PART - 2
Catalysed Reactions
CHAPTER V

Osmium(VIII) catalysed oxidation of L-proline by a new oxidant diperiodatoargentate(III) in aqueous alkaline medium – a free radical intervention

Enzymatic dehydrogenation of α-amino acids by flavoenzymes has attracted considerable attention in recent years. Amino acids have been oxidized by a variety of oxidising agents. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants. The study of amino acids becomes important because of their biological significance and selectivity towards the oxidant to yield different products. L-proline is a non-essential amino acid and is an important constituent of collagen. As per recent report, L-proline is considered to be the world’s smallest natural enzyme and it is used in catalysing the aldol condensation of the acetone to various aldehydes with high stereospecificity that has the pace. Its role in metabolism is crucial and finds extensive applications in pharmaceuticals and medicines.

The importance of diperiodatoargentate(III) (DPA) is given in Chapter II(p.29). In the present investigation, we have obtained the evidence for the reactive species for DPA in alkaline medium. When DPA is the oxidant it needs to be known that which of the species is in active form, since multiple equilibria between different silver(III) species are involved. In the present investigation, we have obtained the evidence for the reactive species for DPA in alkaline medium.
The DPA is a metal complex with Ag in 3+ oxidation state like Cu$^{3+}$ in DPC and Fe$^{3+}$ in hemoglobin.

Osmium(VIII) is known to be an efficient catalyst in several redox reactions, particularly in alkaline solutions$^5$. The mechanism of catalysis can be quite complicated due to the formation of different intermediate complexes, free radicals, and different oxidation states of osmium. The uncatalysed oxidation of L-proline by DPA has been studied$^6$. A micro amount of osmium(VIII) is found to catalyze the reaction. Literature survey reveals that there are no reports on mechanistic study of osmium(VIII) catalysed oxidation of L-proline by diperiodatoargentate(III) (DPA). The present study deals with the title reaction to investigate the redox chemistry of Ag(III), and osmium(VIII) in such media and to arrive at a possible mechanism of the reaction on the basis of kinetic and spectral results.

**EXPERIMENTAL**

**Materials**

All chemicals used were of reagent grade and double distilled water was used throughout the work. A solution of L-proline (Sisco - Chem Ltd.) was prepared by dissolving an appropriate amount of recrystallised sample in double distilled water. The required concentration of L-proline was obtained from its aqueous stock solution. The osmium(VIII) solution was obtained by dissolving osmium(VIII) oxide (Johnson Matthey) in 0.50 mol dm$^{-3}$ in KOH. The concentration was ascertained by known method$^7$. The solution of IO$_4^-$ was prepared by dissolving a known weight of KIO$_4$ (Riedel-de Haen) in hot water,
and used after 24 hrs. Its concentration was ascertained iodometrically at neutral pH maintained using phosphate buffer. KNO$_3$ and KOH were used to maintain ionic strength and alkalinity of the reaction respectively. Aqueous solution of AgNO$_3$ was used to study the product effect, Ag (I).

The preparation of DPA and its characterization and standardization is carried as given in Chapter II (p.31). The aqueous solution of DPA was used for the required [DPA] in the reaction mixture.

**Kinetic measurements**

Kinetic measurements were performed on a Varian CARY 50 Bio UV–Vis Spectrophotometer. The kinetics was followed under pseudo first order condition where [L-proline] > [DPA] at 25 ± 0.1 °C, unless specified. The reaction was initiated by mixing the DPA to L-proline solution which also contained required concentration of osmium(VIII), KNO$_3$, KOH and KIO$_4$. The progress of reaction was followed spectrophotometrically at 360 nm by monitoring the decrease in absorbance of DPA. The molar absorbancy index, ‘$\varepsilon$’ at 360 nm was 13900 ± 200 dm$^3$ mol$^{-1}$ cm$^{-1}$ (Chapter II (p.32)). It was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength. An example run is given in Table V (i)(p.132). During the calculation of the pseudo first-order rate constants, ‘$k_c$’, we have to account for the uncatalysed rate also. Due to this, in case of each catalyzed kinetic run under similar conditions in the absence of catalysts were also carried out. In both the catalysed and uncatalysed cases the pseudo-first order rate constants ($k_c$ and $k_u$) were obtained from the plots of log $[\text{DPC}]$ versus time. The plots were linear up to 80%
Table V (i)

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

\[
\begin{align*}
[L\text{-proline}] &= 5.0 \times 10^{-4}; \\
[\text{DPA}] &= 5.0 \times 10^{-5}; \\
[\text{OH}^-] &= 0.40; \\
[\text{IO}_4^-] &= 1.0 \times 10^{-4}; \\
[\text{Os(VIII)}] &= 1.0 \times 10^{-6}; \\
I &= 0.90 / \text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density (360 nm)</th>
<th>[DPA] \times 10^5 (mol dm^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.687</td>
<td>4.94</td>
</tr>
<tr>
<td>0.4</td>
<td>0.608</td>
<td>4.37</td>
</tr>
<tr>
<td>0.8</td>
<td>0.549</td>
<td>3.95</td>
</tr>
<tr>
<td>1.2</td>
<td>0.455</td>
<td>3.27</td>
</tr>
<tr>
<td>1.6</td>
<td>0.368</td>
<td>2.64</td>
</tr>
<tr>
<td>2.0</td>
<td>0.287</td>
<td>2.06</td>
</tr>
<tr>
<td>2.4</td>
<td>0.189</td>
<td>1.36</td>
</tr>
<tr>
<td>2.8</td>
<td>0.067</td>
<td>0.48</td>
</tr>
</tbody>
</table>
completion of reaction under the range of [OH⁻] used. The catalysed rate\( (k_c) \) can be calculated as follows: As the DPC oxidation of L-lysine in basic medium proceeds with a measurable rate in the absence of catalyst, ruthenium(III), catalyzed reaction is understood to occur in parallel paths with contributions from both the catalyzed and uncatalysed paths. Thus, the total rate constant\( (k_t) \) is equal to the sum of the rate constants of the catalyzed \( (k_c) \) and uncatalysed \( (k_u) \) reactions.

