2.1. INTRODUCTION

Ornithine (OMH) is a non-protein amino acid\textsuperscript{1}, derived from the breakdown of arginine during the citric acid cycle. It helps to build muscle and reduce body fat, especially when combined with the amino acids, arginine and carnitine. Ornithine helps to remove toxic ammonia from the liver, and reduce the effects of cirrhosis of the liver and disorders associated with liver malfunction. Ornithine is the major source of polyamines in mammalian physiological systems\textsuperscript{2}. Increased urinary polyamine levels have been demonstrated in humans with varied types of cancers. The metabolism of DL-[1-\textsuperscript{14}C]ornithine monohydrochloride in rats with either Walker 256 carcinoma or chemically induced methylcholanthrene tumors was studied, whose attempts showed to develop ornithine as a biological marker of cancer\textsuperscript{3,4}.

Transition metals in their higher oxidation states can generally be stabilized by chelation with suitable polydentate ligands. These metal chelates such as diperiodatocuprate(III)\textsuperscript{5}, diperiodatoargentate(III)\textsuperscript{6} and diperiodatonickelate(IV)\textsuperscript{7} are good oxidants in a medium with an appropriate pH value. Diperiodatocuprate(III) (DPC) is a versatile one-electron oxidant and the oxidation study of DPC is scanty in view of its limited solubility and stability in aqueous medium. Its use as an analytical reagent is now well recognized\textsuperscript{8}. Copper complexes have a major role in oxidation chemistry due to their abundance and relevance in biological chemistry\textsuperscript{9-11}. Copper(III) is involved in many biological electron transfer reactions\textsuperscript{12}. When Copper(III)
periodate complex is the oxidant and multiple equilibria between different copper(III) species are involved, it would be interesting to know which of the species is the active oxidant.

Transition metals are known to catalyze many oxidation-reduction reactions since they involve multiple oxidation states. In recent years the use of transition metal ions such as ruthenium, osmium, palladium, manganese, chromium, iridium, either alone or as binary mixtures, as catalysts in various redox processes have attracted considerable interest\textsuperscript{13}. Ru(III) acts as catalyst in the oxidation of many organic and inorganic substrates\textsuperscript{14, 15}. Although the mechanism of catalysis depends on the nature of the substrate, oxidant and experimental conditions, it has been shown\textsuperscript{16} that metal ions act as catalysts by one of these different paths such as the formation of complexes with reactants or oxidation of the substrate itself or through the formation of free radicals. Ruthenium(III) catalysis in redox reactions involves different degrees of complexity, due to the formation of different intermediate complexes and different oxidation states of ruthenium.

Literature survey revealed that no attention has been paid towards the oxidation of DL-ornithine monohydrochloride [(\(\pm\)-2, 5-Diaminopentanoic acid monohydrochloride] with any oxidant from the kinetic and mechanistic point of view. It is also observed that, no one has examined the role of any catalyst on the oxidation of this ubiquitous amino acid. We have observed that ruthenium(III) in micro amounts catalyzes the oxidation of OMH by DPC in alkaline medium. Such studies are of much significance in understanding the
mechanistic profile of ornithine in redox reactions and provide an insight into the interaction of metal ions with the substrate and its mode of action in biological systems. Also to know the active species of Cu(III) and catalyst Ru(III) and to resolve the complexity of the reaction, a detailed study of the title reaction becomes important. Hence, the present investigation in this chapter is aimed at checking the reactivity of OMH towards DPC in both uncatalyzed and ruthenium(III) catalyzed reactions and to arrive at the plausible mechanisms.

2.2. EXPERIMENTAL

2.2.1. Chemicals and solutions

All reagents were of analytical reagent grade and millipore water was used throughout the work. A solution of DL-ornithine monohydrochloride (HiMedia Laboratories) was prepared by dissolving an appropriate amount of recrystallized sample in millipore water. The purity of OMH was checked by comparing its IR spectrum with literature data and with its m.p. 232-234°C. The required concentration of OMH was obtained from its stock solution. A standard stock solution of Ru(III) was prepared by dissolving RuCl₃ (s d fine-chem.) in 0.20 mol dm⁻³ HCl. The concentration was determined by EDTA titration.

The copper(III) periodate complex was prepared and standardized by a standard procedure. The UV-vis spectrum with maximum absorption at 415 nm verified the existence of copper(III) complex. The ionic strength was
maintained by adding KNO$_3$ (AR) solution and the pH value was regulated with KOH (s d fine-chem) solution. A stock solution of IO$_4^-$ was prepared by dissolving a known weight of KIO$_4$ (Riedel-de-Hean) in hot water and used after keeping for 24 h to attain the equilibrium. Its concentration was ascertained iodometrically\textsuperscript{22}, at neutral pH maintained using phosphate buffer. The pH of the medium in the solution was measured by ELICO (LI120) pH meter. Solutions of OMH and DPC were always freshly prepared before use.

