Kinetics and mechanism of oxidation of chromium(III)-L-glutamic acid complex by periodate

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The kinetics of oxidation of the chromium(III)-L-glutamic acid complex, [Cr(III)(L)(H₂O)₃]⁺, by periodate in aqueous solutions has been found to obey the following equation:

\[
d[Cr^{VI}] / dt = k_2 [Cr(III)(H₂O)₃]⁻[1 + ([H⁺]/K_1) + [Cr(III)HL]⁺]
\]

where \(k_2\) is the rate constant for the electron transfer process, \(K_1\) the equilibrium constant for dissociation of \([Cr(III)(L)(H₂O)₃]⁺\) to \([Cr(III)(L)(H₂O)(OH)]⁻ + H⁺\), and \(K_2\) the pre-equilibrium formation constant. Values of \(k_2 = 2.93 \times 10^{-5} \text{s}^{-1}\), \(K_1 = 6.26 \times 10^{-4} \text{mol dm}^{-3}\) and \(K_2 = 88.41 \text{dm}^3 \text{mol}^{-1}\) have been obtained at 30°C and \(I = 0.2 \text{mol dm}^{-3}\). Thermodynamic activation parameters have been calculated. It is proposed that electron transfer proceeds through an inner-sphere mechanism via coordination of IO₄⁻ to chromium(III).

Inorganic substrates are oxidized by periodate through an intermediate, which is formed either through a bridging group or by coordination of IO₄⁻ to the metal ion. Evidence for the fact that the periodate ion is capable of acting as a ligand in this way is furnished by its coordination to copper(III) and nickel(IV).

Oxidation of chromium(III)-tetraoxalylurea and chromium(III)-DL-valine by periodate has also been proposed with the hydroxo-group acting as bridging ligand, or through substitution of coordinated H₂O by IO₄⁻. The kinetics of oxidation of [Cr(III)(L)₂(H₂O)₃]⁺ (L = L-glutamic acid) by periodate is discussed in this note.

Experimental

Chromium(III)-L-glutamic acid was prepared by the reported method. NaIO₄, NaNO₃, NaCl, NaOH and HCl were of reagent grade quality and were used without further purification. A stock solution of NaIO₄ was made up by weight and wrapped with aluminum foil to avoid photochemical decomposition. NaCl/HCl buffers of known pH (2.32-3.48) were used.

Oxidation of L-glutamic acid by periodate was checked, no reaction was observed during the reaction time under our experimental conditions.

Kinetic procedure

The UV-vis absorption spectra of the oxidation products of [Cr(III)(L)₂(H₂O)₃]⁺ by IO₄⁻ were recorded using a Shimadzu UV-160 IPC spectrophotometer. The reaction mixture was prepared as follows: 4.0 ml (0.2 M HCl + 0.2 M NaCl) + 1.6 ml (0.2 M NaNO₃ + 1.0 ml 0.01 M Cr(III)-complex + 4.0 ml 0.2 M IO₄⁻ (added at the beginning of reaction) were made up to a total volume of 40 ml by deionized water, thermally equilibrated for about 15 min, thoroughly mixed and quickly transferred to an absorption cell. Initial oxidation rates were measured by monitoring chromium(VI) absorbance at 350 nm on a Milton-Roy 601 spectrophotometer. The pH of the reaction mixture was measured using a Chertsey, Surrey, 7065 pH-meter.

Pseudo-first order conditions were maintained in all runs using a large excess of IO₄⁻ (> 10-fold). Ionic strength was kept constant by the addition of NaN₃ solution. The pH of the reaction mixture was found to be always constant during the reaction run.

Potentiometric measurements were performed with a Metrohm 686 titroprocessor equipped with 665 Domsimat (Metrohm, Herisau).

Oxidation products

During the oxidation, the violet solution of [Cr(III)(L)₂(H₂O)₃]⁺ in H₂O gradually turned to yellow and its original absorption maxima, at 572 and 413 nm, were replaced by a single peak at 350 nm with molar absorption coefficient \(\varepsilon_{350} = 1600 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^{-3}\). The UV-visible spectrum of the final product was the same as that of chromate ion (Fig. 1). Proving that chromium(VI) is the essential oxidation product.

