CHAPTER VII

Kinetics and Mechanism of Ruthenium(III) Catalysed Oxidation of L-proline by Copper(III): A Free Radical Intervention and Decarboxylation (Stopped flow technique)

The general importance of diperiodatocuprate(III) (DPC) and L-proline are given in chapter II (p.27 and p.28). Ruthenium(III) acts as an efficient catalyst in many redox reactions, particularly in alkaline medium. The mechanism of catalysis can be quite complicated due to the formation of different intermediate complexes, free radicals and multiple oxidation states of ruthenium. The uncatalysed reaction between L-proline and DPC in alkaline medium has been studied previously. A micro amount of ruthenium(III) is sufficient to catalyze the reaction and a variety mechanisms are possible. In this chapter, we describe the results of title reaction in order to understand the active species of oxidant, reductant and catalyst in such a medium and to arrive a plausible mechanism.

EXPERIMENTAL

Materials

All chemicals used were of reagent grade. Stock solution of L-proline (sd-fine chem) was prepared by dissolving the appropriate amount of recrystallised sample in double distilled water. The preparation and standardization of copper(III) periodate complex and other materials are as given in chapter II (p.30,31). The purity of the complex was checked by its UV-Visible spectrum, which showed a broad absorption band at 415 nm. The ruthenium(III) solution
was prepared by dissolving a known weight of RuCl₃ (sd- fine chem.) in HCl(0.20 mol dm⁻³) and standardized by EDTA titration. All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts of the samples in double distilled water. KOH and KNO₃ (BDH, AR) were employed to maintain the required alkalinity and ionic strength respectively in reaction solutions.

**Kinetic Procedure**

Since the initial reaction was too fast to monitor by the usual method, measurements were made on a Hitachi 150-20 spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12). All kinetic measurements were performed under pseudo - first order conditions with [L-proline] excess over [DPC] at a constant ionic strength of 0.10 mol dm⁻³. The reaction was initiated by mixing previously thermostatted solutions of DPC, and L-proline, which also contained the necessary quantities of Ru(III), KOH and KNO₃. The first order rate constants, (kₑ) were evaluated by plots of log [Absorbance] versus time. The first order plots in almost all cases were linear upto 80% completion of the reaction and kₑ were reproducible within ± 5% error. An example run is given in Table VII(i) (p.190).

Since periodate is present in excess in DPC, the possibility of oxidation of L-proline by periodate in alkaline medium at 25°C was tested. The progress of the reaction was followed iodometrically. However, it was found that there was no significant reaction under the experimental conditions employed compared to the DPC oxidation of L-proline.
Table VII (i)

Example run for the Ru(III) catalysed oxidation of L-proline by diperiodatocuprate(III) in aqueous alkaline medium at 25 °C.

\[
\begin{align*}
[L\text{-proline}] &= 6.0 \times 10^{-4}; \\
[DPC] &= 1.0 \times 10^{-4}; \\
[OH^-] &= 0.02 \text{ mol dm}^{-3}; \\
[IO_4^-] &= 1.0 \times 10^{-5} \\
[Ru(III)] &= 4.0 \times 10^{-6}; \\
I &= 0.10 / \text{mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density (415 nm)</th>
<th>([DPC] \times 10^5) (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.6212</td>
<td>9.97</td>
</tr>
<tr>
<td>0.05</td>
<td>0.6002</td>
<td>9.63</td>
</tr>
<tr>
<td>0.25</td>
<td>0.5095</td>
<td>8.18</td>
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<tr>
<td>0.45</td>
<td>0.4231</td>
<td>6.80</td>
</tr>
<tr>
<td>0.65</td>
<td>0.3563</td>
<td>5.72</td>
</tr>
<tr>
<td>0.85</td>
<td>0.2985</td>
<td>4.80</td>
</tr>
<tr>
<td>1.05</td>
<td>0.2588</td>
<td>4.15</td>
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<td>1.25</td>
<td>0.2172</td>
<td>3.49</td>
</tr>
<tr>
<td>1.45</td>
<td>0.1901</td>
<td>3.05</td>
</tr>
<tr>
<td>1.65</td>
<td>0.1659</td>
<td>2.66</td>
</tr>
<tr>
<td>1.85</td>
<td>0.1399</td>
<td>2.25</td>
</tr>
<tr>
<td>2.00</td>
<td>0.1235</td>
<td>1.98</td>
</tr>
</tbody>
</table>
As in chapter II (p.31), the role of surface, effect of dissolved oxygen, added carbonate have been studied but found no effect on the rate of reaction. Regression analysis of experimental data to obtain the regression coefficient r and standard deviation S of points from the regression line was performed using a programme Microsoft Excel 2000.