\[
i.e \quad k_t = k_c + k_u
\]

Therefore, \( k_c = k_t - k_u \)

During the kinetics a constant concentration viz. \( 1.0 \times 10^{-4} \text{ mol dm}^{-3} \) of KIO\(_4\) was used throughout the study unless otherwise stated. Thus, the possibility of oxidation of L-proline by periodate was tested. We found that there was no significant interference due to KIO\(_4\) under experimental condition. 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. However, it was found that there was no significant reaction under the experimental conditions employed compared to the DPC oxidation of L-proline. Similarly for OH⁻ also above test was carried out and there was no significant reaction under the experimental conditions employed. Kinetics runs were also carried out in N\(_2\) atmosphere in order to understand the effect of dissolved oxygen on the rate of reaction. No significant difference in the results was obtained under a N\(_2\) atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of
carbonate was also studied. Added carbonate had no effect on the reaction rates. Regression analysis of experimental data to obtain the regression coefficient $r$ and standard deviation $S$ of point from the regression line was performed using Microsoft Excel programme.

RESULTS

Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPA to L-proline in the presence of constant amounts of $\mathrm{OH}^-$, Os(VIII) and KNO$_3$ were kept for 6 hrs in closed vessels under nitrogen atmosphere. The remaining concentration of DPA was estimated by spectrophotometrically at 360 nm. (Table V (ii)(p.135)). The results indicate a 1:2 stoichiometry as given in equation (1):

$$
\begin{align*}
&\text{COO}^- + 2 \left[\text{Ag(H}_2\text{O}_6\right](\text{H}_2\text{O})_2] + 4 \text{OH}^- \rightarrow \\
&\text{H}_2\text{N} - \text{COOH} + 2\text{Ag (I)} \\
&+ \text{HCO}_3^- + 2 \text{H}_2\text{O}_6^3^- + 5 \text{H}_2\text{O}
\end{align*}
$$

(1)

The stoichiometric ratio suggests that the main reaction product was identified as 4-aminobutyric acid by spot tests. It was extracted with ether and recrystallised from aqueous alcohol and characterized by IR spectrum and melting point, 192 $^\circ$C (Literature value 195$^\circ$C). The presence of carboxylic acid was confirmed by IR spectroscopy which showed bands at 3444 cm$^{-1}$ for NH stretching, 1742 cm$^{-1}$ due to $>\text{C}=\text{O}$ stretching of carboxylic acid, and 2840 cm$^{-1}$ for OH stretching of carboxylic acid. 4-aminobutyric acid was further characterized by $^1\text{H}$ NMR spectrum (CDCl$_3$) two triplet at 2.31 $\delta$ (a) and 2.69 $\delta$ (c) and multiplet at 1.84 $\delta$. 

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Table V (ii)

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

\[
[\text{OH}^-] = 0.40; \quad [\text{IO}_4^-] = 1.0 \times 10^{-4}; \\
I = 0.90 \text{ mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Taken [DPA] \times 10^5 (mol dm(^3))</th>
<th>Taken [L-pro] \times 10^4 (mol dm(^3))</th>
<th>Found [DPA] \times 10^5 (mol dm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>0.02</td>
</tr>
<tr>
<td>3.0</td>
<td>1.0</td>
<td>1.03</td>
</tr>
<tr>
<td>4.0</td>
<td>2.0</td>
<td>0.02</td>
</tr>
<tr>
<td>6.0</td>
<td>2.0</td>
<td>2.04</td>
</tr>
<tr>
<td>8.0</td>
<td>2.0</td>
<td>4.01</td>
</tr>
<tr>
<td>4.0</td>
<td>1.0</td>
<td>2.05</td>
</tr>
</tbody>
</table>
(due to (b) CH₂), 5.44 δ (s, 2H due to -NH₂) and 11.6 δ (s, H due to -COOH), -NH₂ and -OH were vanished on adding D₂O. The only organic product obtained in the oxidation is 4-aminobutyric acid, which is confirmed by single spot in TLC. The product CO₂ was quantitatively detected by bubbling N₂ gas through the acidified reaction mixture and passing the liberated gas through tube containing limewater. The formation of free Ag⁺ in solution was detected by adding KCl solution to the reaction mixture, which produced white turbidity due to formation of AgCl. It was observed that 4-aminobutyric acid does not undergo further oxidation under the present kinetic conditions.

**Reaction order**

The reaction orders have been determined from the slopes of log kᵣ versus log (concentration) plots by varying the concentrations of L-proline, Os(VIII) and alkali in turn while keeping the others constant.

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

The DPA concentration was varied in the range of 1.0 x 10⁻⁵ to 1.0 x 10⁻⁴ mol dm⁻³ under constant concentrations of L-proline, OH⁻, Os(VIII) with constant ionic strength. The linearity of the plots of log (absorbance) versus time, indicates a reaction order of unity in [DPA] (Fig. V (i)(p.137)) (r ≥ 0.9984, S ≤ 0.0027). This is also confirmed by varying of [DPA], which did not result in any change in the pseudo-first order rate constants, kᵣ (Table V (iii)(p.138)).