Stoichiometry

A known excess of chromium(III)-complex over that of periodate was mixed. The absorbance of chromium(VI) produced was measured at 350 nm after 24 hours from the onset of the reaction. The consumed number of moles of chromium(III)-
complex was calculated using the molar absorptivity of chromium(VI).

**Results and discussion**

Oxidation of \([\text{Cr}^{III}(L_2(H_2O))_2]^+\) by periodate was studied in the pH range 2.32-3.48, and 20-40°C for a range of periodate and complex concentrations. The concentration ratio of IO₄⁻ (initially present) to chromium(VI) produced was found to be 3:2 (Table 1). Therefore, the stoichiometry of the reaction can be represented by Eq. (1)

\[
2\text{Cr}^{III}\text{-complex} + 3\text{I}^{VII} \rightarrow 2\text{Cr}^{VI} + 3\text{I}^+ + \text{other product}
\]  

where \(\text{Cr}^{III}\text{-complex}\) and \(\text{I}^{VII}\) represented total chromium(III)-complex and periodate respectively. The stoichiometry is also consistent with the observation that \(\text{I}^0\) does not oxidize the chromium(III) complex over the pH range studied.

Plots of \(\ln(A_- - A_1)\) versus time and \(1/(A_- - A_t)\) versus time, where \(A_-\) and \(A_t\) are absorbances at infinity and time \(t\), respectively, showed marked deviations from linearity (linear only up to 50%). The order with respect to the complex is thus neither first nor second. The initial rate method was thus employed to determine the order with respect to the complex concentration. The initial oxidation rates \((d[\text{Cr}^{III}] / dt)\) at all \([\text{Cr}^{III}]\) used were obtained from the tangents of the absorbance versus time plots employing the appropriate molar absorptivity for chromium(VI). The pseudo-first order rate constant, \(k_{obs}\), was calculated from the slopes of these plots. The results in Table 2 show that \(k_{obs}\) was unaffected when

\[
\begin{array}{cccccc}
[\text{Cr}^{III}(L_2(H_2O)_2)]^+ & 10^4 & [\text{IO}_4^-] & 10^5 & [\text{Cr}^{VI}] & [\text{IO}_4^-]:[\text{Cr}^{VI}] \\
& \text{mol dm}^{-3} & \text{mol dm}^{-3} & \text{mol dm}^{-3} & \text{mol dm}^{-3} & \\
2.5 & 2.5 & 1.60 & 1.56 \\
5.0 & 5.0 & 3.22 & 1.55 \\
7.5 & 7.5 & 4.74 & 1.58 \\
\end{array}
\]

Table 2—Dependence of the rate on \([\text{Cr}^{III}(L_2(H_2O)_2)]^+\), \([\text{IO}_4^-]\) and temperature at \(pH = 3.12\) and \(I = 0.2\) mol dm⁻³

<table>
<thead>
<tr>
<th>(10^2 [\text{IO}_4^-]) mol dm⁻³</th>
<th>(T = 20^\circ)</th>
<th>(25^\circ)</th>
<th>(30^\circ)</th>
<th>(35^\circ)</th>
<th>(40^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.29</td>
<td>0.38</td>
<td>0.50</td>
<td>0.56</td>
<td>0.62</td>
</tr>
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<td>1.0</td>
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<td>0.63</td>
<td>0.80</td>
<td>0.96</td>
<td>1.16</td>
</tr>
<tr>
<td>2.0</td>
<td>0.90</td>
<td>1.10</td>
<td>1.25</td>
<td>1.50</td>
<td>1.79</td>
</tr>
<tr>
<td>3.0</td>
<td>1.08</td>
<td>1.32</td>
<td>1.50</td>
<td>1.83</td>
<td>2.04</td>
</tr>
<tr>
<td>4.0</td>
<td>1.25</td>
<td>1.55</td>
<td>1.79</td>
<td>2.00</td>
<td>2.29</td>
</tr>
<tr>
<td>5.0</td>
<td>1.33</td>
<td>1.75</td>
<td>2.03</td>
<td>2.25</td>
<td>2.58</td>
</tr>
<tr>
<td>6.0</td>
<td>1.51</td>
<td>1.87</td>
<td>2.21</td>
<td>2.41</td>
<td>2.76</td>
</tr>
<tr>
<td>7.0</td>
<td>1.64</td>
<td>2.02</td>
<td>2.42</td>
<td>2.57</td>
<td>2.90</td>
</tr>
</tbody>
</table>