RESULTS

Stoichiometry and Product Analysis

The reaction mixtures containing an excess DPC concentration over L-proline, in presence of constant amount of Ru(III) and 0.02 mol dm⁻³ KOH and adjusted ionic strength (0.10 mol dm⁻³) was allowed to react for 2 hrs at 25 ± 0.1°C. The remaining DPC was then analysed spectrophotometrically. The results showed 2:1 stoichiometry as given in equation (1). (Table VII (ii)(p.192)).

\[
\begin{align*}
\text{CH}_2&-\text{CH}_2 \\
\text{CH}&-\text{COOH} + 2\text{Cu(III)} + 2\text{OH}^- \\
&\xrightarrow{\text{Ru(III)}} \text{H}_2\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHO} \\
&\quad + 2\text{Cu(II)} + \text{H}_2\text{O} + \text{CO}_2 \uparrow
\end{align*}
\]

The main reaction products were identified as the 4-aminobuteraldehyde by spot test⁴ for amine and aldehyde groups. The product 4-aminobuteraldehyde was also confirmed by IR spectroscopy⁵ which showed bands at 3443 cm⁻¹ for –NH stretching, 1733 cm⁻¹ for aldehydic >CO stretching, and 2919 cm⁻¹ for aldehydic –CH stretching respectively. The only organic product obtained in the oxidation is 4-aminobuteraldehyde, which is further confirmed by single spot in
### Table VII (ii)

Stoichiometry of Ru(III) catalysed oxidation of L-proline by diperiodatocuprate(III) in aqueous alkaline medium at 25°C.

\[
[\text{OH}^-] = 0.02; \quad [\text{IO}_4^-] = 1.0 \times 10^{-5};
\]

\[
[\text{Ru(III)}] = 4.0 \times 10^{-6}; \quad I = 0.10 \text{ /mol dm}^3.
\]

<table>
<thead>
<tr>
<th>Taken [DPC] \times 10^4 (mol dm(^{-3}))</th>
<th>Taken [L-proline] \times 10^4 (mol dm(^{-3}))</th>
<th>Found [DPC] \times 10^4 (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>0.03</td>
</tr>
<tr>
<td>3.0</td>
<td>1.0</td>
<td>1.05</td>
</tr>
<tr>
<td>4.0</td>
<td>2.0</td>
<td>0.03</td>
</tr>
<tr>
<td>6.0</td>
<td>2.0</td>
<td>2.01</td>
</tr>
<tr>
<td>8.0</td>
<td>2.0</td>
<td>4.03</td>
</tr>
<tr>
<td>4.0</td>
<td>1.0</td>
<td>2.03</td>
</tr>
</tbody>
</table>
However, the other product in alkaline medium is copper(II), identified by spot test and UV-Visible spectra. Test for the corresponding acid was negative. It was further observed that the aldehyde does not undergo further oxidation under prevailing kinetic conditions.

**Reaction Order**

As the reduction of diperiodatocuprate(III) by L-proline in alkaline medium proceeds with a measurable rate in the absence of ruthenium(III), the catalysed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus, the total rate constant \( k_T \) is equal to the sum of the rate constants of the catalysed \( k_c \) and uncatalysed \( k_u \) reactions, so \( k_c = k_T - k_u \). Hence the reaction orders have been determined from the slopes of \( \log(k_c) \) versus \( \log(\text{concentration}) \) plots by varying the concentrations of L-proline, Ru(III) and alkali in turn while keeping the others constant.

**Effect of [Diperiodatocuprate(III)]**

The DPC concentration was varied in the range of \( 2 \times 10^{-5} \) to \( 2 \times 10^{-4} \) mol dm\(^{-3} \) and the linearity of plots of \( \log[DPC] \) versus time (Fig. VII(i)(p.194)) \( (r \geq 0.9985, S \leq 0.027) \) indicated a reaction order of unity in [DPC]. This was also confirmed by variation of [DPC], which did not result any change in the pseudo-first order rate constants, \( k_c \) (Table VII (iii)(p.195)).

**Effect of [L-proline]**

The substrate, [L-proline] was varied in the range of \( 3.0 \times 10^{-4} \) to \( 3.0 \times 10^{-3} \) mol dm\(^{-3} \) at 25 °C keeping all other reactants concentrations and conditions constant (Table VII(iii)(p.195)). The \( k_c \) values increased with increase in
Figure VII (i)

First order plots of Ru(III) catalysed oxidation of diperiodatocuprate(III) by L-proline in aqueous alkaline medium at 25°C.