2.2.2. Instruments used

(i) For kinetic measurements, a Peltier Accessory (temperature control) attached Varian CARY 50 Bio UV-vis Spectrophotometer (Varian, Victoria-3170, Australia) connected to a rapid kinetic accessory (HI-TECH SFA-12) was used.

(ii) For product analysis, a QP-2010S Shimadzu gas chromatograph mass spectrometer, Nicolet 5700-FT-IR spectrometer (Thermo, U.S.A.), 300 MHz $^1$H NMR spectrophotometer (Bruker, Switzerland) were used and for pH measurement, an Elico pH meter model LI120 was used.

2.2.3. Kinetic measurements

Since the initial rate was too fast to be monitored by usual methods in the catalyzed reaction, the kinetic measurements were performed on a Varian CARY 50 Bio UV-vis Spectrophotometer attached to a rapid kinetic accessory (HI-TECH SFA-12). The oxidation of OMH by DPC was followed under pseudo-first order conditions, where [OMH] > [DPC] in both uncatalyzed and
catalyzed reactions at 25.0 ± 0.1°C, unless otherwise specified. In the absence of catalyst, the reaction was initiated by mixing DPC with the OMH solution which also contained required concentrations of KNO₃, KOH, and KIO₄. The reaction in the presence of catalyst Ru(III) was initiated by mixing DPC with the OMH solution which also contained the required concentration of KNO₃, KOH, KIO₄, and Ru(III) catalyst. The progress of the reaction was monitored spectrophotometrically at 415 nm. The application of Beer’s law to DPC at 415 nm was verified and molar absorbency index, ‘ε’ was found to be 6231 ± 100 dm³ mol⁻¹ cm⁻¹ as shown in Figure II (i) (p. 30), in both uncatalyzed and catalyzed reaction. It was verified that there was almost no interference from other species in the reaction mixture at this wavelength. The reaction was followed to more than 75% completion of reaction. An example run is given in Table II (i) (p. 31). The pseudo-first order rate constants, (kᵢ or kᵢₓ), in both the cases were determined from the log( absorbance) versus time plots. The plots were linear upto 75% completion (Fig. II (ii) (p. 32) for uncatalyzed as an example) of reaction under the range of [OH⁻] used (r ≥ 0.9549, S ≤ 0.016). The rate constants were reproducible to within ± 5%. The spectral changes during the chemical reaction for the standard condition at 298 K are shown in Figure II (iii) (p. 33) (for uncatalyzed as an example). It is evident from the figure that the concentration of DPC decreases at 415 nm.

During the kinetics, a constant concentration viz. 1.0 x 10⁻⁵ mol dm⁻³ of KIO₄ was used throughout the study unless otherwise stated. Since excess of
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Figure II (i)

Verification of Beer’s law for DPC in aqueous alkaline medium at 298 K

\[ [\text{OH}^-] = 0.08 \text{ and } I = 0.20 / \text{mol dm}^{-3} \]
**Table II (i)**

Example run for the oxidation of DL-ornithine by alkaline diperiodatocuprate(III) at 298 K. \([\text{DPC}] = 5.0 \times 10^{-5}; \ [\text{OMH}] = 5.0 \times 10^{-4}; \ [\text{OH}^-] = 0.08; \ [\text{IO}_4^-] = 1.0 \times 10^{-5}\) and \(I = 0.20\ /\ \text{mol dm}^{-3}\)

<table>
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<tr>
<th>Time (min)</th>
<th>Absorbance (415 nm)</th>
<th>([\text{DPC}] \times 10^5) (mol dm(^{-3}))</th>
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</thead>
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<td>0.95</td>
</tr>
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</table>
Figure II (ii)

First order plots for the oxidation of DL-ornithine by alkaline diperiodatocuprate(III) at 298 K. \([\text{DPC}] \times 10^5 = (1) 1.0; (2) 3.0; (3) 5.0; (4) 8.0\) and (5) 10.0 / mol dm\(^{-3}\)

(Conditions as in Table II (ii) (p. 38))
Figure II (iii)

UV-vis. spectral changes during the oxidation of DL-ornithine by alkaline diperiodatocuprate(III) at 298 K. [DPC] = 5.0 \times 10^{-5}; [OMH] = 5.0 \times 10^{-4}; [OH^-] = 0.08 and I = 0.20 / mol dm^{-3} with scanning time of: (1) 1.0, (2) 2.0, (3) 3.0, (4) 4.0, (5) 5.0 and (6) 6.0 min
periodate is present in DPC, the possibility of oxidation of OMH by periodate in alkaline medium at 25ºC was verified and found that there was no significant interference due to KIO₄ under experimental conditions. The total concentrations of periodate and OH⁻ was calculated by considering the amount present in DPC solution and that additionally added.