**Effect of [L-proline]**

The L-proline concentration was varied in the range 1.0 x 10⁻⁴ to 1.0 x 10⁻³ mol dm⁻³ at 25 °C while keeping other reactants concentrations and conditions
Figure V (i)

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

$[\text{DPA}] \times 10^5 \text{ (mol dm}^{-3})$: (1) 1.0, (2) 3.0, (3) 5.0, (4) 8.0, (5) 10

(Conditions as in Table V (iii) (p.138))
Table V (iii)
Effect of variation of [DPA] and [L-pro] on the osmium(VIII) catalysed oxidation of L-proline by diperiodatoargentate(III) in aqueous alkaline medium at 25 °C.

\[
[\text{Os(VIII)}] = 1.0 \times 10^{-6}; \quad [\text{OH}^-] = 0.40; \\
[\text{IO}_4^-] = 1.0 \times 10^{-4}; \quad I = 0.90 \text{ mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>[DPA] \times 10^5 (mol dm(^{-3}))</th>
<th>[L-pro] \times 10^4 (mol dm(^{-3}))</th>
<th>(k_T \times 10^2) (s(^{-1}))</th>
<th>(k_U \times 10^3) (s(^{-1}))</th>
<th>(k_C \times 10^2) (s(^{-1}))</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>5.0</td>
<td>1.63</td>
<td>3.22</td>
<td>0.98</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>5.0</td>
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<td>2.66</td>
<td>0.97</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>1.18</td>
<td>2.01</td>
<td>0.98</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
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<td>1.59</td>
<td>1.41</td>
<td>0.96</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>1.56</td>
<td>1.35</td>
<td>0.97</td>
<td>0.97</td>
<td></td>
</tr>
</tbody>
</table>

| 5.0             | 1.0             | 0.51            | 1.02            | 0.41            | 0.40   |        |
| 5.0             | 3.0             | 0.90            | 1.43            | 0.76            | 0.79   |        |
| 5.0             | 5.0             | 1.18            | 2.01            | 0.98            | 0.98   |        |
| 5.0             | 8.0             | 1.39            | 2.56            | 1.13            | 1.13   |        |
| 5.0             | 10              | 1.53            | 3.13            | 1.22            | 1.19   |        |

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constant. (Table V (iii)(p.138)). The $k_c$ values increased with the increase in concentration of L-proline and found that an apparent less than unit order dependence on [L-proline] (Fig. V (ii)(p.140)) ($r>0.9964$, $S\leq0.017$). However, at lower concentration of L-proline, the reaction was first-order in L-proline and at high concentration of L-proline, the reaction was independent of [L-proline]. The order in L-proline changes from first-order to zero order as [L-proline] increases.

**Effect of [alkali]**

The effect of alkali on the reaction has been studied in the range of 0.1 to 0.8 mol dm$^{-3}$ at constant concentrations of L-proline, DPA and a constant ionic strength of 0.90 mol dm$^{-3}$ in presence of Os(VIII) catalyst at 25 °C. The rate constants increased with increasing [alkali] and an apparent less than unit order dependence on [alkali] (Table V (iv)(p.141)). The order in [alkali] also changes from first order to zero order as [alkali] increases. (Fig. V (ii)(p.140)) ($r > 0.9969$, $S < 0.013$).

**Effect of [Os(VIII)]**

The osmium(VIII) concentration was varied from 8.0x10$^{-7}$ to 9.0x10$^{-6}$ mol dm$^{-3}$ range, at constant concentration of diperiodatoargentate(III), L-proline, alkali and at constant ionic strength (Table V (iv)(p.141)). The order in [Os(VIII)] was found to be unity from the linearity of the plots of log $k_c$ versus log [Os(VIII)] (Fig. V (iii)(p.142)) ($r \geq 0.9967$, $S \leq 0.015$).

**Effect of [periodate]**

The periodate was varied from 8.0 x 10$^{-5}$ to 9.0 x 10$^{-4}$ at constant concentrations of DPA, L-proline, OH$^-$, osmium(VIII) and at constant ionic
Figure V (ii)
Order plots with respect to [L-pro], [OH'] and [IO₄⁻] on the Os(VIII) catalysed oxidation of L-proline by alkaline diperiodatoargentate(III) at 25° C and I = 0.90 mol dm⁻³.

(Conditions as in Table V (iii)(p.138); V (iv)(p.141)).
Table V (iv)

Effect of variation of [OH'], [Os(VIII)] and [IO₄'] on the osmium(VIII) catalysed oxidation of L-proline by diperiodatoargentate(III) in aqueous alkaline medium at 25 °C.

\[
\text{[L-proline] = } 5.0 \times 10^4; \quad \text{[DPA] = } 5.0 \times 10^5; \\
I = 0.90 / \text{mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>[OH'] (mol dm(^{-3}))</th>
<th>[Os(VIII)] \times 10^6 (mol dm(^{-3}))</th>
<th>[IO₄'] \times 10^4 (mol dm(^{-3}))</th>
<th>(k_T \times 10^4) (s(^{-1}))</th>
<th>(k_U \times 10^3) (s(^{-1}))</th>
<th>(k_C \times 10^2) (s(^{-1}))</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
</tr>
<tr>
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<td>1.0</td>
<td>0.89</td>
<td>1.45</td>
<td>0.74</td>
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<td></td>
</tr>
<tr>
<td>0.4</td>
<td>1.0</td>
<td>1.0</td>
<td>1.18</td>
<td>2.01</td>
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</tr>
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<tr>
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<td>0.89</td>
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<td>0.78</td>
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<td>1.0</td>
<td>1.0</td>
<td>1.18</td>
<td>2.01</td>
<td>0.98</td>
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</tr>
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<td>5.89</td>
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</tr>
<tr>
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<td>1.0</td>
<td>9.77</td>
<td>2.01</td>
<td>9.10</td>
<td>8.84</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
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<td>0.8</td>
<td>1.21</td>
<td>1.29</td>
<td>1.08</td>
<td>1.05</td>
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</tr>
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<td>1.18</td>
<td>2.01</td>
<td>0.98</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
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</tr>
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</tr>
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<td>0.49</td>
<td>1.50</td>
<td>0.34</td>
<td>0.29</td>
<td></td>
</tr>
</tbody>
</table>
Figure V (iii)

Order plot with respect to [Os(VIII)] on the Os(VIII) catalysed oxidation of L-proline by alkaline diperiodatoargentate(III) at 25 °C.
strength. It was observed that the rate constants decreased by increasing \([\text{IO}_4^-]\) (Table V (iv)(p.141) (Fig. V (ii)(p.140)) \((r \geq 0.9970, S \leq 0.011)\).