[DPC] ×10^4 (mol dm^-3): (1) 0.2 , (2) 0.4 , (3) 0.8 , (4) 1.0 , (5) 2.0

(Conditions as in Table VII (iii) (p.195))
Table VII (iii)

Effect of variation of [DPC] and [L-proline] on the ruthenium(III) catalysed oxidation of L-proline by diperiodatocuprate(III) in aqueous alkaline medium at 25 °C.

\[ [\text{Ru(III)}] = 4.0 \times 10^{-6}; \quad [\text{OH}^-] = 0.05; \]
\[ [\text{IO}_4^-] = 1.0 \times 10^{-3}; \quad I = 0.10 \text{ mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>[DPC] x 10^4 (mol dm^{-3})</th>
<th>[L-proline] x 10^3 (mol dm^{-3})</th>
<th>( k_T \times 10^2 ) (s^{-1})</th>
<th>( k_U \times 10^2 ) (s^{-1})</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.6</td>
<td>1.31</td>
<td>0.24</td>
<td>1.07</td>
<td>1.09</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>1.33</td>
<td>0.22</td>
<td>1.11</td>
<td>1.09</td>
</tr>
<tr>
<td>0.8</td>
<td>0.6</td>
<td>1.33</td>
<td>0.25</td>
<td>1.08</td>
<td>1.09</td>
</tr>
<tr>
<td>1.0</td>
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<td>1.34</td>
<td>0.25</td>
<td>1.09</td>
<td>1.09</td>
</tr>
<tr>
<td>2.0</td>
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<td>1.32</td>
<td>0.23</td>
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<tr>
<td>1.0</td>
<td>0.3</td>
<td>0.91</td>
<td>0.20</td>
<td>0.71</td>
<td>0.70</td>
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<tr>
<td>1.0</td>
<td>0.6</td>
<td>1.34</td>
<td>0.25</td>
<td>1.09</td>
<td>1.09</td>
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<td>0.8</td>
<td>1.59</td>
<td>0.35</td>
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<td>1.26</td>
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<tr>
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<td>1.98</td>
<td>0.62</td>
<td>1.36</td>
<td>1.40</td>
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<tr>
<td>1.0</td>
<td>3.0</td>
<td>2.91</td>
<td>0.81</td>
<td>2.10</td>
<td>1.96</td>
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</tbody>
</table>
concentration of L-proline and found that an apparent less than unit order dependence on [L-proline] (Fig. VII(ii)(p.197)).

**Effect of [Alkali]**

The alkali, [OH'] was varied in the range of 0.01 to 0.10 mol dm^{-3} at 25 °C keeping all other reactants concentrations and conditions constant(Table VII(iv)(p.198)). The rate increases with increase in the concentrations of alkali. The order with respect to [OH'] was found to be less than unity (Fig. VII(ii)(p.197)).

**Effect of [Ruthenium(III)]**

The catalyst, Ru(III) was varied in the range of $2.0 \times 10^{-6}$ to $2.0 \times 10^{-5}$ mol dm^{-3} (Table VII(iv)(p.198)) at constant concentration of DPC, L-proline and at constant ionic strength of 0.1 mol dm^{-3}. The order with respect to [Ru(III)] was found to be unity (Fig. VII(iii)(p.199)).

**Effect of [Periodate]**

The effect of [IO_4^-] was observed by varying the concentration from $1.0 \times 10^{-5}$ to $1.0 \times 10^{-4}$ mol dm^{-3} at constant concentrations of diperiodatocuprate(III), [L-proline], alkali and constant ionic strength. It was found that the added periodate did not show any significant effect on the rate of reaction (Table VII (iv)(p.198)).

**Effect of Initially Added Products**

The effect of initially added reaction products such as Cu(II) in the form of CuSO_4 and 4-amino butalaraldehyde were studied in concentration ranges from $1.0 \times 10^{-5}$ to $1.0 \times 10^{-4}$ mol dm^{-3}, keeping all other reactant concentrations constant.
Order with respect to [L-proline] and [OH'] on the Ru(III) catalysed diperiodatocuprate(III) oxidation of L-proline in aqueous alkaline medium at 25°C.

(Conditions as in Table VII(iii) (p.195); (iv)(p.198))
Table VII (iv)

Effect of variation of $[\text{OH}^-]$, $[\text{Ru(III)}]$ and $[\text{IO}_4^-]$ on the ruthenium(III) catalysed oxidation of L-proline by diperiodatocuprate(III) in aqueous alkaline medium at 25 °C.

