CHAPTER IV

KINETICS AND MECHANISM OF L-ISOLEUCINE OXIDATION BY ALKALINE DIPERIODATOARGENTATE(III)
L-isoleucine (ISL) is an essential amino acid. It forms active sites of enzymes and helps in maintaining their proper conformation by keeping them in proper ionic states. So, oxidation of ISL may help in understanding some aspects of enzyme kinetics. Amino acids not only act as the building blocks in protein synthesis but also play a significant role in metabolism. Amino acids can undergo many types of reaction depending on whether a particular amino acid contains non-polar groups or polar substituents. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants\textsuperscript{1, 2}. Thus, the study of amino acids becomes important because of their biological significance and selectivity towards the oxidant.

Diperiodatoargentate(III) (DPA) is a powerful oxidizing agent in alkaline medium with the reduction potential\textsuperscript{3} $1.74\text{V}$. It is widely used as a volumetric reagent for the determination of various organic and inorganic species\textsuperscript{4}. Jaya Prakash Rao\textsuperscript{5, 6} et al. have used DPA as an oxidizing agent for the kinetics of oxidation of various organic substrates. They normally found that order with respect to both oxidant and substrate concentrations was unity and $[\text{OH}^+]$ was found to enhance the rate of reaction. It was also observed that they did not arrive at the possible active species of DPA in alkali and on the other hand they proposed mechanisms by generalizing the DPA as $[\text{Ag(HL)L}]^{(x+1)^-}$. However, Anil Kumar\textsuperscript{7, 9} et al. put an effort to give an evidence for the reactive form of DPA in the large scale of alkaline pH. In the present investigation, we have obtained the evidence for the reactive species for DPA in alkaline medium. DPA is a metal complex with Ag in +3 oxidation state like Cu\textsuperscript{3+} in
diperiodatocuprate(III) (DPC) and Fe$^{3+}$ in haemoglobin and Ni$^{4+}$ in diperiodatonickelate(IV) (DPN).

The literature survey reveals that there are no reports on mechanistic studies of L-isoleucine oxidation by DPA. Thus, ISL has been selected as a substrate in order to explore the mechanism of oxidation by DPA in alkaline medium and to check the reactivity of amino acids towards DPA. The title reaction studied in this chapter investigates the redox chemistry of the Ag(III) in such media and to arrive at a plausible mechanism.

**EXPERIMENTAL**

All chemicals used were of reagent grade and double distilled water was used throughout the work. A solution of L-isoleucine (Sisco-Chem) was prepared by dissolving an appropriate amount of recrystallised sample in double distilled water. The required concentration of ISL was used from its aqueous stock solution. A stock solution of IO$_4^-$ was prepared by dissolving a known weight of KIO$_4$ (Riedel-de Haen) in hot water, the stock solution was used after 24h. Its concentration was ascertained iodometrically$^{10}$ 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).

**Preparation of DPA**

DPA was prepared by oxidizing Ag(I) as described elsewhere$^{11}$: The mixture of 28g of KOH and 23g of KIO$_4$ in 100 cm$^3$ of water along with 8.5g AgNO$_3$ was heated just to boiling and 20g of K$_2$S$_2$O$_8$ was added in several lots.
with stirring then allowed to cool. It was filtrated through a medium porosity fritted glass filter and 40g of NaOH was added slowly to the filtrate, whereupon a voluminous orange precipitate agglomerates. The precipitate is filtered as above and washed three to four times with cold water. The pure crystals were dissolved in 50 cm$^3$ water and warmed to 80 °C with constant stirring thereby some solid was dissolved to give a red solution. The resulting solution was filtered when it was hot and on cooling at room temperature, the orange crystals separated out and were recrystallised from water.

The complex was characterized from its U.V. spectrum, exhibited three peaks at 216, 255 and 362 nm. These spectral features were identical to those reported earlier for DPA$^{11}$. The magnetic moment study revealed that the complex is diamagnetic. The compound prepared was analyzed$^{12}$ for silver and periodate by acidifying a solution of the material with HCl, recovering and weighing the AgCl for Ag and titrating the iodine liberated when excess KI was added to the filtrate for IO$_4^−$. The aqueous solution of DPA was used for the required DPA concentration in the reaction mixture. During the kinetics a constant concentration viz. 1.0 x 10$^{-5}$ mol dm$^{-3}$ of KIO$_4$ was used throughout the study unless otherwise stated. Thus, the possibility of oxidation of ISL by periodate was also tested and found that there was no significant interference due to KIO$_4$ under experimental condition.