Kinetic runs were also carried out in N₂ atmosphere in order to understand the effect of dissolved oxygen on the rate of the reaction. No significant difference in the results was obtained under a N₂ 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. The added carbonate had no effect on the reaction rates. Regression analysis of experimental data to obtain regression coefficient r and the standard deviation S, of points from the regression line was performed with the Microsoft office Excel 2003 program.

2.3. RESULTS

2.3.1. Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPC to OMH in presence of constant amount of OH⁻, KIO₄, and KNO₃ in uncatalysed reaction and a constant amount of Ru(III) in catalysed reaction were kept for 6 hrs in a closed vessel under nitrogen atmosphere. The remaining concentration of DPC was assayed by measuring the absorbance at 415 nm. The results indicated 1:4 stoichiometry for both the reactions as given in equation (1).
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After completion of reaction, the reaction mixture was acidified, concentrated and extracted with ether. The reaction product was further recrystallized from aqueous alcohol. The main reaction product was identified as 4-aminobutyric acid. This was the only organic product obtained in the oxidation which was confirmed by a single spot on thin layer chromatography and was characterized by FT-IR, GC-MS and $^1$H NMR spectral studies.

The IR spectroscopy showed a $>\text{C} = \text{O}$ stretching of carboxylic acid at 1708 cm$^{-1}$ indicating the presence of acidic C=O group, O-H stretching of carboxylic acid at 2848 cm$^{-1}$ indicating the presence of acidic –OH group, and also N-H stretching at 3427 cm$^{-1}$ indicating the presence of -NH$_2$ group in 4-aminobutyric acid. GC-MS data was obtained on a QP-2010S Shimadzu gas chromatograph mass spectrometer. The mass spectral data showed a molecular ion peak at 103 m/z confirming the presence of 4-aminobutyric acid (Fig. II (iv) (p. 36)). All other peaks observed in GC-MS can be interpreted in accordance with the observed structure of 4-aminobutyric acid. It was also subjected to $^1$H NMR spectrum (CDCl$_3$), two triplet at 2.31 $\delta$ (a) and 2.69 $\delta$ (c) and a multiplet at 1.84 $\delta$ (due to (b) CH$_2$), 5.44 $\delta$ (s, 2H due to -NH$_2$) and 11.6 $\delta$ (s, H due to –COOH). -NH$_2$ and –OH disappeared on D$_2$O exchange.
Figure II (iv)

Mass spectrum of reaction product, 4-aminobutyric acid with its molecular ion peak at 103 m/z.
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The byproducts were identified as ammonia by Nessler’s reagent\(^1\) and CO\(_2\) was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through the tube containing limewater. Finally copper(II) was identified by UV-vis spectra.

2.3.2. Reaction orders

As the diperiodatocuprate(III) oxidation of DL-ornithine in alkaline medium proceeds with a measurable rate in the absence of Ru(III), the catalysed reaction is understood to occur in parallel paths with contribution 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 (\(k_U\) or \(k_C\)) versus respective concentration of OMH, IO\(_4^-\), OH\(^-\) and catalyst Ru(III) except for [DPC], in turn while keeping others constant.

2.3.3. Effect of varying [DPC]

The oxidant [DPC] was varied in the range of 1.0 \(\times\) 10\(^{-5}\) to 1.0 \(\times\) 10\(^{-4}\) at fixed [OMH], [KOH] and [KIO\(_4\)] and a constant ionic strength of 0.20 mol dm\(^{-3}\) in uncatalysed and with constant concentration of Ru(III) in catalysed reaction. The fairly constant pseudo-first order rate constants, \(k_U\) (Table II (ii) (p. 38)) and \(k_C\) (Table II (iii) (p. 39)) indicate that the order with respect to [DPC] was unity. This was also confirmed by linearity of plots of log (absorbance) versus time (Fig. II (ii) (p. 32)).
Table II (ii)

Effect of variation of DPC and OMH concentrations on the oxidation of DL-ornithine by diperiodatocuprate (III) in aqueous alkaline medium at 298 K.