$L\text{-proline}=6.0 \times 10^{-4}; \quad [\text{DPC}]=1.0 \times 10^{-4};$

$I=0.10 \text{ mol dm}^{-3}.$

<table>
<thead>
<tr>
<th>$[\text{OH}^-]$ (mol dm$^{-3}$)</th>
<th>$[\text{Ru(III)}] \times 10^6$ (mol dm$^{-3}$)</th>
<th>$[\text{IO}_4^-] \times 10^5$ (mol dm$^{-3}$)</th>
<th>$k_T \times 10^2$ (s$^{-1}$)</th>
<th>$k_U \times 10^4$ (s$^{-1}$)</th>
<th>$k_C \times 10^2$ (s$^{-1}$)</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
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</tr>
<tr>
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<td>3.02</td>
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<td>1.0</td>
<td>4.08</td>
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<td>3.69</td>
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</tr>
<tr>
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<td>0.74</td>
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<td>0.54</td>
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</tr>
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<td>4.0</td>
<td>1.0</td>
<td>1.34</td>
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<td>1.09</td>
<td>1.09</td>
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</tr>
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<td>6.25</td>
<td>0.25</td>
<td>6.00</td>
<td>5.46</td>
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</tr>
<tr>
<td>0.02</td>
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<tr>
<td>0.02</td>
<td>4.0</td>
<td>2.0</td>
<td>1.33</td>
<td>0.25</td>
<td>1.08</td>
<td>1.09</td>
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</tr>
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<td>1.30</td>
<td>0.20</td>
<td>1.10</td>
<td>1.09</td>
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</tr>
<tr>
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<td>8.0</td>
<td>1.34</td>
<td>0.26</td>
<td>1.08</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>4.0</td>
<td>10.0</td>
<td>1.34</td>
<td>0.25</td>
<td>1.09</td>
<td>1.09</td>
<td></td>
</tr>
</tbody>
</table>

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Figure VII (iii)

Order with respect to [Ru(III)] on ruthenium(III) catalysed oxidation of L-proline by alkaline diperiodatocuprate(III) at 25°C and I = 0.10 mol dm\(^{-3}\).

(Conditions as in Table (VII)(iv)(p.198)).
was found that the added products had negligible effect on rate of reaction.

**Effect of Ionic Strength and Solvent Polarity**

The effect of ionic strength was studied by varying the potassium nitrate concentration from 0.1 to 1.0 mol dm\(^{-3}\) at constant concentrations of diperiodatocuprate(III), L-proline, ruthenium(III), periodate and alkali (Table VII(v) (p.201)). It was found that the rate constants, \(k_c\) increased with increase in the concentration of KNO\(_3\). The plot of log \(k_c\) versus \(I^{1/2}\) was linear with positive slope as shown in Fig. VII(iv)(p.202) \((r \geq 0.9312, S \leq 0.089)\).

The effect of relative permittivity \((\varepsilon_r)\) was studied by varying the t-butanol-water content in the reaction mixture with all other conditions being maintained constant (Table VII(v) (p.201)). Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquid\(^7\) as given in chapter II (p.45). The solvent did not react with the oxidant under the experimental conditions. The rate constant, \(k_c\) increased with decrease in the dielectric constant of the medium. The plot of log \(k_c\) versus \(1/\varepsilon_r\) was linear with a positive slope as shown in Fig. VII(iv)(p.202) \((r \geq 0.9872, S \leq 0.016)\).

**Polymerisation Study**

The intervention of free radicals in the reaction was examined as follows: The reaction mixture, to which a known quantity of acrylonitrile scavenger had been initially added was kept for 1 hr in an inert atmosphere. On diluting the reaction mixture with methanol, a precipitate resulted, suggesting the possibility of free radical intervention. The blank experiments of either DPC or L-proline with acrylonitrile alone did not induce polymerization under the same conditions.
Table VII (v)

Effect of variation of ionic strength (I) and solvent polarity ($\varepsilon_T$) on the Ru(III) catalysed oxidation of L-proline by aqueous alkaline diperiodatocuprate(III) at 25°C.

\[
\begin{align*}
\text{[DPC]} &= 1.0 \times 10^{-4}; \\
\text{[L-proline]} &= 1.0 \times 10^{-3}; \\
\text{[Ru(III)]} &= 4.0 \times 10^{-6}; \\
\text{[OH]} &= 0.02; \\
\text{[IO}_4^-\text{]} &= 1.0 \times 10^{-5} / \text{mol dm}^{-3}; \\
I &= 0.10 / \text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>I (mol dm$^{-3}$)</th>
<th>$k_c \times 10^2$ (s$^{-1}$)</th>
<th>%of *t-butanol-water</th>
<th>$\varepsilon_T$</th>
<th>$k_c \times 10^2$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.05</td>
<td></td>
<td>5.0</td>
<td>75.12</td>
</tr>
<tr>
<td>0.10</td>
<td>1.09</td>
<td></td>
<td>10.0</td>
<td>71.74</td>
</tr>
<tr>
<td>0.15</td>
<td>1.12</td>
<td></td>
<td>15.0</td>
<td>68.36</td>
</tr>
<tr>
<td>0.20</td>
<td>1.53</td>
<td></td>
<td>20.0</td>
<td>64.98</td>
</tr>
<tr>
<td>0.25</td>
<td>1.86</td>
<td></td>
<td>25.0</td>
<td>61.60</td>
</tr>
</tbody>
</table>

* *t-butanol-water(v/v)
Effect of ionic strength ($I$) and dielectric constant ($\varepsilon_r$) on the Ru(III) catalysed oxidation of L-proline by aqueous alkaline diperiodatocuprate(III) at 25°C.