**Kinetic studies**

The kinetics was followed under pseudo-first order condition where concentration of isoleucine was excess over concentration of DPA at 25 ±
0.1°C unless otherwise stated ([ISL] > [DPA]). The reaction was initiated by mixing the required quantities of previously thermostatted solutions of isoleucine and DPA, which also contained definite quantities of periodate, potassium hydroxide and potassium nitrate to maintain the required alkalinity and ionic strength. The total hydroxide ion concentration was calculated by considering the potassium hydroxide in DPA as well as potassium hydroxide additionally added. Similarly, the total metaperiodate concentration was calculated by considering metaperiodate present in solution of DPA and additionally added. It was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength. The progress of reaction was followed by measuring the absorbance of unreacted DPA in the reaction mixture present in 1 cm cell in a thermostatted compartment of a Varian CARY 50 Bio UV-Vis. spectrophotometer at 415 nm. Peltier accessory was used to control the temperature of cell holder and cell.

The obedience of Beer's law by DPA at 360 nm had been verified, giving molar absorbance coefficient, 13900 ± 100 dm³ mol⁻¹ cm⁻¹ (Fig. IV (i) (p.103)). An example run is given in Table IV (i) (p.104). The first order rate constants, k₀ˢ, were obtained from the plots of log(Absorbance) versus time. The plots were linear up to 80% completion of the reaction and the rate constants were reproducible within ± 5%. The effect of dissolved oxygen on the rate of reaction was studied by preparing the reaction mixture and following the reaction in an atmosphere of the nitrogen. No significant difference between the results was observed in presence and absence of nitrogen. In view
Verification of Beer’s law with freshly prepared diperiodatoargentate(III) in aqueous alkaline medium at 25°C

\[ [\text{DPA}] = 5.0 \times 10^{-5}; \ [\text{OH}^-] = 0.60; \ [\text{IO}_4^-] = 1.0 \times 10^{-5}; \ I = 0.80 \text{ mol dm}^{-3} \]
Table IV (i)

Example run for the oxidation of isoleucine by diperiodatoargentate(III) in aqueous alkaline medium at 25ºC

\[
\begin{align*}
[DPA] &= 5.0 \times 10^{-5}; \\
[\text{Isoleucine}] &= 5.0 \times 10^{-4}; \\
[\text{IO}_4^-] &= 1.0 \times 10^{-5}; \\
[\text{OH}^-] &= 0.60; \\
1 &= 0.80 \text{ / mol dm}^3
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Absorbance</th>
<th>[DPA] x 10^5 (mol dm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.701</td>
<td>5.04</td>
</tr>
<tr>
<td>0.2</td>
<td>0.684</td>
<td>4.92</td>
</tr>
<tr>
<td>0.4</td>
<td>0.661</td>
<td>4.76</td>
</tr>
<tr>
<td>0.6</td>
<td>0.652</td>
<td>4.69</td>
</tr>
<tr>
<td>0.8</td>
<td>0.606</td>
<td>4.36</td>
</tr>
<tr>
<td>1.0</td>
<td>0.570</td>
<td>4.10</td>
</tr>
<tr>
<td>1.2</td>
<td>0.539</td>
<td>3.88</td>
</tr>
<tr>
<td>1.4</td>
<td>0.499</td>
<td>3.59</td>
</tr>
<tr>
<td>1.6</td>
<td>0.469</td>
<td>3.37</td>
</tr>
<tr>
<td>1.8</td>
<td>0.437</td>
<td>3.14</td>
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<td>0.405</td>
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<td>0.373</td>
<td>2.68</td>
</tr>
<tr>
<td>2.4</td>
<td>0.342</td>
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</tr>
<tr>
<td>2.6</td>
<td>0.314</td>
<td>2.26</td>
</tr>
<tr>
<td>2.8</td>
<td>0.287</td>
<td>2.06</td>
</tr>
<tr>
<td>3.0</td>
<td>0.261</td>
<td>1.88</td>
</tr>
<tr>
<td>3.2</td>
<td>0.237</td>
<td>1.71</td>
</tr>
<tr>
<td>3.4</td>
<td>0.213</td>
<td>1.53</td>
</tr>
<tr>
<td>3.6</td>
<td>0.184</td>
<td>1.33</td>
</tr>
</tbody>
</table>
of ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. However, fresh solutions were used during the experiments. In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the rate. However, fresh solutions were used during the experiments.

Regression analysis of experimental data to obtain the regression coefficient, $r$ and standard deviation, $S$ of points from the regression line was performed using Microsoft Excel-2003 programme.

RESULTS

Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPA to ISL in presence of constant amount of OH$^-$ and KNO$_3$ were kept for 3 h at 298K in a nitrogen atmosphere in a closed vessel. The remaining concentration of DPA was estimated spectrophotometrically at 360 nm. The results indicate that two moles of DPA consumed one mole of ISL (2:1) as in equation (1).

$$
\begin{align*}
\text{C}_2\text{H}_5\text{COO}^- + 2[\text{Ag(H}_2\text{IO}_6)(\text{H}_2\text{O})_2] + 4\text{OH}^- & \rightarrow \text{H}_3\text{C}--\text{CH}--\text{COO}^+ + 2\text{Ag}^+(l) + \text{NH}_3 \\
\text{CH}_3\text{NH}_2 + \text{HC}O_3^- + 2(\text{H}_2\text{IO}_6)^3^- + 5\text{H}_2\text{O} & \\
\end{align*}
$$

The main oxidation products were identified as 2-methyl butyric acid by spot test$^{13}$, ammonia by Nessler’s reagent and the product CO$_2$ was detected.
qualitatively by bubbling N₂ gas through the acidified reaction mixture and passing the liberated gas through tube containing limewater. The nature of the carboxylic acid was confirmed by the IR spectrum (p. 107), which showed a carbonyl (˃C=O) stretch at 1705 cm⁻¹ and O-H stretching of the acid at 2934 cm⁻¹. 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 product does not undergo further oxidation under the present kinetic conditions.