$[\text{OH}^-] = 0.08$; $[\text{IO}_4^-] = 1.0 \times 10^{-5}$; $I = 0.20$ / mol dm$^{-3}$

<table>
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<th>[DPC] $\times 10^5$ (mol dm$^{-3}$)</th>
<th>[OMH] $\times 10^4$ (mol dm$^{-3}$)</th>
<th>$k_U \times 10^3$(s$^{-1}$) Found</th>
<th>Calculated</th>
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<tr>
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Table II (iii)

Effect of variation of DPC and OMH concentrations on the ruthenium(III) catalysed oxidation of DL-ornithine by diperiodatocuprate (III) in aqueous alkaline medium at 298 K. [OH⁻] = 0.08; [Ru(III)] = 8.0 x 10⁻⁷; [IO₄⁻] = 1.0 x 10⁻⁵; I = 0.20 / mol dm⁻³

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<th>[DPC] x 10⁵ (mol dm⁻³)</th>
<th>[OMH] x 10⁴ (mol dm⁻³)</th>
<th>kₜ x 10² (s⁻¹)</th>
<th>kₜ⁺ x 10³ (s⁻¹)</th>
<th>kC x 10²(s⁻¹)</th>
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<td>2.06</td>
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2.3.4. Effect of varying [DL-ornithine]

The effect of OMH was studied for both the cases in the range of $6.0 \times 10^{-5}$ to $6.0 \times 10^{-4}$ mol dm$^{-3}$ at constant concentrations of DPC, OH$^-$, IO$_4^-$ and a constant ionic strength of 0.20 mol dm$^{-3}$ in uncatalysed and with constant concentration of Ru(III) in catalysed reaction. In the case of uncatalysed reaction as well as catalysed reaction, at constant temperature, the $k_U$ (Table II (ii) (p. 38)) and $k_C$ (Table II (iii) (p. 39)) values increased with increase in [OMH]. The order with respect to [OMH] was less than unity (Fig. II (v a) (p. 41)) ($r \geq 0.9810$, $S \leq 0.009$) (Fig. II (v b) (p. 41)) ($r \geq 0.9855$, $S \leq 0.006$). This was also confirmed by the plots of $k_U$ versus [OMH]$^{0.56}$ and $k_C$ versus [OMH]$^{0.61}$ which were linear rather than the direct plot of $k_U$ versus [OMH] and $k_C$ versus [OMH] (Fig. II (vi a and b) (p. 42))

2.3.5. Effect of varying [alkali]

The effect of alkali concentration was studied for both the cases in the range of 0.02 to 0.20 mol dm$^{-3}$ at constant concentrations of DPC, OMH, IO$_4^-$ and ionic strength in uncatalysed and with constant concentration of Ru(III) in catalysed reaction. The rate constants increased with increase in [alkali] (Table II (iv) (p. 43)) and (Table II (v) (p. 44)). The order was found to be less than unity i.e., 0.41 in uncatalysed (Fig. II (vii a) (p. 45)) ($r \geq 0.972$, $S \leq 0.008$) and 0.39 in Ru(III) catalysed reaction (Fig. II (vii b) (p. 45)) ($r \geq 0.96$, $S \leq 0.007$)

2.3.6. Effect of varying [periodate]

The effect of periodate concentration was studied for both the cases in
Figure II (v)

(a) Order with respect to OMH concentration on the oxidation of DL-ornithine by DPC in aqueous alkaline medium at 298 K

(Conditions as in Table II (ii) (p. 38))

(b) Order with respect to OMH concentration on the oxidation of Ru(III) catalysed oxidation of DL-ornithine by DPC in aqueous alkaline medium at 298 K

(Conditions as in Table II (iii) (p. 39))
Figure II (vi)

(a) Plot of $k_U$ versus $[\text{OMH}]^{0.56}$ and $k_U$ versus $[\text{OMH}]$

![Graph showing plots of $k_U$ versus $[\text{OMH}]^{0.56}$ and $k_U$ versus $[\text{OMH}]$.]

(b) Plot of $k_C$ versus $[\text{OMH}]^{0.61}$ and $k_C$ versus $[\text{OMH}]$

![Graph showing plots of $k_C$ versus $[\text{OMH}]^{0.61}$ and $k_C$ versus $[\text{OMH}]$.]
Table II (iv)

Effect of variation of OH$^-$ and IO$_4^-$ concentrations on the oxidation of DL-ornithine by diperiodatocuprate (III) in aqueous alkaline medium at 298 K. 