(Conditions as in Table VII(v) (p.201))
as those induced with reaction mixture. Initially added acrylonitrile decreases the rate indicating the free radical intervention, which is the case in earlier work.

**Effect of Temperature**

The rate of the reaction was measured at four different temperatures with varying [OH'] and [L-proline] keeping other conditions constant. The rate was found to increase with increase in temperature. The rate constants, k, of the slow step of Scheme were obtained from the intercept of the plots of [Ru(III)]/kC versus 1/[OH'](Fig.VII(vi)(p.213) (r ≥ 0.989, S ≤ 0.0118) at four different temperatures. The values of k at different temperatures are tabulated in Table VII(vi a)(p.204). The data are subjected to least square analysis as in chapter II (p.48 and 50) and were tabulated in Table III (vi a) (p.204). The energy of activation corresponding to these constants were evaluated from the Arrhenius plot of log k (Y*cal) versus 1/T (Fig.VII(v)(p.205);(r ≥ 0.979, S ≤ 0.0098)) and other activation parameters with respective slow step were calculated as in chapter II(p.45) and are tabulated in Table VII(vib)(p. 204).

The title reaction obeys following experimental rate law,

\[ -\frac{d[DPC]}{dt} = k [DPC][L-Proline]^{0.46}[OH]^{0.77}[Ru(III)] \]

**DISCUSSION**

The water soluble Cu(III) periodate complex is reported to be [Cu(HIO₆)₂(OH)₂]⁻. However, in an aqueous alkaline medium and over the high pH range employed in this study, periodate is unlikely to exist as HIO₆⁻ (as
(a) Effect of temperature on the slow step of the mechanism of Ru(III) catalysed oxidation of L-proline by alkaline diperiodatocuprate(III).

\[ [\text{L-proline}] = 1.0 \times 10^{-3}; \quad [\text{DPC}] = 1.0 \times 10^{-4}; \]
\[ [\text{OH}^-] = 0.02 \text{mol dm}^{-3}; \quad [\text{IO}_4^-] = 1.0 \times 10^{-5}; \]
\[ I = 0.10 \text{ /mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( \log k ) ( \times 10^4 )</th>
<th>( 1/T \times 10^3 )</th>
<th>( Y^* ) calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>3.61</td>
<td>4.557</td>
<td>4.553</td>
</tr>
<tr>
<td>298</td>
<td>4.10</td>
<td>4.613</td>
<td>4.617</td>
</tr>
<tr>
<td>303</td>
<td>4.74</td>
<td>4.675</td>
<td>4.679</td>
</tr>
<tr>
<td>308</td>
<td>5.54</td>
<td>4.743</td>
<td>4.739</td>
</tr>
</tbody>
</table>

*Calculated

(b) Activation parameter with respect to slow step of Scheme 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a ) (kJ mol(^{-1}))</td>
<td>21.5 ± 1.0</td>
</tr>
<tr>
<td>( \log A )</td>
<td>8.3 ± 0.3</td>
</tr>
<tr>
<td>( \Delta H^# ) (kJ mol(^{-1}))</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>( \Delta S^# ) (J K(^{-1}) mol(^{-1}))</td>
<td>-93 ± 4</td>
</tr>
<tr>
<td>( \Delta G^# ) (kJ mol(^{-1}))</td>
<td>47 ± 2</td>
</tr>
</tbody>
</table>
Figure VII (v)

Effect of temperature on the Ru(III) catalysed oxidation of L-proline by diperiodatocuprate(III) in aqueous alkaline medium

(Conditions as in Table VII(vi) (p.204))
present in the complex) as is evident from its involvement in the multiple equilibria\(^\text{10}\) (2)-(4) depending on the pH of the solution.

\[
\begin{align*}
\text{H}_5\text{IO}_6 & \rightleftharpoons \text{H}_4\text{IO}_5^- + \text{H}^+ & K_1 = 5.0 \times 10^{-4} \\
\text{H}_4\text{IO}_6^- & \rightleftharpoons \text{H}_3\text{IO}_5^{2-} + \text{H}^+ & K_2 = 4.9 \times 10^{-9} \\
\text{H}_3\text{IO}_5^{2-} & \rightleftharpoons \text{H}_2\text{IO}_4^{3-} + \text{H}^+ & K_3 = 2.5 \times 10^{-12}
\end{align*}
\]

Periodic acid (H\(_5\)IO\(_6\)) exists in acid medium and also as H\(_4\)IO\(_6\) at pH 7. Thus, under alkaline conditions, the main species are expected to be H\(_3\)IO\(_5^{2-}\) and H\(_2\)IO\(_4^{3-}\). At higher concentrations, periodate also tends to dimerise. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III), [Cu(H\(_3\)IO\(_6\))\(_2\)(OH)\(_2\)]\(^{3-}\) in aqueous alkaline medium, a conclusion also supported by earlier work\(^\text{11}\).