**Reaction orders**

The reaction orders with respect to isoleucine, alkali and periodate concentrations were determined from the slope of log kₐobs versus log (concentration) plots by varying the concentrations of one of the reactant at a time keeping all other concentrations and conditions 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 and the linearity and parallelism of the plots of log (absorbance) versus time up to 80% completion of the reaction as in Fig.IV (ii) (p.108) indicates a reaction order of unity in DPA concentration. This is also confirmed by varying DPA concentration, which did not result in any change in the pseudo-first order rate constants, kᵦobs as in Table IV (ii) (p.109).

**Effect of [isoleucine]**

The effect of isoleucine concentration on the reaction was studied at constant concentrations of alkali, DPA and periodate and constant ionic
IR spectra of 2-methyl butyric acid
First order plots of the oxidation of isoleucine by diperiodatoargentate(III) in aqueous alkaline medium at 25°C

\[ [\text{ISL}] = 5.0 \times 10^{-3}; \ [\text{OH}^-] = 0.60; \ [\text{IO}_4^-] = 1.0 \times 10^{-5}; \ I = 0.80 \text{ / mol dm}^{-3} \]

\[ [\text{DPA}] \times 10^{-5} \text{ (mol dm}^{-3} \text{): (1) 1.0, (2) 2.0, (3) 4.0, (4) 8.0, (5) 10} \]
Table IV (ii)

Effect of DPA and ISL concentrations on diperiodatoargentae(III) oxidation of ISL in alkaline medium at 25°C

\[ [\text{IO}_4^-] = 1.0 \times 10^{-5}; [\text{OH}^-] = 0.60; I = 0.80 /\text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>[DPA] \times 10^5 (mol dm(^{-3}))</th>
<th>[ISL] \times 10^4 (mol dm(^{-3}))</th>
<th>(k_{\text{obs}}\times10^3) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>5.0</td>
<td>5.88</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>5.90</td>
</tr>
<tr>
<td>4.0</td>
<td>5.0</td>
<td>5.85</td>
</tr>
<tr>
<td>8.0</td>
<td>5.0</td>
<td>5.88</td>
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<td>10</td>
<td>5.0</td>
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<td>2.0</td>
<td>3.26</td>
</tr>
<tr>
<td>5.0</td>
<td>4.0</td>
<td>5.37</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>5.88</td>
</tr>
<tr>
<td>5.0</td>
<td>8.0</td>
<td>7.42</td>
</tr>
<tr>
<td>5.0</td>
<td>10</td>
<td>7.66</td>
</tr>
</tbody>
</table>
strength of 0.80 mol dm$^{-3}$ at 25° C. The ISL concentration was varied in the range $1.0 \times 10^{-4}$ to $1.0 \times 10^{-3}$ mol dm$^{-3}$ at 25° C. The $k_{obs}$ values increased with the increase in concentration of ISL and found an apparent less than unit order dependence on ISL concentration. (Fig.IV (iii) (p.111) ($r \geq 0.9842$, $S \leq 0.0009$) and (Table IV (ii) (p.109)).

Effect of [periodate]

The effect of increasing concentration of periodate was studied by varying the periodate concentration from $1.0 \times 10^{-5}$ to $1.0 \times 10^{-4}$ at constant DPA, ISL concentrations and at constant ionic strength. It was observed that the rate constants decreased by increasing $IO_4^-$ ion concentration and the values are reported in Table IV (iii) (p.112). The order with respect to periodate was found to be negative and less than unity (Fig.IV (iv) (p.113))

Effect of [alkali]

The effect of increase in concentration of alkali on the reaction rate was studied at constant concentrations of isoleucine, DPA and periodate and constant ionic strength of 0.80 mol dm$^{-3}$ at 25° C. The alkali concentration was varied in the range of 0.08 to 0.80 mol dm$^{-3}$. The rate constants increased with increasing alkali concentration (Table IV (iii) (p.112)) and the order was found to be less than unity (Fig. IV (iv) (p.113)) ($r \geq 0.9808$, $S \leq 0.00081$).