$\text{[DPC]} = 5.0 \times 10^{-5}; \text{[OMH]} = 5.0 \times 10^{-4}; \text{I} = 0.20 \text{ / mol dm}^{-3}$

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<thead>
<tr>
<th>[OH$^-$] $\times 10^1$ (mol dm$^{-3}$)</th>
<th>[IO$_4^-$] $\times 10^5$ (mol dm$^{-3}$)</th>
<th>$k_U \times 10^3$ (s$^{-1}$)</th>
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Table II (v)

Effect of variation of OH\(^-\), IO\(_4\)\(^-\) and Ru(III) concentrations on the ruthenium(III) catalysed oxidation of DL-ornithine by diperiodatocuprate (III) in aqueous alkaline medium at 298 K. [DPC] = 5.0 \times 10^{-5}; [OMH] = 5.0 \times 10^{-4}; I = 0.20 / mol dm\(^{-3}\)

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<tr>
<th>[OH(^-)]×10(^1) (mol dm(^{-3}))</th>
<th>[IO(_4)(^-)]×10(^5) (mol dm(^{-3}))</th>
<th>[Ru(III)]×10(^7) (mol dm(^{-3}))</th>
<th>k(_T)×10(^2) (s(^{-1}))</th>
<th>k(_U)×10(^3) (s(^{-1}))</th>
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<td>8.0</td>
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<td>2.88</td>
<td>1.87</td>
<td>1.84</td>
</tr>
<tr>
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<td>8.0</td>
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<td>2.29</td>
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<td>3.80</td>
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<td>2.21</td>
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<td>0.8</td>
<td>8.0</td>
<td>2.40</td>
<td>3.30</td>
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<td>1.98</td>
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<tr>
<td>0.8</td>
<td>1.0</td>
<td>8.0</td>
<td>2.16</td>
<td>2.88</td>
<td>1.87</td>
<td>1.84</td>
</tr>
<tr>
<td>0.8</td>
<td>3.0</td>
<td>8.0</td>
<td>1.32</td>
<td>1.85</td>
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<td>1.11</td>
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<td>0.80</td>
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<td>2.88</td>
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<td>1.43</td>
<td>2.88</td>
<td>1.14</td>
<td>1.15</td>
</tr>
<tr>
<td>0.8</td>
<td>1.0</td>
<td>8.0</td>
<td>2.16</td>
<td>2.88</td>
<td>1.87</td>
<td>1.84</td>
</tr>
<tr>
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<td>10.0</td>
<td>2.61</td>
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<tr>
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<td>4.80</td>
<td>2.88</td>
<td>4.51</td>
<td>4.62</td>
</tr>
</tbody>
</table>
(a) Order with respect to OH\(^-\) concentration on the oxidation of DL-ornithine by DPC in aqueous alkaline medium at 298 K

(Conditions as in Table II (iv) (p. 43))

(b) Order with respect to OH\(^-\) concentration on the oxidation of Ru(III) catalysed oxidation of DL-ornithine by DPC in aqueous alkaline medium at 298 K

(Conditions as in Table II (v) (p. 44))
the range of $5.0 \times 10^{-6}$ to $5.0 \times 10^{-5}$ mol dm$^{-3}$ at constant concentrations of DPC, OMH, OH$^-$ and ionic strength in uncatalysed and with constant concentration of Ru(III) in catalysed reaction. The experimental results indicated that the $k_U$ and $k_C$ values decreased with increase in [IO$_4^-$] (Table II (iv) (p. 43)) and (Table II (v) (p. 44)). The order with respect to IO$_4^-$ was negative fractional i.e., -0.45 in uncatalysed (Fig. II (viii a) (p. 47)) ($r \geq 0.9898$, $S \leq 0.006$) and -0.44 in Ru(III) catalysed reaction (Fig. II (viii b) (p. 47)) ($r \geq 0.9899$, $S \leq 0.004$)

2.3.7. Effect of varying [Ru(III)]

The Ru(III) concentration was varied from $2.0 \times 10^{-7}$ to $2.0 \times 10^{-6}$ mol dm$^{-3}$ range, at constant concentration of DPC, OMH, OH$^-$ and ionic strength. The rate constants increased with increase in [Ru(III)] (Table II (v) (p. 44)). The order in [Ru(III)] was found to be unity from the linearity of the plot of $k_C$ versus [Ru(III)] (Fig. II (ix) (p. 48)) ($r \geq 0.9992$, $S \leq 0.006$)

2.3.8. Effect of varying ionic strength and dielectric constant

The effect of ionic strength (I) was studied by varying [KNO$_3$]. It was found that there was no significant effect of ionic strength on the rate of reaction in both the cases of uncatalyzed and catalyzed reactions.