It is known that L-proline exists in the form of Zwitter ion\(^\text{12}\) in aqueous medium. In highly acidic medium, it exists in the protonated form, whereas in highly basic medium, it is in the fully deprotonated form\(^\text{12}\).

\[
\text{CH}_2 \quad - \quad \text{CH}_2
\]
\[
\text{CH}_2 \quad \text{CH} \quad \text{COO}^- \quad \text{N} \quad \text{H}
\]

The reaction between the L-proline and diperiodatocuprate(III) complex in alkaline medium has the stoichiometry 1:2 with a first order dependence on the [DPC] and a less than unit order dependence on the [alkali] and [substrate]. In most of the reports\(^\text{11}\) on DPC oxidation, periodate had retarding effect and order in the [OH\(^-\)] was found to be less than unity and monoperiodatocuprate(III) is
considered to be the active species. However, in the present kinetic study, different observations have been obtained i.e., periodate has totally no effect on the rate of the reaction. Accordingly, the DPC is considered to be the active species. No effect of added product such as copper(II) was observed. The observed fractional order in $[\text{OH}^-]$ indicate that first alkali combines with DPC to form an deprotonated species of DPC $([\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)_{\text{H}_2\text{IO}_6})]^+$ in a pre-equilibrium step$^{13}$, which is also supported by the Michaelis-Menten plot. L-proline in the deprotonated form reacts with deprotonated form of DPC species $[\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^+$, to form a complex C. This complex C further reacts with one mole of protonated DPC, in a slow step to give a free radical derived from decarboxylated L-proline with regeneration of catalyst, Ru(III). This radical in turn reacts with another molecule of DPC species in a fast step to yield the products (Scheme 1).

$$[\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)_2]^3^+ + \text{OH}^- \rightleftharpoons \frac{K_4}{[\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^+ + \text{H}_2\text{O}}$$

$$[\text{Ru(H}_2\text{O})_5\text{OH}]^{2^+} \xrightarrow{K_5} \text{Complex (C)} + \text{H}_2\text{O}$$

Complex (C) + $[\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^+$ $\xrightarrow{k_{\text{slow}}}$

$\text{CH}_2$-$\text{CH}_2$

$\text{CH}_2$-$\text{CH}^+$-$\text{COO}^-$

$\text{N}$

$\text{H}$

$\text{CH}_2$-$\text{CH}_2$

$\text{CH}_2$-$\text{CH}_2$

$\text{N}$

$\text{H}$

$\text{Cu(OH)}_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)^+ + \text{OH}^-$ $\xrightarrow{\text{fast}}$

$\text{H}_2\text{N}$-$\text{H}_2\text{C}$-$\text{CH}_2$-$\text{CH}_2$-$\text{CHO} + \text{Cu(OH)}_2 + \text{H}_2\text{IO}_6^-$ + $\text{H}_3\text{IO}_6^{2^-}$

Scheme 1
The probable structure of complex (C) is

\[
\begin{array}{c}
\text{CH—CH} \\
\text{OH} \\
\text{O—Ru—OH2} \\
\text{OH2} \\
\text{N—H} \\
\end{array}
\]

Spectral evidence for complex formation between catalyst and substrate was obtained from the UV-Vis spectra of the ruthenium(III) species and mixture of ruthenium(III) and L-proline. A bathochromic shift, \( \lambda_{\text{max}} \), of ca 6nm from 224 to 230 nm is observed, together with hyperchromicity at \( \lambda_{\text{max}} \) 230 nm. Analogous effects upon complex formation between a ruthenium(III) and substrate have been observed in other investigations\(^{14}\). Furthermore, the formation of the complex is proved kinetically by the non zero intercept of the plot of \([\text{Ru(III)}]/k_c\) versus \(1/[\text{proline}]\) (Fig.VII(vi)(p.213)) \((r \geq 0.9935, S<0.043)\). The mechanism is also supported by moderate values of activation parameters (Table VII(vi b)(p.204)). A high negative value of \( \Delta S^\# \) suggests that the intermediate complex is more ordered than the reactants. The observed modest enthalpy of activation, and relatively high rate constant of the slow step indicated that oxidation presumably occurs by an inner-sphere mechanism. This conclusion is supported by earlier work\(^{15}\).