\(10^2 [\text{Cr}^{III}(L_2(H_2O)_2)]^+ = 2.5 \times 10^{-4}\) mol dm⁻³; \(10^4 k_{obs} = 1.24, 1.38, 1.35\) and \(1.30\) s⁻¹ at \(10^4 [\text{Cr}^{III}(L_2(H_2O)_2)]^+\) of 1.25, 3.75, 5.0 and 6.25 mol dm⁻³, respectively at 30°C and \([\text{IO}_4^-] = 0.02\) mol dm⁻³.
the concentration of the chromium(III)-complex was varied at a constant periodate concentration, indicating first order dependence on the complex concentration.

At constant \([H^+]\) and ionic strength, \(1/k_{\text{obs}}\) varies linearly with \(1/[\text{IO}_4^-]\) at different temperatures (Fig. 2), and the kinetics of the reaction are described by Eq. (2)

\[
d[\text{Cr}^{\text{III}}]/dt = a[\text{IO}_4^-][\text{Cr}^{\text{III}}]/(1 + b[\text{IO}_4^-][\text{Cr}^{\text{III}}])
\]

or

\[
1/k_{\text{obs}} = 1/a[\text{IO}_4^-] + b/a
\]

The values of \((a)\) and \((b)\) were obtained from the slope and intercept as 0.12 dm\(^3\)mol\(^{-1}\) s\(^{-1}\) and 40.96 dm\(^3\)mol\(^{-1}\) respectively at 30°C and pH = 3.12. Plots of \(1/k_{\text{obs}}\) versus \(1/[\text{IO}_4^-]\) at different pHs (2.32-3.48) (Fig. 3), show that the rate of reaction increases with increase in pH (Table 3).

The composition of the chromium(III)-L-glutamic acid complex, as determined by Job’s method of continuous variation\(^{15}\), was found to be 1:2 (metal : ligand). Thus the formula of the chromium(III)-L-glutamic acid complex is \([\text{Cr}^{\text{III}}(\text{L})(\text{H}_2\text{O})_2]\). In acid medium the chromium(III)-L-glutamic acid complex is in equilibrium.

\[
[\text{Cr}^{\text{III}}(\text{L})(\text{H}_2\text{O})_2] \rightleftharpoons [\text{Cr}^{\text{III}}(\text{L})(\text{H}_2\text{O})(\text{OH})]+\text{H}^+(K_1)
\]

\(K_1\) was obtained potentiometrically (Fig. 4) and has the value of 3.07x10\(^{-4}\) at 30°C. From the pH (2.32-3.48) and the \(K_1\) value, it is clear that \([\text{Cr}^{\text{III}}(\text{L})(\text{H}_2\text{O})(\text{OH})]\) may be the reactive species. An inner-sphere process may still be accommodated through replacement of coordinated \(\text{H}_2\text{O}\) in \([\text{Cr}^{\text{III}}(\text{L})(\text{H}_2\text{O})(\text{OH})]\) by \(\text{IO}_4^-\) (refs 11, 16, 17). The hydroxo-group labilises a Cr-OH\(_2\) bond, thus facilitating the substitution of \(\text{H}_2\text{O}\) by \(\text{IO}_4^-\) (refs 6, 17).