Effect of ionic strength and initially added products

Ionic strength was varied from 0.20 to 1.0 mol dm$^{-3}$ at constant concentrations of DPA, isoleucine, periodate and alkali. It was found that
Fig. IV (iii)

Order with respect to concentration for the oxidation of isoleucine by diperiodatoargentate(III) in aqueous alkaline medium at 25° C.

\[
[DPA] = 5.0 \times 10^{-5}; [OH^-] = 0.60; [IO_4^-] = 1.0 \times 10^{-5} \text{ and } I = 0.80 / \text{mol dm}^3
\]
Table IV (iii)

Effect of IO₄⁻ ion and OH⁻ ion concentrations on diperiodatoargentae(III) oxidation of isoleucine in alkaline medium at 25⁰C

[DPA]=5.0 x 10⁻⁵; [ISL]=5.0 x 10⁻⁴; I = 0.80 / mol dm⁻³

<table>
<thead>
<tr>
<th>[IO₄⁻] x10⁵ (mol dm⁻³)</th>
<th>[OH⁻] x10⁻⁵ (mol dm⁻³)</th>
<th>k_obs x10³ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.6</td>
<td>6.29</td>
</tr>
<tr>
<td>2.0</td>
<td>0.6</td>
<td>5.23</td>
</tr>
<tr>
<td>4.0</td>
<td>0.6</td>
<td>4.27</td>
</tr>
<tr>
<td>8.0</td>
<td>0.6</td>
<td>3.25</td>
</tr>
<tr>
<td>10</td>
<td>0.6</td>
<td>2.87</td>
</tr>
<tr>
<td>1.0</td>
<td>0.08</td>
<td>2.99</td>
</tr>
<tr>
<td>1.0</td>
<td>0.2</td>
<td>4.41</td>
</tr>
<tr>
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<td>0.4</td>
<td>5.28</td>
</tr>
<tr>
<td>1.0</td>
<td>0.6</td>
<td>5.78</td>
</tr>
<tr>
<td>1.0</td>
<td>0.8</td>
<td>6.25</td>
</tr>
</tbody>
</table>
Fig. IV (iv)

Order with respect to alkali and periodate concentrations for the oxidation of ISL by DPA in aqueous alkaline medium at 25°C

(Conditions as in Table IV (iii) (p.112))
increasing ionic strength had negligible effect on the rate constant. Initially added products, such as Ag (I) and 2-methyl butyric acid had no effect on the rate of reaction.

Effect of solvent polarity

The effect of relative permittivity (D) was studied by varying the t-butanol- water (v/v) content in the reaction mixture with all other conditions being maintained constant. The solvent did not react with the oxidant under the experimental conditions. Decreasing the dielectric constant of the medium had no effect on the rate of the reaction.

Test for free radicals (Polymerization study)

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. Upon diluting the reaction mixture with methanol, precipitate resulted, suggesting the participation of free radicals in the reaction. The blank experiment of either DPA or ISL alone with acrylonitrile did not induce polymerization under the same condition as those with reaction mixture. Initially added acrylonitrile decreases the rate which also indicates the free radical intervention. Such type of results were also observed in in the literature14.

Effect of temperature

The influence of temperature on the k_{obs} values were studied at 25, 30, 35 and 40 °C under varying concentrations of ISL, alkali and periodate, keeping other conditions constant. The rate constants were found to increase
with increase in temperature. The rate constant (k) of the slow step of Scheme 1 were obtained from the slopes and intercepts of 1/k_{obs} versus 1/[ISL] plots at four different temperatures. The values are given in Table IV (iv) (p.116). The results were subjected to least square analysis as in Chapter II (p.45). The activation parameters were obtained from the plot of log k versus 1/T (Fig. IV (v) (p.117)) and are presented in Table IV (iv) (p.116).

**DISCUSSION**

In the later period of 20th century the kinetics of oxidation of various organic and inorganic substrates by Ag(III) species have been studied which may be due to its strong versatile nature of two electron-oxidant. Among the various species of Ag(III), Ag(OH)$_4$\(^{-}\), diperiodatoargentate(III) and ethylenebis(biguanide), (EBS), silver(III) are of maximum attention to the researchers due to their relative stability\textsuperscript{15}. The stability of Ag(OH)$_4$\(^{-}\) is very sensitive towards traces of dissolved oxygen and other impurities in the reaction medium whereupon it had not drawn much attention. However, the other two forms of Ag(III)$^{4-9,16}$ are considerably stable; the DPA is used in highly alkaline medium and EBS is used in highly acidic medium.

It is known that ISL exists in the form of Zwitterion\textsuperscript{17} in aqueous medium. In highly acidic medium, it exists in the protonated form, whereas in highly basic medium they exist as the anionic form according to the following
(a) Effect of temperature on the oxidation of ISL by DPA in aqueous alkaline medium

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>k x 10^2 (s^-1)</th>
<th>log k</th>
<th>1/T x 10^3</th>
<th>Y*_{calc} (log k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.10</td>
<td>-1.957</td>
<td>3.36</td>
<td>-1.965</td>
</tr>
<tr>
<td>303</td>
<td>1.20</td>
<td>-1.921</td>
<td>3.30</td>
<td>-1.912</td>
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<td>308</td>
<td>1.37</td>
<td>-1.863</td>
<td>3.25</td>
<td>-1.861</td>
</tr>
<tr>
<td>313</td>
<td>1.51</td>
<td>-1.808</td>
<td>3.16</td>
<td>-1.812</td>
</tr>
</tbody>
</table>

