{H}^+] [\text{Cl}^-]}{K} + k_2^{'} K_2 [\text{H}^+] \right) \quad \ldots (6)
\]

The observed second order rate constant, \(k_{\text{obs}}\) is obviously given by

\[
k_{\text{obs}} = k_1^{'} [\text{H}^+] [\text{Cl}^-] + k_2^{'} [\text{H}^+] \quad \ldots (7)
\]

(\text{where } k_1^{'} / K = k_1 \text{ and } k_2^{'} K_2 = k_2)

Eq. (7) indicates that at constant \(pH\), the plot of \(k_{\text{obs}}\) versus \([\text{Cl}^-]\) should be linear as has indeed been observed. Plot of \(k_{\text{obs}}\) versus \([\text{H}^+]\) or \(1/[\text{H}^+]\) was non-linear as expected from the nature of Eq. (7). From the plot of \(k_{\text{obs}}\) versus \([\text{Cl}^-]\) at constant \(pH\), the values of \(k_1\) and \(k_2\) were calculated (slope = \(k_1^{'} [\text{H}^+]\) and intercept = \(k_2^{'} [\text{H}^+]\). \(k_1\), \(k_2\) and the corresponding activation parameters calculated from Eyring equation are incorporated in Table 2.

Data presented in Table 2 indicate that \(k_1^{'} / k_2\) is about \(5 \times 10^8\) and the contribution of the \(k_2\) path to the overall rate appears to be negligible. In this connection the following points may be considered. The values of \(k_1\) and \(k_2\) have been calculated from the \(k_{\text{obs}}\) versus \([\text{Cl}^-]\) plot in \([\text{Cl}^-]\) range 0.05 to 0.4 mol dm\(^{-3}\) at \(pH = 4.4\). Under such experimental conditions it is possible to show, using Eq. (7), that contribution of rate of the \(\text{Cl}_2\) path to the overall rate ranges from about 30 to 75\% and that of the \(\text{OCI}^-\) path from 70 to 25\%. Thus the contributions of the \(\text{Cl}_2\) and the \(\text{OCI}^-\) paths to the overall rate are comparable. But to decide the fate of the overall reaction, besides the rates, the activation parameters should also be considered.

Table 2 indicates that the \(\text{Cl}_2\) path \((k_1\) path\) is associated with lower activation enthalpy which probably makes the reaction in the \(\text{Cl}_2\) path much more favourable than that in \(\text{OCI}^-\) path. The greater reactivity of \(\text{Cl}_2\) may be due to the fact that \(\text{Cl}_2\) is a much stronger oxidant\(^8\) than \(\text{OCI}^-\). The rate is almost unaffected by the variation in ionic strength. This further indicates that the major portion of the reaction proceeds via the \(\text{Cl}_2\) path.

When carboxylatopentaamminecobalt(III) complexes are oxidised, the products formed are either \((\text{NH}_3)_5 \text{Co(H}_2\text{O})_3^{3+}\) or \(\text{Co}^{2+}\) or both depending on the nature of the oxidant used and the life period of the reaction intermediate generated\(^6\). In the present investigation \((\text{NH}_3)_5 \text{Co(H}_2\text{O})_3^{3+}\) was shown to be the only reaction product\(^3\).

Compared to the \(k_1\) path, the lower value of \(\Delta S^*\) for the \(k_2\) path implies that the transition complex is more ordered. The opposite charges associated with the substrate and the oxidant (\(\text{OCI}^-\)) are probably responsible for the formation of a more ordered transition complex for the \(k_2\) path.

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References