**Effect of products**

Initially added products, such as \(\text{Ag(I)}\) and 4-aminobutyric acid did not affect the rate of reaction.

**Effect of ionic strength**

The addition of \(\text{KNO}_3\) was used to increase the ionic strength of the reaction medium. There is increasing effect on the rate of reaction at constant \([\text{DPA}], [\text{L-proline}], [\text{OH}^-], \text{Os(VIII)}\) and \([\text{IO}_4^-]\) (Table V (v)(p.144)). The plot of \(\log k_C\) vs \(1/2\) was linear with positive slope (Fig. V (iv)(p.145)) \((r \geq 0.9965, S \leq 0.016)\).

**Dielectric constant of the medium**

The dielectric constant of the medium, \(\mathcal{D}\) was varied by varying the \(t\)-butyl alcohol and water percentage. The \(\mathcal{D}\) values were calculated as in earlier Chapter II(p.43). The decrease in dielectric constant of the reaction medium increases the rate (Table V (v)(p.144)) the plot of \(\log k_C\) versus \(1/\mathcal{D}\) was linear with positive slope as shown in Fig. V (iv)(p.145) \((r \geq 0.9962, S \leq 0.019)\).

**Test for free radicals**

The intervention of free radicals was examined as follows, the reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept in an inert atmosphere for 1h. When the reaction mixture was diluted with methanol, precipitate resulted, suggesting that there is participation of free radicals in the reaction.
Table V (ν)

Effect of variation of ionic strength and solvent polarity on the Os(VIII) catalysed oxidation of L-proline by diperiodatoargentate(III) in aqueous alkaline medium at 25° C.

\[
\begin{align*}
[DPA] &= 5.0 \times 10^{-5}; \\
[L\text{-proline}] &= 5.0 \times 10^{-4}; \\
[Os(\text{VIII})] &= 1.0 \times 10^{-6}; \\
[OH^-] &= 0.40 \text{ mol dm}^{-3} \\
I &= 0.90 \text{ mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>I (mol dm(^{-3}))</th>
<th>(k_c \times 10^2) (s(^{-1}))</th>
<th>%of t-butyl alcohol-water (v/v)</th>
<th>(k_c \times 10^2) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
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<td>0.5</td>
<td>0.67</td>
<td>5.0 75.12</td>
<td>1.10</td>
</tr>
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<td>0.7</td>
<td>0.79</td>
<td>10.0 71.74</td>
<td>1.19</td>
</tr>
<tr>
<td>0.9</td>
<td>0.98</td>
<td>15.0 68.36</td>
<td>1.34</td>
</tr>
<tr>
<td>1.1</td>
<td>1.18</td>
<td>20.0 64.98</td>
<td>1.48</td>
</tr>
<tr>
<td>1.3</td>
<td>1.41</td>
<td>25.0 61.04</td>
<td>1.72</td>
</tr>
</tbody>
</table>

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Figure V (iv)
Effect of variation of ionic strength and solvent polarity on the osmium(VIII) catalysed oxidation of L-proline by diperiodatoargentate(III) in aqueous alkaline medium at 25° C.

(Conditions as in Table V (v) (p.144))
Catalytic activity

It has been pointed out by Moelwyn-Hughes¹¹ that, in the presence of the catalyst, the uncatalysed and catalysed reactions proceed simultaneously, so that

\[ k_T = k_U + K_C [\text{catalyst}]^x \]  

(2)

Here \( k_T \) is the observed pseudo first-order rate constant in the presence of Os(VIII) catalyst, \( k_U \) is the pseudo first-order rate constant for the uncatalysed reaction, \( K_C \) is the catalytic constant and ‘\( x \)’ is the order of the reaction with respect to [Os(VIII)]. In the present investigations, \( x \) values for the standard run were found to be 1.0. Then the value of \( K_C \) can be calculated using the equation

\[ K_C = \frac{k_T - k_U}{[\text{Catalyst}]^x} = \frac{k_C}{[\text{Catalyst}]^x} \quad \text{(where, } k_T - k_U = k_C) \]  

(3)

The values of \( K_C \) were evaluated at different temperatures and found to vary with temperatures. Further, plots of log \( K_C \) versus 1/T were linear and the values of energy of activation and other activation parameters with reference to catalyst were computed. These results are summarized in Table V (vi)(p.147).

Effect of temperature

The influence of temperature on the \( K_C \) values were studied at 25, 30, 35 and 40 °C by varying L-proline concentrations. The rate constants, \( k \), of the slow step of Scheme 2 were obtained from the intercepts of [Os(VIII)]/ \( K_C \) versus 1/[L-proline] plots at four different temperatures and were used to calculate the activation parameters. The values are given in Table V (vii)(p.148). The data are subjected to least square analysis as in Chapter II (p.47). The energy of activation corresponding to these constants was evaluated from the plot of log \( k \) (\( Y^\text{cal} \)) versus 1/T (Fig. V (v)(p.149)) and other activation parameters are obtained as in Chapter II (p.48) and are presented in Table V (vii)(p.148).
Table V (vi)

Values of catalytic constant ($K_C$) at different temperatures and activation parameters calculated using $K_C$ values.