Also, it may be concluded that from the reported equilibrium constants of aqueous periodate solutions over the pH range used that periodate species likely to be present\(^{18}\) are \(\text{IO}_4^-\), \(\text{H}_2\text{IO}_6^-\) and \(\text{H}_3\text{IO}_5^2^-\).

\[
\text{H}_3\text{IO}_6^- \rightleftharpoons \text{H}_2\text{IO}_6^- + \text{H}^+ (K_2 = 1.98x10^{-3} \text{ dm}^3 \text{ mol}^{-1})
\]

\[
\text{H}_2\text{IO}_6^- \rightleftharpoons 2\text{H}_2\text{O} + \text{IO}_4^- (K_3 = 0.025)
\]

\[
\text{H}_3\text{IO}_6^- \rightleftharpoons \text{H}_3\text{IO}_5^2^- + \text{H}^+ (K_4 = 5x10^6 \text{ dm}^3 \text{ mol}^{-1})
\]

From the \(K_4\) value, \(\text{H}_3\text{IO}_6^2^-\) is not the predominant species (\(\text{I}^\text{VII}\) will be used to represent \(\text{H}_3\text{IO}_6^2^-\)).

A possible mechanism is described by Eqs (8-12):

\[
\text{Cr}^{\text{III}}(\text{L})(\text{H}_2\text{O})_2] + \text{I}^\text{VII} \rightleftharpoons [\text{Cr}^{\text{III}}(\text{L})(\text{H}_2\text{O})(\text{OH})] + \text{H}^+(K_1)
\]

\[
[\text{Cr}^{\text{III}}(\text{L})(\text{H}_2\text{O})(\text{OH})] + \text{I}^\text{VII} \rightleftharpoons [\text{Cr}^{\text{III}}(\text{L})(\text{OH})+\text{I}^\text{VII}^+]
\]

\[
+ \text{H}_2\text{O} (K_3)
\]

\[
[\text{Cr}^{\text{III}}(\text{L})(\text{OH})+\text{I}^\text{VII}^+] \rightarrow \text{Cr}^\text{IV}+\text{OH}^-+2\text{L}+\text{IO}_5^-.
\]
From the above mechanism, the rate of the reaction is given by:

$$\frac{d[Cr^{VI}]}{dt} = k_2 K_5 [Cr^{III}(L)_2(H_2O)(OH)] [I^{VIII}]$$  \hspace{1cm} (13)

If $[Cr^{III}]_T$ represents the total concentration of $Cr^{III}$ species, then

$$[Cr^{III}]_T = [Cr^{III}(L)_2(H_2O)(OH)][H^+]/K_1 + [Cr^{III}(L)_2(H_2O)(OH)] + K_3 [Cr^{III}(L)_2(H_2O)(OH)] [I^{VIII}]_T$$  \hspace{1cm} (14)

Substitution for $[Cr^{III}(L)_2(H_2O)(OH)]$ from Eq. (14) into Eq. (13) gives Eqs (15) and (16).

$$\text{Rate} = k_2 K_5 [Cr^{III}]_T [I^{VIII}] / 1 + ([H^+] / K_1) + K_5 [I^{VIII}]_T$$  \hspace{1cm} (15)

and

$$k_{obs} = k_2 K_5 [I^{VIII}]_T / 1 + ([H^+] / K_1) + K_5 [I^{VIII}]_T$$  \hspace{1cm} (16)

which on rearrangement gives

$$1/k_{obs} = (K_1 + [H^+]) / k_2 K_5 K_3 [I^{VIII}]_T + 1/k_2$$  \hspace{1cm} (17)

At constant $[H^+]$, Eq. (18) follows, in which $A$ is a constant:

$$1/k_{obs} = A/k_2 K_1 K_3 [I^{VIII}]_T + 1/k_2$$  \hspace{1cm} (18)

which is identical to the experimental results shown by Eq. (2) where $a = k_2 K_1 K_3 / A$ and $b = K_1 K_3 / A$.

The calculated values of $10^3 k_2$ are 2.39, 2.84, 2.93, 3.39 and 4.05 s$^{-1}$ at 20, 25, 30, 35 and 40 °C respectively. The activation parameters obtained from a least-squares fit applied to the transition state theory equation are $\Delta H^a = 16.54$ kJ mol$^{-1}$ and $\Delta S^a = -238.08$ J K$^{-1}$mol$^{-1}$. The high negative entropies of activation for these reactions were largely due to the result of the charge concentration on encounter complex formation, which causes substantial mutual ordering of the solvated water molecules$^{19}$.