* Calculated

(b) Activation parameters with respect to the slow step of Scheme 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH^# (kJ mol^-1)</td>
<td>14.9 ± 0.4</td>
</tr>
<tr>
<td>ΔS^# (JK^-1 mol^-1)</td>
<td>-231 ± 22</td>
</tr>
<tr>
<td>ΔG^# (kJ mol^-1)</td>
<td>83.9 ± 5.0</td>
</tr>
<tr>
<td>log A</td>
<td>1.09 ± 0.04</td>
</tr>
</tbody>
</table>
Fig. IV (v)

Effect of temperature on the oxidation of isoleucine by aqueous alkaline diperiodatoargentate(III).

(Conditions as in Table IV (iv) (p. 116))
equilibria. A literature survey\textsuperscript{11} reveals that the water soluble diperiodatoargentate(III) (DPA) has a formula \([\text{Ag(\text{IO}_6)_2}]^{7-}\) with dsp\textsuperscript{2} configuration of square planar structure, similar to diperiodatocopper(III) complex with two bidentate ligands, periodate to form a planar molecule. When the same molecule is used in alkaline medium, it is unlikely to exist as \([\text{Ag(\text{IO}_6)_2}]^{7-}\) as periodate is known to be in various protonated forms\textsuperscript{18} depending on pH of the solution as given in following multiple equilibria (2)-(4).

\[
\begin{align*}
\text{H}_3\text{IO}_6 & \rightleftharpoons \text{H}_4\text{IO}_6^- + \text{H}^+ & (2) \\
\text{H}_4\text{IO}_6^- & \rightleftharpoons \text{H}_2\text{IO}_6^{2-} + \text{H}^+ & (3) \\
\text{H}_3\text{IO}_6^{2-} & \rightleftharpoons \text{H}_2\text{IO}_6^{3-} + \text{H}^+ & (4)
\end{align*}
\]

Periodic acid exists as \(\text{H}_3\text{IO}_6\) in acid medium and as \(\text{H}_4\text{IO}_6^{4-}\) around 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\textsuperscript{3(b)}. However the formation of this species is negligible under conditions employed for kinetic studies. On contrary, the authors\textsuperscript{5,6} in their recent studies have proposed the DPA as \([\text{Ag(\text{HL})}_2]^{x-}\) in which ‘L’ is a periodate with uncertain number of protons and ‘HL’ is a protonated periodate of uncertain number of protons. This can be ruled out by considering the alternative form\textsuperscript{18} of \(\text{IO}_4^-\) at pH > 7 which is in the form \(\text{H}_3\text{IO}_6^{2-}\) or \(\text{H}_2\text{IO}_6^{3-}\). Hence, DPA could be as \([\text{Ag(\text{H}_3\text{IO}_6)_2}]^\cdot\) or \([\text{Ag(\text{H}_2\text{IO}_6)_2}]^{3\cdot}\) in alkaline medium. Therefore, under the present condition, diperiodatoargentate(III), may be
depicted as $[\text{Ag(H}_3\text{IO}_6\text{)}_2]^{-}$. The similar speciation of periodate in alkali was proposed\textsuperscript{19} for diperiodatonicelate(IV).

Since, the rate of reaction was enhanced by increasing OH\textsuperscript{-} ion concentration, added periodate concentration retarded the rate and first order dependency in DPA concentration and less than unit order in ISL concentration, the following mechanism has been proposed by considering ISL in anionic form which explains all other experimental observations.

\[
\begin{align*}
\text{K}_1 & \quad [\text{Ag(H}_3\text{IO}_6\text{)}_2]^{-} + \text{OH}^{-} \rightarrow [\text{Ag(H}_2\text{IO}_6\text{)}(\text{H}_3\text{IO}_6\text{})]^2^{-} + \text{H}_2\text{O} \\
\text{K}_2 & \quad [\text{Ag(H}_2\text{IO}_6\text{)}(\text{H}_3\text{IO}_6\text{})]^2^{-} + 2\text{H}_2\text{O} \rightarrow [\text{Ag(H}_2\text{IO}_6\text{)}(\text{H}_2\text{O})_2]^{-} + \text{H}_3\text{IO}_6^{2-} \\
\text{K}_3 & \quad \text{R}--\text{CH}--\text{COO}^{-} + [\text{Ag(H}_2\text{IO}_6\text{)}(\text{H}_2\text{O})_2] \rightarrow \text{Complex (C)}
\end{align*}
\]

\[
\text{Complex (C)} \overset{k}{\underset{\text{slow}}{\rightarrow}} \text{R}--\text{CH} + \text{Ag(OH)}^{+} + \text{HCO}_3^{-} + 2\text{H}^{+} + \text{H}_3\text{IO}_6^{2-}
\]

\[
\text{R}--\text{CH} + \text{Ag(OH)}^{+} \rightarrow \text{R}--\text{CHO} + \text{Ag(l)} + \text{NH}_3
\]

\[
\text{R}--\text{CHO} + [\text{Ag(H}_2\text{IO}_6\text{)}(\text{H}_2\text{O})_2] \rightarrow \text{R}--\text{COOH} + \text{Ag(l)} + \text{H}_2\text{IO}_6^{3-} + 2\text{H}^{+} + \text{H}_2\text{O}
\]

\[
4\text{H}^{+} + 4\text{OH}^{-} \rightarrow \text{H}_2\text{O}
\]