\[
[DPA] = 5.0 \times 10^{-5}; \quad [L\text{-pro}] = 5.0 \times 10^{-4};
\]
\[
[OH^-] = 0.40; \quad [IO_4^-] = 1.0 \times 10^{-4};
\]
\[
[Os(VIII)] = 1.0 \times 10^{-6}; \quad I = 0.90 /\text{mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$10^3 K_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>9.8</td>
</tr>
<tr>
<td>303</td>
<td>14.8</td>
</tr>
<tr>
<td>308</td>
<td>19.9</td>
</tr>
<tr>
<td>313</td>
<td>24.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>47.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^#$ (kJ mol$^{-1}$)</td>
<td>45.2</td>
</tr>
<tr>
<td>$\Delta S^#$ (JK$^{-1}$mol$^{-1}$)</td>
<td>-16.2</td>
</tr>
<tr>
<td>$\Delta G^#$ (kJ mol$^{-1}$)</td>
<td>50</td>
</tr>
<tr>
<td>$\log A$</td>
<td>12.3</td>
</tr>
</tbody>
</table>
(a) Effect of temperature on the slow step of the mechanism of Os(VIII) catalysed oxidation of L-proline by alkaline diperiodatoargentate(III).

\[
[L\text{-pro}] = 5.0 \times 10^{-4}; \quad [\text{OH}^-] = 0.40;
\]
\[
[DPA] = 5.0 \times 10^{-5}; \quad [\text{Os(VIII)}] = 1.0 \times 10^{-6};
\]
\[
I = 0.90 /\text{mol dm}^{-3}.
\]

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>(k \times 10^3) (s(^{-1}))</th>
<th>(\log k)</th>
<th>(1/T \times 10^3)</th>
<th>(Y_{\text{calc}}^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.51</td>
<td>4.1794</td>
<td>3.35</td>
<td>4.1616</td>
</tr>
<tr>
<td>303</td>
<td>1.91</td>
<td>4.2818</td>
<td>3.30</td>
<td>4.2030</td>
</tr>
<tr>
<td>308</td>
<td>2.65</td>
<td>4.4238</td>
<td>3.25</td>
<td>4.4379</td>
</tr>
<tr>
<td>313</td>
<td>3.85</td>
<td>4.5859</td>
<td>3.19</td>
<td>4.5694</td>
</tr>
</tbody>
</table>

(b) Thermodynamic activation parameters with respect to slow step of Scheme 1.

<table>
<thead>
<tr>
<th>Activation parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_a) (kJ mol(^{-1}))</td>
<td>48 ± 1</td>
</tr>
<tr>
<td>(\Delta H^#) (kJ mol(^{-1}))</td>
<td>46 ± 1</td>
</tr>
<tr>
<td>(\Delta S^#) (J K(^{-1})mol(^{-1}))</td>
<td>-10 ± 0.2</td>
</tr>
<tr>
<td>(\Delta G^#) (kJ mol(^{-1}))</td>
<td>49 ± 2</td>
</tr>
<tr>
<td>(\log A)</td>
<td>12.6 ± 0.4</td>
</tr>
</tbody>
</table>
Effect of temperature on the Os(VIII) catalysed oxidation of diperiodatoargentate(III) by L-proline in aqueous alkaline medium.

(Conditions as in Table V (vii)(p.148)
DISCUSSION

In the later period of the 20th century, the kinetics of oxidation of various organic and inorganic substrates have been studied by Ag(III) species, this strategy may be due to its strong and versatile nature as a two-electron oxidant. Among the various species of Ag(III), Ag(OH)$_4^-$; diperiodatoargentate(III) and ethylenebis (biguanide), (EBS), silver(III) atoms are of maximum interest to the researchers due to their relative stability$^{12}$. The stability of Ag(OH)$_4^-$ is very sensitive towards traces of dissolved oxygen and other impurities in the reaction medium; so it had not drawn much attention. However, the other two forms of Ag(III) are quite stable$^{13}$; the DPA is used in highly alkaline medium and EBS is used in highly acidic medium.

It is known that L-proline exists in the form of Zwitterion$^{14}$ 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$^{14}$.

\[
\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-COO}^-
\]

A literature survey$^{15}$ reveals that the water soluble diperiodatoargentate (III) (DPA) has a formula [Ag (IO$_6$)$_2$]$^7$ with dsp$^2$ configuration of square planar structure, similar to diperiodatocopper (III) complex with two bidentate ligands: a periodate to form a planar molecule. When the same molecule is used in alkaline medium, it is unlikely to exist as [Ag (IO$_6$)$_2$]$^7$ though periodate is known to be in various protonated forms$^{16,17}$ depending on pH of the solution as given in the following multiple equilibria (4)-(6):

\[
\]
Periodic acid exists as $\text{H}_5\text{IO}_6$ in acid medium and as $\text{H}_4\text{IO}_6^-$ at pH 7. Thus under the present alkaline conditions, the main species are expected to be $\text{H}_3\text{IO}_6^{2-}$ and $\text{H}_2\text{IO}_6^{3-}$. At higher concentrations, periodate also tends to dimerise. On the contrary, the authors in their recent studies have proposed the DPA as $[\text{Ag (HL)}_2]^-$ in which ‘L’ is a periodate with an uncertain number of protons and ‘HL’ is a protonated periodate of an uncertain number of protons. This can be ruled out by considering the alternative form $^{16}$ of $\text{IO}_4^-$ at pH $>7$ which is in the form $\text{H}_3\text{IO}_6^{2-}$ and $\text{H}_2\text{IO}_6^{3-}$. Hence, DPA could be present as $[\text{Ag (H}_3\text{IO}_6)_2]^-$ or $[\text{Ag (H}_2\text{IO}_6)_2]^{3-}$ in alkaline medium. Therefore, under the present condition, diperiodatoargentate(III) may be depicted as $[\text{Ag (H}_3\text{IO}_6)_2]^-$ or $[\text{Ag (H}_2\text{IO}_6)_2]^{3-}$. A similar speciation of periodate in alkali was proposed for diperiodatonicelate(IV).