The thermodynamic quantities for the first equilibrium steps in Scheme 1 can be evaluated as follows: The hydroxyl ion concentration and L-proline concentration as in Table VII(iv)(p.198);(iii)(p.195) were varied at four different
temperatures and the $K_4$ and $K_5$ were determined and are given in Table VII (viia) (p.210). A vant Hoff's plot was made for the variation of $K_4$ with temperature (i.e., log $K_4$ versus $1/T$) ($r \geq 0.9781$, $S \leq 0.0108$) and the corresponding thermodynamic quantities are given in Table VII (viib) (p.210). A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step is fairly rapid and involves only high activation energy$^{16}$.

The DPC oxidation of L-proline in aqueous alkaline medium proceeds at a measurable rate in the absence of Ru(III) catalyst. Hence, in the presence of catalyst the reaction is understood to occur in parallel paths with contribution from the uncatalysed and catalysed paths. Thus, the total rate constants ($k_T$) is equal to the sum of the rate constants of the catalysed ($k_c$) and uncatalysed ($k_u$) reactions.

Since Scheme 1 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in sequences of one-electron steps, the reaction would involve a radical intermediate. A free radical scavenging experiment revealed such a possibility (vide infra). This type of radical intermediate has also been observed in earlier work$^{17}$.

Scheme 1 leads to the rate law as follows,

$$\text{Rate} = \frac{d[DPC]}{dt} = k[C] [Cu(OH)_2(H_3IO_6)(H_2IO_6)]^4.$$
Table VII(vii)

(a) Effect of temperature to calculate $K_4$ and $K_5$ on ruthenium(III) catalysed oxidation of DPC by L-proline in alkaline medium.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$K_4$ (dm$^3$ mol$^{-1}$)</th>
<th>$K_5 \times 10^{-3}$ (dm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>8.13</td>
<td>1.39</td>
</tr>
<tr>
<td>303</td>
<td>8.77</td>
<td>1.34</td>
</tr>
<tr>
<td>308</td>
<td>9.81</td>
<td>1.23</td>
</tr>
<tr>
<td>313</td>
<td>11.03</td>
<td>1.18</td>
</tr>
</tbody>
</table>

(b) Thermodynamic quantities for the oxidation of L-proline by DPC in aqueous alkaline medium for the first equilibrium step ($K_4$ values)

<table>
<thead>
<tr>
<th>Thermodynamic quantities</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (kJ mol$^{-1}$)</td>
<td>15.4 $\pm$ 0.5</td>
</tr>
<tr>
<td>$\Delta S$ (J K$^{-1}$ mol$^{-1}$)</td>
<td>70 $\pm$ 8</td>
</tr>
<tr>
<td>$\Delta G$ (kJ mol$^{-1}$)</td>
<td>-20.7 $\pm$ 0.6</td>
</tr>
</tbody>
</table>
The total \([DPC]\) is given by (where \(t\) and \(f\) stand for total and free)

\[
[DPC]_t = [Cu(OH)_2(H_3IO_6)_2]^3^- + [Cu(OH)_2(H_2IO_6)(H_3IO_6)]^4^-
\]

\[
= [Cu(OH)_2(H_3IO_6)_2]^3^- + K_d[OH^-][Cu(OH)_2(H_2IO_6)(H_3IO_6)]^3^-
\]

\[
= [Cu(OH)_2(H_3IO_6)_2]^3^- \{1+K_d[OH^-]\}
\]

Therefore,

\[
[DPC]_t = \frac{[DPC]_f}{1+K_d[OH^-]} \tag{6}
\]

Similarly,

\[
[L-proline]_t = [L-proline]_f + [C]
\]

\[
= [L-proline]_f + K_5[L-proline][Ru(III)]
\]

\[
= [L-proline]_f \{1+K_5[Ru(III)]\}
\]

Therefore,

\[
[L-proline]_f = \frac{[L-proline]_f}{1+K_5[Ru(III)]} \tag{7}
\]

Similarly,

\[
[OH^-]_t = [OH^-]_f + [Cu(OH)_2(H_2IO_6)(H_3IO_6)]^4^-
\]

\[
= [OH^-]_f + K_d[OH^-][Cu(OH)_2(H_2IO_6)(H_3IO_6)]^3^-
\]

\[
= [OH^-]_f \{1+K_d[OH^-][Cu(OH)_2(H_2IO_6)(H_3IO_6)]^3^-\}
\]

Therefore,

\[
[OH^-]_t = \frac{[OH^-]_f}{1+K_d[DPC]} \tag{8}
\]

Similarly,

\[
[Ru(III)]_t = [Ru(H_2O)_5OH]^2^+ + [Complex]
\]

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\[
\begin{align*}
[\text{Ru}(\text{II})_2\text{O}_3\text{OH}]_t^{2+} + K_5[\text{Ru}(\text{II})_2\text{O}_3\text{OH}]^{2+} & \rightarrow [\text{L-proline}]_t \\
= [\text{Ru}(\text{H}_2\text{O})_5\text{OH}]_t^{2+} \{1 + K_5[\text{L-proline}]_t\}
\end{align*}
\]