\textbf{Scheme 1}

where $\text{R} = --\text{CHMeEt}$

In the prior equilibrium step 1, the OH\textsuperscript{-} ion deprotonates the DPA to give a deprotonated diperiodatometricate(III); in the second step displacement of a ligand, periodate takes place to give free periodate which is evidenced by
decrease in the rate with increase in periodate concentration. It may be expected that lower Ag (III) periodate species such as MPA is more important in the reaction than the DPA. The inverse fractional order in H$_2$IO$_6^{2-}$ concentration might also be due to this reason. In the pre rate determining stage, this monoperiodatoargentate(III) (MPA), combines with a molecule of anionic species of ISL to give a complex, which decomposes in a slow step to give the free radical derived from ISL and Ag (II) species. The formation of intermediate Ag(II) species is evidenced by earlier work$^{7-9}$. This free radical of ISL combines with Ag(II) species in a fast step to give an aldehyde, which reacts with another molecule of MPA in a fast step to give the products. Thus, all these results indicate a mechanism of the type as in Scheme 1.

Since Scheme 1 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$^{20}$. The Michaelis-Menten plot also proved the complex formation between oxidant and reductant, which explains less than unit order in ISL concentration. The structures of DPA, MPA and complex could be as shown below:

\[
\begin{align*}
\text{DPA} & \quad \begin{array}{c}
\text{OH} \\
\text{OH} \\
\text{OH} \\
\text{OH} \\
\text{OH}
\end{array} \\
\text{SHown below} & \quad \begin{array}{c}
\text{Ag} \\
\text{O} \\
\text{O}
\end{array} \\
\text{MPA} & \quad \begin{array}{c}
\text{OH} \\
\text{OH} \\
\text{OH} \\
\text{OH} \\
\text{OH}
\end{array} \\
\text{Complex} & \quad \begin{array}{c}
\text{OH} \\
\text{OH} \\
\text{OH} \\
\text{OH} \\
\text{OH}
\end{array}
\end{align*}
\]
The rate law for the Scheme 1 could be derived as follows:

\[
\text{Rate} = \frac{-d[DPA]}{dt} = k \text{ [Complex (C)]}
\]

\[
= k K_3 [\text{ISL}][\text{Ag}(H_2IO_6)(H_2O)_2]
\]

\[
= \frac{k K_2 K_3 [\text{ISL}][\text{Ag}(H_2IO_6)(H_2IO_6)]^2}{[H_3IO_6^{2-}]}
\]

\[
= \frac{kK_2K_3[DPA][OH^-][\text{ISL}]}{[H_3IO_6^{2-}]} \quad (5)
\]

The total [DPA]_T, is given as (where the T and f stands for total and free respectively).

\[
[DPA]_T = [DPA]_T + [\text{Ag}(H_3IO_6)(H_2IO_6)]^2 + [\text{Ag}(H_3IO_6)(H_2O)_2] + \text{Complex (C)}
\]

\[
= [DPA]_T + K_1 [DPA]_T[OH^-] + \frac{K_2[\text{Ag}(H_2IO_6)(H_2IO_6)]^2}{[H_3IO_6^{2-}]} + \frac{K_1K_2K_3[\text{ISL}][DPA]_T[OH^-]}{[H_3IO_6^{2-}]} \quad (6)
\]

Similarly,

\[
[\text{OH}]_T = [\text{OH}]_T + [\text{Ag}(H_3IO_6)(H_2IO_6)]^2 + [\text{Ag}(H_3IO_6)(H_2O)_2]
\]

Therefore, \[
[DPA]_T = \frac{[DPA]_T [H_3IO_6^{2-}]}{[H_3IO_6^{2-}] + K_1 [OH^-] [H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-] \text{ [ISL]}}
\]

Similarly, \[
[\text{OH}]_T = [\text{OH}]_T + [\text{Ag}(H_3IO_6)(H_2IO_6)]^2 + [\text{Ag}(H_3IO_6)(H_2O)_2]
\]

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In view of the low concentrations of DPA and H₃IO₆²⁻ used in the experiment second and third terms may be neglected.