Osmuim(VIII) is known to form different complexes$^{20}$ at different $\text{OH}^-$ concentrations, $[\text{OsO}_4(\text{OH})_2]^{2-}$ and $[\text{OsO}_5(\text{OH})]^{3-}$. At higher concentrations of $\text{OH}^-$ i.e.$>0.15$ mol dm$^3$, $[\text{OsO}_5(\text{OH})]^{3-}$ is significant. At lower concentrations of $\text{OH}^-$, as employed in the present study, and since the rate of oxidation increased with increase in [OH$^-$], it is reasonable that $[\text{OsO}_4(\text{OH})_2]^{2-}$ was operative and that its formation is importance in the reaction$^{20}$. Based on the experimental rate law, a general mechanism can be proposed (Scheme 1).
Scheme 1. General mechanistic scheme for the L-proline oxidation by diperiodatoargentate (III)

Since, the reaction was enhanced by [OH'], and added periodate retarded the rate and first-order dependency in [DPA] and fractional order in [L-proline], the following mechanism has been proposed by considering [L-proline] in anionic form which also explains all other experimental observations (Scheme 2).

\[
\begin{align*}
\text{Ag (HL)}_2 + \text{OH}^- & \quad \rightleftharpoons \quad \text{Ag L(HL)} + \text{H}_2\text{O} \\
\text{Ag L (HL)} + 2 \text{H}_2\text{O} & \quad \rightleftharpoons \quad \text{Ag L(H}_2\text{O)}_2 + \text{L} \\
\text{Catalyst} + \text{S} & \quad \rightleftharpoons \quad \text{Complex (C)} \\
\text{Complex (C)} + \text{Ag L(H}_2\text{O)}_2 & \quad \rightleftharpoons \quad \text{S}^- + \text{Ag (I)} + \text{L} + \text{Catalyst} \\
\text{S}^- + \text{Ag(OH)}^+ & \quad \text{fast} \quad \rightarrow \quad \text{I} \quad (\text{I= Intermediate form}) \\
\text{I} + \text{Ag L(H}_2\text{O)}_2 & \quad \text{fast} \quad \rightarrow \quad \text{Products}
\end{align*}
\]
Complex(C) + Ag(H2O6)(H2O)2 \xrightarrow{k_{slow}}

\[ + Ag(OH)^+ + 2H^+ + HCO_3^- + H_2O_6^{3-} + \{Os_4(OH)_2\}^{2-} \]

\[ H + Ag(OH)^+ \rightarrow \text{CHO} + Ag(l) \]

\[ H_2N - \text{CHO} + [Ag(H_2O_6)(H_2O)_2] \xrightarrow{k_{fast}} H_2N - \text{COOH} \]

\[ + Ag(l) + H_2O_6^{3-} + 2H^+ + H_2O \]

\[ 4 H^+ + 4 OH^- \xrightarrow{k_{fast}} 4 H_2O \]

Scheme 2. Detailed Scheme for the oxidation of L-proline by alkaline diperiodatoargentate (III)

The reaction between DPA and L-proline in alkaline medium in the presence of osmium(VIII) presents a 2:1 stoichiometry of oxidant to reductant, with first order dependence on both [DPA] and [osmium(VIII)] and an apparent order of less than unity in [OH'] and [L-proline], monoperiodatoargentate(III) (MPA) is considered to be the active species in view of the observed experimental results. In the prior equilibrium step 1, the [OH'] deprotonates the DPA to give a deprotonated diperiodatoargentate (III); in the second step, displacement of a ligand, periodate from deprotonated DPA takes place to give free periodate which is evidenced by decrease in the rate with increase in [periodate]. It may be
expected that lower Ag(III) periodate species such as monoperiodatoargentate(III) (MPA) will be more important in the reaction than the DPA. The inverse fractional order in $[\text{H}_3\text{IO}_6\quad 2^+]$ might also be due to this reason. In the pre rate determining stage, Os(VIII) catalyst, combines with a molecule of anionic species of L-proline to give a complex, which reacts with monoperiodatoargentate(III) MPA in a slow step to give the free radical derived from L-proline with generation of Ag(II) species. This free radical of L-proline combines with Ag(II) species in a fast step to give 4-aminobutaraldehyde, which reacts with another molecule of MPA in a fast step to give the 4-aminobutyric acid. Thus, all these results indicate a mechanism of the type as in Scheme 2.

Since Scheme 2 is in accordance with generally well accepted principle of non-complementary oxidations taking place in sequence of one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility as given in experimental section. This type of radical intermediate has been observed in earlier work 21. The Michaelis-Menten plot proved the complex formation between oxidant and reductant, which explains less than unit order in [L-proline].

Thus, in Scheme 2, the parallel reaction and involvement of two molecules of L-proline in the intermediate complex are excluded.

The probable structure of the complex (C) is given below:
Spectroscopic evidence for the complex formation between osmium(VIII) and L-proline was obtained from UV-Vis spectra of L-proline (5.0 x 10⁻⁴), Os (VIII) (1.0 x 10⁻⁶, [OH⁻] = 0.40 mol dm⁻³) and a mixture of both. A bathochromic shift of about 8 nm from 437 nm to 445 nm in the spectra of L-proline was observed. Such a complex between a substrate and a catalyst has been observed in other studies²².