The dielectric constant of the medium (D) was studied varying the t-butanol-water (v/v) content in the reaction mixture with all the other conditions maintained constant. Attempts to measure the relative permittivity were not successful. However, they were computed from the values of pure liquids$^{23}$. The dielectric constants of the reaction medium at various composition of t-
Figure II (viii)

(a) Order with respect to IO₄⁻ ion concentration on the oxidation of DL-ornithine by DPC in aqueous alkaline medium at 298 K

(Conditions as in Table II (iv) (p. 43))

(b) Order with respect to IO₄⁻ ion concentration on the oxidation of Ru(III) catalysed oxidation of DL-ornithine by DPC in aqueous alkaline medium at 298 K

(Conditions as in Table II (v) (p. 44))
Figure II (ix)

Order with respect to Ru(III) concentration on the oxidation of Ru(III) catalysed oxidation of DL-ornithine by DPC in aqueous alkaline medium at 298 K

(Conditions as in Table II (v) (p. 44))
butyl alcohol-water (v/v) were calculated by the following equation,

\[ D = V_1 D_1 + V_2 D_2 \]

Where, \( V_1 \) and \( V_2 \) are volume fractions and \( D_1 \) and \( D_2 \) are dielectric constants of water and t-butyl alcohol as 78.5 and 10.9 at 25°C respectively.

For example at 10% t-butyl alcohol in water,

\[ D = 78.5 \times \frac{90}{100} + 10.9 \times \frac{10}{100} = 71.74 \]

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 reaction in both the cases of uncatalyzed and catalyzed reactions.

2.3.9. Effect of initially added products

Initially added products, Copper(II) (\( \text{CuSO}_4 \)) and 4-aminobutyric acid did not have any significant effect on the rate of reaction (for both the cases).

Thus, from the observed experimental results-

The rate law for uncatalyzed reaction is given as:

\[ \text{Rate} = k_U [\text{DPC}]^{1.0} [\text{OMH}]^{0.56} [\text{OH}^-]^{0.41} [\text{IO}_4^-]^{-0.45} \]

The rate law for Ru(III) catalyzed reaction is given as:

\[ \text{Rate} = k_C [\text{DPC}]^{1.0} [\text{OMH}]^{0.61} [\text{OH}^-]^{0.39} [\text{Ru(III)}]^{1.0} [\text{IO}_4^-]^{-0.44} \]

2.3.10. Polymerization study

For both uncatalyzed and catalyzed reactions the possibility of free radicals was detected as follows: the reaction mixture, to which a known quantity of acrylonitrile (scavenger) had been added initially, was kept for 2 h
in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the intervention of free radicals in the reactions. The blank experiments of either DPC or DL-ornithine alone with acrylonitrile did not induce any polymerization under the same condition as those induced for the reaction mixture. Also, initially added acrylonitrile decreases the rate of reaction indicating free radical intervention, which is the case in earlier work\textsuperscript{24}.

### 2.3.11. Effect of temperature

The activation parameters for the reaction were studied by using linear regression analysis (also known as the method of least squares). In generalized notation, the formula for a straight line is \( y = ax + b \). The most tractable form of linear regression analysis assumes that values of the independent variables ‘\( x \)’ are known without error and that experimental error is manifested only in values of the dependent variable ‘\( y \)’. Most sets of kinetic data approximate this situation, in as much as times of observation are more accurately measurable than the chemical or physical quantities related to reactant concentrations. The straight line selected by common linear regression analysis is that which minimizes the sum of the squares of the derivatives of the ‘\( y \)’ variable from the line. The slope ‘\( a \)’ and the intercept ‘\( b \)’ parameters for the above equation can be calculated by linear regression analysis by any of several mathematically equivalent but different looking experiments. Most familiar are:

\[
\text{Slope: } a = \frac{n\sum x y - \sum x \sum y}{n\sum x^2 - (\sum x)^2}
\]
The activation energy of the reaction was calculated by,
\[ E_a = -2.303 \times R \times \text{slope} \]

The Arrhenius factor ‘A’ was calculated by,
\[ \log A = \log k + \frac{E_a}{2.303RT} \]

The entropy of activation was calculated by,
\[ \frac{\Delta S^\#}{4.576} = \log k - 10.753 - \log T + \frac{E_a}{4.576T} \]

where, k is in sec\(^{-1}\), temperature in Kelvin and \(E_a\) in calories.