Therefore,

\[
[\text{Ru}(\text{III})]_t = \frac{[\text{Ru}(\text{III})]_t}{1 + K_5[\text{L-proline}]}
\] (9)

Substituting the equations (6), (7), (8) and (9) in equation (5) (omitting subscripts \(t\) and \(f\)), we get,

\[
\text{rate}_{\text{cat}} = \frac{kK_4K_5[\text{DPC}][\text{L-proline}][\text{OH}'][\text{Ru(III)}]}{(1 + K_4[\text{OH}']) (1 + K_4[\text{Ru(III)}]) (1 + K_4[\text{DPC}]) (1 + K_4[\text{L-proline}])}
\] (10)

In view of the low concentration of catalyst and oxidant used, the terms \((1 + K_5[\text{Ru(III)}])\) and \((1 + K_4[\text{DPC}])\) are neglected.

The equation (9) becomes (10),

\[
\text{rate} = \frac{kK_4K_5[\text{L-proline}][\text{Cu(OH)}_2(\text{H}_2\text{IO}_6)_2][\text{OH}'][\text{Ru(III)}]}{(1 + K_5[\text{L-proline}]) (1 + K_4[\text{OH}'])}
\] (11)

Equation (11) becomes equation (12).

\[
k_c = \frac{\text{rate}}{[\text{DPC}]} = \frac{kK_4K_5[\text{L-proline}][\text{OH}'][\text{Ru(III)}]}{1 + K_4K_5[\text{L-proline}][\text{OH}'] + K_5[\text{L-proline}] + K_4[\text{OH}']}
\] (12)

The above equation (12) can be rearranged to the following form (13), which is used for the verification of the rate law,

\[
\frac{[\text{Ru(III)}]}{k_c} = \frac{1}{kK_4K_5[\text{L-proline}][\text{OH}']} + \frac{1}{kK_5[\text{L-proline}]} + \frac{1}{kK_4[\text{OH}']} + \frac{1}{k}
\] (13)

According to equation (13), other conditions being constant, the plots of \([\text{Ru(III)}]/k_c\) versus \(1/\text{L-proline}\). (Fig. VII (vi) (p. 213)) \((r \geq 0.997, S \leq 0.050)\) and
Verification of rate law (12) in the form of (13). Plots of $[\text{Ru(III)}]/k_c$ versus $1/[\text{L-proline}]$ and $[\text{Ru(III)}]/k_c$ versus $1/[\text{OH}^-]$.

(Conditions as in Table VII(iii)(p.195);(iv)(p.198)).
[Ru(III)]/k c versus 1/[OH'] be linear (Fig.VII(vi)(p.213)) \((r \geq 0.997, S \leq 0.050)\). From the slopes and intercept of such plots, the values of \(K_4\), \(K_5\) and \(k_c\) were found to be \(8.77 \pm 0.50 \text{ dm}^3\text{mol}^{-1}\), \((1.34 \pm 0.05) \times 10^3 \text{ dm}^3\text{mol}^{-1}\) and \((4.10 \pm 0.2) \times 10^4 \text{ dm}^3\text{mol}^{-1} \text{ s}^{-1}\), respectively. Using these values, the rate constants under different experimental conditions were calculated by equation (12) and compared with experimental data (Table VII (iii)(p.195));(iv) (p.198)). Experimental and calculated values agreed reasonably well supporting the assumptions of Scheme 1. The value of \(K_4\) is in good agreement with earlier work\(^{18}\). The difference in the activation parameters for the catalysed and uncatalysed reactions\(^2\) explains the catalytic effect on the reaction. The catalyst Ru(III) forms the complex with L-proline, which shows more reducing property than L-proline itself. Hence the catalyst, Ru(III) lowers the energy of activation, i.e. it provides an alternative pathway with lower activation parameters for the reaction.

The effect of increasing ionic strength on the rate explains qualitatively the reaction between two negatively charged ions, as seen in Scheme 1. A plot of \(\log k_c\) versus \(1/\varepsilon_r\) gives a straight line with negative slope for a reaction between negative ions and a neutral molecule, whereas positive slope results for a positive ion and neutral molecule. In our present study, the plot of \(\log k_c\) versus \(1/\varepsilon_r\) \((r \geq 0.9938, S \leq 0.0184)\) was linear with a positive slope (Table VII (v)(p.201)) (Fig. VII (iv) (p.202)) which is in accordance with the involvement of negative ions as given in Scheme 1.
Importance of Chapter VII

Among various species of DPC in alkaline medium, in earlier reports the mono periodatocuprate(III) was the active species, whereas, deprotonated diperiodatocuprate(III) is considered to be the active species for the title reaction. Rate constants of slow step and other equilibrium constants involved in the mechanism are evaluated and activation parameters with respect to slow step of reaction were computed.