The rate equation can be derived as follows,

\[
\text{Rate} = \frac{-d[DPA]}{dt} = k \frac{[C][Ag(H_2IO_6)(H_2O)_2]}{[H_3IO_6^2]} = \frac{k K_2 K_3 [L-pro][Os(VIII)][DPA]}{[H_3IO_6^2]} \quad [\text{eqn } 7]
\]

The total concentration of DPA, \([DPA]_T\) is given by (subscripts t and f stand for total and free respectively).

\[
[DPA]_T = [DPA]_f + [Ag(H_2IO_6)(H_3IO_6)]^2 + [Ag(H_2IO_6)(H_2O)_2]
\]

\[
= [DPA]_f + K_1 [OH][DPA] + \frac{K_2 [Ag(H_2IO_6)(H_3IO_6)]^2}{[H_3IO_6^2]}
\]

\[
= [DPA]_f + K_1 [OH][DPA] + \frac{K_1 K_2 [DPA][OH]}{[H_3IO_6^2]}
\]
\[ [DPA]_f \{ 1 + K_1 [OH^-] + \frac{K_1 K_2 [OH^-]}{[H_3IO_6^{2-}]} \} \]

\[ = [DPA]_f \{ \frac{[H_3IO_6^{2-}] + K_1 [OH^-] [H_3IO_6^{2-}] + K_1 K_2 [OH^-]}{[H_3IO_6^{2-}]} \} \]

Therefore,

\[ [DPA]_f = \frac{[DPA]_f [H_3IO_6^{2-}]}{[H_3IO_6^{2-}] + K_1 [OH^-] [H_3IO_6^{2-}] + K_1 K_2 [OH^-]} \]

Similarly,

\[ [L-pro]_f = [L-pro]_f + [\text{complex}] \]

\[ = [L-pro]_f + K_3 [L-pro] [Os(VIII)] \]

\[ = [L-pro]_f \{ 1 + K_3 [Os(VIII)] \} \]

\[ [L-pro]_f = \frac{[L-pro]_f}{1 + K_3 [Os(VIII)]} \]  \hspace{1cm} (8)

In view of low concentrations of osmium(VIII) used,

\[ [L-pro]_f = [L-pro]_f \]  \hspace{1cm} (9)

\[ [Os(VIII)]_f = [Os(VIII)]_f + [\text{complex}] \]

\[ = [Os(VIII)]_f + K_3 [L-pro] [Os(VIII)] \]

\[ = [Os(VIII)]_f \{ 1 + K_3 [L-pro] \} \]

\[ [Os(VIII)]_f = \frac{[Os(VIII)]_f}{1 + K_3 [L-pro]} \]  \hspace{1cm} (10)

\[ [OH^-]_f = [OH^-]_f + [Ag(H_2IO_6)(H_3IO_6)]^2 + [Ag(H_2IO_6)(H_2O)_2] \]

\[ = [OH^-]_f + K_1 [OH^-][DPA] + \frac{K_2 [Ag(H_2IO_6)(H_3IO_6)]^2}{[H_3IO_6^{2-}]} \]

\[ = [OH^-]_f + K_1 [OH^-][DPA] + \frac{K_1 K_2 [DPA][OH^-]}{[H_3IO_6^{2-}]} \]
\[ [\text{OH}^-]_t = \frac{[\text{OH}^-]_T [\text{H}_3\text{IO}_6^{2-}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1 [\text{DPA}] [\text{H}_3\text{IO}_6^{2-}] + K_1 K_2 [\text{DPA}]} \]

In view of low concentrations of DPA and H$_3$IO$_6^{2-}$ used,

\[ [\text{OH}^-]_t = [\text{OH}^-]_T \tag{11} \]

Substituting equation (8), (9), (10) and (11) in equation (7) and omitting the $T$ and $f$ subscripts, we get,

\[
\frac{d[DPA]}{dt} = \frac{k K_1 K_2 K_3 [\text{DPA}] [\text{L-pro}] [\text{OH}^-] [\text{Os(VIII)}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1 [\text{OH}^-] [\text{H}_3\text{IO}_6^{2-}] + K_1 K_2 [\text{OH}^-] + K_1 K_2 K_3 [\text{OH}^-] [\text{L-pro}] + K_3 [\text{H}_3\text{IO}_6^{2-}] [\text{L-pro}] + K_1 K_3 [\text{L-pro}] [\text{OH}] [\text{H}_3\text{IO}_6^{2-}]} \tag{12}
\]

The terms ($K_3 [\text{H}_3\text{IO}_6^{2-}][\text{L-pro}]$ and ($K_1 K_3 [\text{L-pro}] [\text{OH}^-] [\text{H}_3\text{IO}_6^{2-}]$) are neglected in the view of low concentrations of L-proline and periodate used in the study and therefore equation (12) becomes,

\[
\frac{Rate}{[\text{DPA}]} = k_C = k_T - k_U = \frac{k K_1 K_2 K_3 [\text{L-pro}] [\text{OH}^-] [\text{Os(VIII)}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1 [\text{OH}^-] [\text{H}_3\text{IO}_6^{2-}] + K_1 K_2 [\text{OH}^-] + K_1 K_2 K_3 [\text{OH}^-] [\text{L-pro}]} \tag{13}
\]

which explains all the observed kinetic orders of different species.

The rate law (13) can be rearranged into the following form suitable for verification

\[
\frac{[\text{Os(VIII)}]}{k_C} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{k K_1 K_2 K_3 [\text{OH}^-] [\text{L-pro}]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{k K_3 K_3 [\text{L-pro}]} + \frac{1}{k K_3 [\text{L-pro}]} + \frac{1}{k} \tag{14}
\]

The plots of $[\text{Os(VIII)}]/k_C$ versus $[\text{H}_3\text{IO}_6^{2-}]$, $[\text{Os(VIII)}]/k_C$ versus $1/[\text{OH}^-]$ and $[\text{Os(VIII)}]/k_C$ versus $1/[\text{L-proline}]$ were linear with an intercept supporting the Os(VIII)-L-proline complex, as verified in Fig. V (vi)(p.158). From the intercept
Figure V (vi)

Verification of rate law (13) for the oxidation of L-proline by diperiodatoargentate (III) at 25 °C.