The enthalpy of activation was calculated by,
\[ \Delta H^\# = E_a - RT \]

and, the free energy of activation was calculated by,
\[ \Delta G^\# = \Delta H^\# - T \Delta S^\# \]

The kinetics was studied at four different temperatures viz. 288 K, 298 K, 308 K and 318 K under varying concentrations of DL-ornithine, alkali and periodate, keeping other conditions constant for uncatalyzed reaction. The rate constants, (\(k_i\)), of the slow step of Scheme 1 were obtained from the slopes and the intercepts of the plots of \(1/k_U\) versus \(1/[OMH]\) at four different temperatures. The values are given in Table II (vi a) (p. 52). The energy of activation for the rate determining step was obtained by the least-squares...
Table II (vi)

(a) Effect of temperature on slow step of the mechanism (Scheme 1) for the oxidation of OMH by diperiodatocuprate(III) in aqueous alkaline medium

<table>
<thead>
<tr>
<th>T (K)</th>
<th>k₁ × 10^2 (s⁻¹)</th>
<th>log k₁ (Y)</th>
<th>1/T × 10³ (X)</th>
<th>Y*_{calc} (log k₁)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>0.23</td>
<td>-2.6241</td>
<td>3.47</td>
<td>-2.6337</td>
</tr>
<tr>
<td>298</td>
<td>0.47</td>
<td>-2.3231</td>
<td>3.35</td>
<td>-2.3127</td>
</tr>
<tr>
<td>308</td>
<td>0.95</td>
<td>-2.0221</td>
<td>3.24</td>
<td>-2.0125</td>
</tr>
<tr>
<td>318</td>
<td>1.90</td>
<td>-1.7210</td>
<td>3.14</td>
<td>-1.7312</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>Eₐ (kJ mol⁻¹)</td>
<td>52.7 ± 2.0</td>
</tr>
<tr>
<td>△H# (kJ mol⁻¹)</td>
<td>50.2 ± 2.0</td>
</tr>
<tr>
<td>△S# (JK⁻¹ mol⁻¹)</td>
<td>-121 ± 5</td>
</tr>
<tr>
<td>△G# (kJ mol⁻¹)</td>
<td>86 ± 4</td>
</tr>
<tr>
<td>log A</td>
<td>6.9 ± 0.2</td>
</tr>
</tbody>
</table>
method of plot of log \( k_1(Y^* \text{calc}) \) versus \( 1/T \) as shown in Figure II (x) (p. 54) (r \( \geq 0.9998, S \leq 0.005 \)) and other activation parameters calculated are presented in Table II (vi b) (p. 52).

For catalyzed reaction the influence of temperature on the rate of reaction was studied at 288 K, 298 K, 308 K and 318 K. The rate constants, \( (k_2) \), of the slow step of Scheme 2 were obtained from the slopes and the intercepts of the plots of \([\text{Ru(III)}]/k_C \) versus \( 1/\text{[OMH]} \) at four different temperatures (Table II (vii a) (p. 55)). The energy of activation for the rate determining step was obtained by the least-squares method of plot of log \( k_2(\text{Y}^* \text{calc}) \) versus \( 1/T \) as shown in Figure II (xi) (p. 56) (r \( \geq 0.9999, S \leq 0.006 \)) and other activation parameters calculated for the reaction are presented in Table II (vii b) (p. 55).

2.3.12. Catalytic activity

It has been pointed out by Moelwyn-Hughes\(^2\) that in the presence of catalyst, the uncatalyzed and catalyzed reactions proceed simultaneously, so that,

\[
k_T = k_U + K_C[Ru(III)]^x
\]

Here \( k_T \), the total rate constant; \( k_U \), the pseudo-first order rate constant for uncatalyzed; \( K_C \), the catalytic constant and ‘x’ the order of the reaction with respect to Ru(III). In the present investigations; x values for the standard run were found to be unity.
Figure II (x)

Effect of temperature on the oxidation of OMH by DPC in aqueous alkaline medium

(Conditions as in Table II (vi a) (p. 52))
Table II (vii)

(a) Effect of temperature on slow step of the mechanism (Scheme 2) of Ru(III) catalysed oxidation of DL-ornithine by DPC in aqueous alkaline medium

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( k_2 \times 10^5 ) (dm³ mol⁻¹ s⁻¹)</th>
<th>log ( k_2 ) (Y)</th>
<th>( 1/T \times 10^3 ) (X)</th>
<th>( Y^\text{calc} ) (log ( k_2 ))</th>
</tr>
</thead>
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<tr>
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<td>3.47</td>
<td>4.3356</td>
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<tr>
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</tr>
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<td>0.73</td>
<td>4.8684</td>
<td>3.24</td>
<td>4.8766</td>
</tr>
<tr>
<td>318</td>
<td>1.35</td>
<td>5.1318</td>
<td>3.14</td>
<td>5.1216</td>
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</table>