Therefore \([\text{OH}]_T = [\text{OH}]_f\)

Similarly,

\([\text{ISL}]_T = [\text{ISL}]_f + \text{Complex (C)}\)

\[
[\text{ISL}]_T = [\text{ISL}]_f + \frac{K_1K_2K_3[DPA][OH^-][\text{ISL}]}{[H_3IO_6^{2-}]} \tag{7}
\]

In view of the low concentrations of DPA, OH⁻ and H₃IO₆²⁻ used,

\([\text{ISL}]_T = [\text{ISL}]_f\)

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

\[
\text{rate} = -\frac{d[DPA]}{dt} = \frac{kK_1K_2K_3[DPA][\text{ISL}][OH^-]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][\text{ISL}]} \tag{9}
\]

\[
k_{obs} = \frac{kK_1K_2K_3[\text{ISL}][OH^-]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][\text{ISL}]} \tag{10}
\]

The rate law (9) can be rearranged into the following form (10), which is suitable for verification

\[
\frac{1}{k_{obs}} = \frac{[H_3IO_6^{2-}]}{kK_1K_2K_3[OH^-][\text{ISL}]} + \frac{[H_3IO_6^{2-}]}{kK_2K_3[\text{ISL}]} + \frac{1}{kK_3[\text{ISL}]} + \frac{1}{k} \tag{10}
\]

According to equation (10), other conditions being constant, the plots of \(1/k_{obs}\) versus \([H_3IO_6^{2-}]\), \(1/[OH^-]\) and \(1/[\text{ISL}]\) were linear as shown in Fig.IV(vi) (p.123). From the intercepts and slopes of such plots, the reaction constants \(K_1\),
Fig. IV (vi)

Rate law (9) verified in the form of (10) for the oxidation of isoleucine by diperiodatoargentate(III). $\frac{1}{k_{\text{obs}}} \text{ versus } \frac{1}{[\text{ISL}]}$ (■) $\frac{1}{k_{\text{obs}}} \text{ versus } [\text{H}_3\text{IO}_6]^{2-}$ (●) and $\frac{1}{k_{\text{obs}}} \text{ versus } \frac{1}{[\text{OH}^{-}]}$ (♦).

(Conditions as in Table IV (ii) (p.109) and (iii) (p.112))
K₂, K₃ and k were calculated as (1.15 ± 0.03) \times 10⁻¹ dm³ mol⁻¹, (3.1 ± 0.12) \times 10⁻⁴ mol dm⁻³, (3.35 ± 0.10) \times 10² dm³ mol⁻¹, (1.1 ± 0.04) \times 10⁻² s⁻¹ respectively. The values of K₁ and K₂ obtained are also in agreement with earlier literature²¹. The equilibrium constant K₁ is far greater than K₂. This may be attributed to the greater tendency of DPA to undergo deprotonation compared to the formation of hydrolysed species in alkaline medium. The negligible effect of ionic strength and dielectric constant of medium, on the rate of reaction explains qualitatively the involvement of neutral molecule, as seen in Scheme 1.

The thermodynamic quantities for the different equilibrium steps, in Scheme 1 can be evaluated as follows. The ISL, periodate and hydroxide ion concentrations were varied at different temperatures as given in Table IV (ii)p. 109. The plots of 1/k_{obs} versus 1/[ISL] (r ≥ 0.9958, S ≤ 0.0014), 1/k_{obs} versus [H₃IO₆]²⁻ (r ≥ 0.9949, S ≤ 0.0062) and 1/k_{obs} versus 1/[OH⁻] (r ≥ 0.9863, S ≤ 0.0011) should be linear as shown in Fig.IV (vi) (p.123). From the slopes and intercepts, the values of K₁ are calculated at different temperatures. A van’t Hoff plot was made for the variation of K₁ with temperature (i.e., log K₁ versus 1/T (r ≥ 0.9837, S ≤ 0.1101)) and the values of the enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG, were calculated. These values are also given in Table IV (v) (p.125). 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 energy²². In the same manner, K₂ and K₃ values were calculated at different temperatures.
Table IV(v)

(a) Effect of temperature on equilibrium constants $K_1$, $K_2$ and $K_3$ for the oxidation of ISL by diperiodatoargentate (III) in alkaline medium

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_1 \times 10^4$ (dm$^3$ mol$^{-1}$)</th>
<th>$K_2 \times 10^4$ (mol dm$^{-3}$)</th>
<th>$K_3 \times 10^2$ (dm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.15 ± 0.006</td>
<td>3.1 ± 0.15</td>
<td>3.35 ± 0.10</td>
</tr>
<tr>
<td>303</td>
<td>1.38 ± 0.01</td>
<td>2.01 ± 0.12</td>
<td>4.52 ± 0.11</td>
</tr>
<tr>
<td>308</td>
<td>1.80 ± 0.02</td>
<td>1.03 ± 0.10</td>
<td>6.31 ± 0.24</td>
</tr>
<tr>
<td>313</td>
<td>2.09 ± 0.05</td>
<td>0.64 ± 0.03</td>
<td>8.83 ± 0.32</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Quantity</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>32 ± 4</td>
<td>-84 ± 0.8</td>
<td>50 ± 3.1</td>
</tr>
<tr>
<td>$\Delta S$ (J K$^{-1}$ mol$^{-1}$)</td>
<td>89 ± 15</td>
<td>-349 ± 10</td>
<td>217 ± 15</td>
</tr>
<tr>
<td>$\Delta G$ (kJ mol$^{-1}$)</td>
<td>4.7 ± 0.2</td>
<td>22.5 ± 0.8</td>
<td>-16 ± 0.5</td>
</tr>
</tbody>
</table>
The corresponding thermodynamic quantities are given in Table IV (v) p.125.