The intramolecular electron transfer step is endothermic, hence the contributions of $H^a$ and $S^a$ to the rate constant seem to compensate each other. This suggests that the factors controlling $\Delta H^a$ must be closely related to those controlling $\Delta S^a$; therefore, the solvation state of the encounter complex would be important$^{19}$ in determining $\Delta H^a$. Thus the relatively small enthalpy of activation, $\Delta H^a$, can be explained in

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**Table 3**—Effect of pH on $k_{obs}$ at $[Cr^{III}(L)_2(H_2O)] = 2.5 \times 10^{-4}$ mol dm$^{-3}$, $I = 0.2$ mol dm$^{-3}$ and $T = 30^\circ$C.

<table>
<thead>
<tr>
<th>$10^3 [IO_3^-]$ mol dm$^{-3}$</th>
<th>$pH = 3.48$</th>
<th>$3.12$</th>
<th>$2.60$</th>
<th>$2.32$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.83</td>
<td>0.50</td>
<td>0.21</td>
<td>0.13</td>
</tr>
<tr>
<td>1.0</td>
<td>1.37</td>
<td>0.80</td>
<td>0.37</td>
<td>0.29</td>
</tr>
<tr>
<td>2.0</td>
<td>1.66</td>
<td>1.25</td>
<td>0.75</td>
<td>0.54</td>
</tr>
<tr>
<td>3.0</td>
<td>1.87</td>
<td>1.50</td>
<td>0.96</td>
<td>0.71</td>
</tr>
<tr>
<td>4.0</td>
<td>2.16</td>
<td>1.79</td>
<td>1.17</td>
<td>0.87</td>
</tr>
<tr>
<td>5.0</td>
<td>2.42</td>
<td>2.03</td>
<td>1.33</td>
<td>1.08</td>
</tr>
<tr>
<td>6.0</td>
<td>2.57</td>
<td>2.21</td>
<td>1.47</td>
<td>1.26</td>
</tr>
<tr>
<td>7.0</td>
<td>2.84</td>
<td>2.42</td>
<td>1.69</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>1.96 ± 0.668</td>
<td>1.56 ± 0.68</td>
<td>0.991 ± 0.524</td>
<td>0.787 ± 0.457</td>
</tr>
</tbody>
</table>
terms of the formation of a more solvated complex, \([\text{Cr}^{III}(\text{L})_2(\text{OH})]-\text{II}\).

From Eq. (17), it follows that the slope of the plots can be represented by Eq. (19):

\[
\text{slope} = \frac{\text{[H}^+\text{]}}{k_2 K_1 K_3} + \frac{1}{k_2 K_3} \quad \ldots (19)
\]

Hence, the slope is dependent on \([\text{H}^+\text{]})\). This plot can be given as the linear equation \(y = mx + c\), with a correlation coefficient of 0.9836. The values of \(K_1\) and \(K_3\) were calculated from Eq. (19) as \(6.26 \times 10^{-4}\) mol dm\(^{-3}\) and \(88.41\) dm\(^3\) mol\(^{-1}\), at 30°C and \(I = 0.2\) mol dm\(^{-3}\), respectively. The value of \(K_1\) is in good agreement with that obtained potentiometrically (\(K_1 = 3.07 \times 10^{-4}\)) at 30°C. This indicates the validity of our proposed mechanism.

From the above discussion, the following mechanism is proposed for oxidation of the chromium(III)-L-glutamic acid complex by periodate which is supported by the observation that the ion is capable of acting as a ligand, as is apparent from its coordination to copper(III)\(^8\) and nickel(IV)\(^9\). The oxidation of \([\text{Cr}^{III}(\text{L})_2(\text{H}_2\text{O})_2]\) \(1\text{O}_4\) may proceed via one or two electron transfer giving chromium(IV) or chromium(V), respectively in the rate determining step leading to chromium(VI). The fact that acrylonitrile was not polymerized seems to support two electron transfer process.

References