(Conditions as in Table III (iii)(p.138); (iv)(p.141))
and slope of such plots, the reaction constants $K_1$, $K_2$, $K_3$ and $k$ were calculated as $(8.0 \pm 0.2) \times 10^2$ dm$^3$ mol$^{-1}$, $(1.8 \pm 0.1) \times 10^4$ mol dm$^{-3}$, $(6.4 \pm 0.3) \times 10^4$ dm$^3$ mol$^{-1}$, $(1.5 \pm 0.06) \times 10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ respectively. These constants were used to calculate the rate constants and compared with the experimental values and found to be in reasonable agreement with each other (Table V (iii)(p.138);(iv)(p.141)) which fortifies the Scheme 2.

The increase in the rate, with increasing ionic strength is in the favor of a reaction between two negative charged species as presented in Scheme 2. The effect of solvent on the reaction rate has been described in detail in the literature$^{23}$. In present study, the plot of log $k_C$ versus $1/D$ is linear with positive slope (Fig. V (iv)(p.145)), which seems to be contrary to the expected reaction between neutral and anionic species in media of lower relative permittivity. However, an increase in the rate of the reaction with increasing relative permittivity may be due to stabilization of the complex (C) at high relative permittivity. The complex involved in the Os(VIII) catalyst is expected to lead to negative entropy of activation and this is found to be the case.

The thermodynamic quantities for the different equilibrium steps, in Scheme 2 can be evaluated as follows. The L-proline and hydroxide ion concentrations (Table V (iii)(p.138);(iv)(p.141)) were varied at different temperatures. The plots of $[\text{Os(VIII)}]/k_C$ versus $1/[\text{L-proline}]$ ($r>0.9982$, $S \leq 0.00121$) and $[\text{Os(VIII)}]/k_C$ versus $1/[\text{OH}^-]$ ($r>0.9998$, $S \leq 0.00085$) should be linear as shown in (Fig. V (vi)(p.158)). From the slopes and intercepts, the values of $K_1$ are calculated at different temperatures. A van't Hoff's plot was made for
the variation of $K_1$ with temperature [i.e., log $K_1$ versus $1/T$ ($r > 0.9895$, $S < 0.1106$)] and the values of the enthalpy of reaction $\Delta H$, entropy of reaction $\Delta S$ and free energy of reaction $\Delta G$, were calculated. These values are given in Table V (viii)(p.161). 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 slow and involves high activation energy. In the same manner, $K_2$ and $K_3$ values were calculated at different temperatures and the corresponding values of thermodynamic quantities are given in Table V (viii)(p.161).

The negative value of $\Delta S^*$ suggests that the intermediate complex is more ordered than the reactants $^{24}$. Negative $\Delta S^*$ values for radical reactions have been ascribed to the nature of electron pairing and unpairing reactions and to the loss of degrees of freedom by formation of a rigid transition state $^{25}$. The Os(VIII) catalysed reaction however, is reasonably fast in view of readiness of Os(VIII) to act across the double bond. The activation parameters evaluated for the catalysed and uncatalysed reaction explain the catalytic effect on the reaction. The catalyst Os(VIII) forms a complex (C) with the substrate, which enhances the reducing property of the substrate over that without catalyst (Os(VIII)). Further, the catalyst Os(VIII) modifies the reaction path by lowering the energy of activation.

Importance of chapter V

Among various species of Ag(III) in alkaline medium, monoperiodatoargentate(III) is the active species. This active species involved in
Table V (viii)

(A) Effect of temperature on equilibrium constants $K_1$, $K_2$ and $K_3$ for the osmium(VIII) catalyzed oxidation of L-proline by diperiodatoargentate (III) in alkaline medium.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_1$ (dm$^3$ mol$^{-1}$)</th>
<th>$K_2 \times 10^4$ (mol dm$^{-3}$)</th>
<th>$K_3 \times 10^4$ (dm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.8 ± 0.04</td>
<td>1.8 ± 0.1</td>
<td>6.4 ± 0.3</td>
</tr>
<tr>
<td>303</td>
<td>1.8 ± 0.06</td>
<td>2.8 ± 0.1</td>
<td>6.0 ± 0.2</td>
</tr>
<tr>
<td>308</td>
<td>2.6 ± 0.1</td>
<td>3.3 ± 0.2</td>
<td>5.8 ± 0.2</td>
</tr>
<tr>
<td>313</td>
<td>3.8 ± 0.2</td>
<td>4.2 ± 0.2</td>
<td>5.4 ± 0.2</td>
</tr>
</tbody>
</table>

(B) Thermodynamic quantities using $K_1$, $K_2$ and $K_3$

<table>
<thead>
<tr>
<th>Thermodynamic quantities</th>
<th>Values from $K_1$</th>
<th>Values from $K_2$</th>
<th>Values from $K_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (kJ mol$^{-1}$)</td>
<td>75.5 ± 2.0</td>
<td>41.1 ± 0.8</td>
<td>-114 ± 6.0</td>
</tr>
<tr>
<td>$\Delta S$ (J K$^{-1}$ mol$^{-1}$)</td>
<td>234 ± 10</td>
<td>67 ± 3.0</td>
<td>-291 ± 12</td>
</tr>
<tr>
<td>$\Delta G_{298}$ (kJ mol$^{-1}$)</td>
<td>6.1 ± 0.2</td>
<td>21.2 ± 0.9</td>
<td>-27.4 ± 1.2</td>
</tr>
</tbody>
</table>
the mechanism play an important role in the reaction. And osmium(VIII) is known to be an efficient catalyst & catalyses the reaction with a measurable velocity. The active species of Os(VIII) is found to be \([\text{OsO}_4(\text{OH})_2]^{2-}\). Rate constants and equilibrium constants are evaluated and activation parameters with respect to slow step of the reaction were computed. Catalytic constants and the activation parameters with reference to the catalyst were also computed.
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