The values of $\Delta S^\#$ and $\Delta H^\#$ were both favorable for electron transfer processes. The favorable enthalpy was due to release of energy on solution changes in the transition state. The low value of enthalpy of activation obtained might be due to the involvement of prior equilibrium steps\textsuperscript{23a} as given in Scheme 1. The high negative value of $\Delta S^\#$ (-231 JK\textsuperscript{-1}mol\textsuperscript{-1}) suggests that the intermediate complex is more ordered than the reactants\textsuperscript{23b}. The observed modest enthalpy of activation and a higher rate constant for the slow step indicates that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations\textsuperscript{24}.

The activation parameters for the oxidation of some amino acids by DPA are summarized in Table IV (vi) (p.127). The entropy of the activation for the title reaction falls within the observed range. Variation in the rate within a reaction series may be caused by change in the enthalpy or entropy of activation. Changes in the rate are caused by changes in both $\Delta H^\#$ and $\Delta S^\#$, but these quantities vary extensively in a parallel fashion. A plot of $\Delta H^\#$ versus $\Delta S^\#$ is linear according to equation.

$$\Delta H^\# = \beta \Delta S^\# + \text{constant}$$

$\beta$ is called the isokinetic temperature; it has been asserted that apparently linear correlation of $\Delta H^\#$ with $\Delta S^\#$ are sometimes misleading and the evaluation of $\beta$ by means of the above equation lacks statistical validity\textsuperscript{25}. Exner\textsuperscript{26} advocates an
Table IV (vi)

Activation parameters for some amino acids (for iso kinetic temperature)

<table>
<thead>
<tr>
<th>Amino acids</th>
<th>$k_1 \times 10^3$ (s$^{-1}$) at 25°C</th>
<th>$k_2 \times 10^3$ (s$^{-1}$) at 30°C</th>
<th>$\Delta S^#$ (JK$^{-1}$mol$^{-1}$)</th>
<th>$\Delta H^#$ (kJ mol$^{-1}$)</th>
<th>$\Delta G^#$ (kJ mol$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Proline</td>
<td>3.32</td>
<td>3.84</td>
<td>-211</td>
<td>25.0</td>
<td>88.0</td>
<td>(27)</td>
</tr>
<tr>
<td>L-Alanine</td>
<td>3.04</td>
<td>3.66</td>
<td>-212</td>
<td>24.0</td>
<td>87.2</td>
<td>(28)</td>
</tr>
<tr>
<td>L-Leucine</td>
<td>4.29</td>
<td>4.98</td>
<td>-225</td>
<td>19.4</td>
<td>86.4</td>
<td>(29)</td>
</tr>
<tr>
<td>L-Isoleucine</td>
<td>11</td>
<td>12</td>
<td>-231</td>
<td>14.9</td>
<td>83.9</td>
<td>Present work</td>
</tr>
</tbody>
</table>

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alternative method for the treatment of experimental data. If the rates of several reactions in a series have been measured at two temperatures and log \(k_2\) (at \(T_2\)) is linearly related to log \(k_1\) (at \(T_1\)) i.e. log \(k_2 = a + b \log k_1\), he proposes that \(\beta\) can be evaluated from the equation,

\[
\beta = \frac{T_1 T_2 (b-1)}{T_2 b - T_1}
\]

We have calculated the isokinetic temperature as 399.6 K by plotting log \(k_2\) at 303 K versus log \(k_1\) at 298 K \((r \geq 0.9993 \& S \leq 0.008)\) as in Fig. IV (vii) (p.129). The value of \(\beta\) (399.6 K) is higher than experimental temperature (298 K). This indicates that the rate is governed by the enthalpy of activation\(^{30}\). The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow similar mechanism, as previously suggested.

**Importance of Chapter IV**

Among various species of DPA in alkaline medium, monoperiodatoargentate(III) (MPA) is considered as active species for the title reaction. Rate constant 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. Reaction proceeds through intermediate complex, which is more ordered than the reactants. Oxidation presumably occurs via an inner-sphere mechanism. Calculated isokinetic temperature is 399.6 K, which indicates that the rate is governed by the enthalpy of activation. The overall mechanistic sequence described here is consistent with product studies, mechanistic and kinetic studies.
Fig. IV (vii)

Plot of $\log k_2$ at $30^\circ C$ versus $\log k_1$ at $25^\circ C$

(Conditions as given in Table IV (vi) (p. 127))

1. L-alanine; 2. L-proline; 3. L-leucine; 4. L-Isoleucine
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