*Calculated

(b) Activation parameters with respect to the slow step of Scheme 2

<table>
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<th>Parameters</th>
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<tbody>
<tr>
<td>( E_a ) (kJ mol⁻¹)</td>
<td>( 46 \pm 2 )</td>
</tr>
<tr>
<td>( \Delta H^\circ ) (kJ mol⁻¹)</td>
<td>( 43.4 \pm 0.5 )</td>
</tr>
<tr>
<td>( \Delta S^\circ ) (JK⁻¹ mol⁻¹)</td>
<td>( -11.5 \pm 1.0 )</td>
</tr>
<tr>
<td>( \Delta G^\circ ) (kJ mol⁻¹)</td>
<td>( 47 \pm 5 )</td>
</tr>
<tr>
<td>log A</td>
<td>( 12.6 \pm 0.2 )</td>
</tr>
</tbody>
</table>
Effect of temperature on the oxidation of Ru(III) catalysed oxidation of DL-ornithine by DPC in aqueous alkaline medium

(Conditions as in Table II (vii a) (p. 55))
Then, the value of $K_C$ is calculated using the equation,

$$K_C = \frac{k_T - k_U}{[\text{Ru (III)}]^x} = \frac{k_C}{[\text{Ru (III)}]} \quad \text{(where, } k_T - k_U = k_C)$$ \hspace{1cm} (3)

The values of $K_C$ were evaluated for Ru(III) catalyst at different temperatures and were found to vary at different 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 catalytic constant were computed. These results are summarized in Table II (viii) (p. 58). The value of $K_C$ is $2.34 \times 10^4$ at 298 K.

2.4. DISCUSSION

The water-soluble copper(III) periodate complex is reported to be \([\text{Cu(HIO}_6\text{)}_2(\text{OH})_2]^-\). However, in an aqueous alkaline medium and at a high pH range as employed in the study, periodate is unlikely to exist as HIO$_6^4-$ (as present in the complex) as is evident from its involvement in the multiple equilibria depending on the pH of the solution.

$$H_3\text{IO}_6 \quad \leftrightarrow \quad H_4\text{IO}_6^- + H^+ \quad \hspace{1cm} (4)$$

$$H_4\text{IO}_6^- \quad \leftrightarrow \quad H_3\text{IO}_6^{2-} + H^+ \quad \hspace{1cm} (5)$$

$$H_3\text{IO}_6^{2-} \quad \leftrightarrow \quad H_2\text{IO}_6^{3-} + H^+ \quad \hspace{1cm} (6)$$

Periodic acid exists as $H_3\text{IO}_6$ in an acid medium and as $H_4\text{IO}_6^-$ around pH 7. Thus, under the conditions employed in alkaline medium, the main species are expected to be $H_3\text{IO}_6^{2-}$ and $H_2\text{IO}_6^{3-}$. At higher concentrations, periodate also tends to dimerise. However, formation of this species is
Table II (viii)

Values of catalytic constant ($K_C$) at different temperatures and activation parameters calculated using $K_C$ values. $[\text{DPC}] = 5.0 \times 10^{-5}$, $[\text{OMH}] = 5.0 \times 10^{-4}$, $[\text{OH}^-] = 0.08$, $[\text{Ru(III)}] = 8.0 \times 10^{-7}$, $[\text{IO}_4^-] = 1.0 \times 10^{-5}$, $I = 0.20 / \text{mol dm}^{-3}$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_C \times 10^{-4}$</th>
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<tbody>
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<td>288</td>
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</tr>
<tr>
<td>298</td>
<td>2.34</td>
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<td>308</td>
<td>4.68</td>
</tr>
<tr>
<td>318</td>
<td>9.36</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>52</td>
</tr>
<tr>
<td>$\Delta H^#$ (kJ mol$^{-1}$)</td>
<td>50</td>
</tr>
<tr>
<td>$\Delta S^#$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>-110</td>
</tr>
<tr>
<td>$\Delta G^#$ (kJ mol$^{-1}$)</td>
<td>83</td>
</tr>
<tr>
<td>log $A$</td>
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negligible under conditions employed for kinetic study. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III), \([\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_3\text{IO}_6)]^{2-}\), a conclusion also supported by earlier work\(^{28,29}\).

It is known that DL-ornithine exists in the form of Zwitterion\(^{30}\) in aqueous medium. In highly acidic medium it exists in the protonated form, whereas in highly basic medium it is in the deprotonated form\(^{30}\).

\[
\text{H}_2\text{N}-
\begin{array}{c}
\text{O} \\
\text{NH}_2 \\
\text{O}^-
\end{array}
\]

2.4.1. Mechanism for uncatalyzed reaction

The reaction between DPC and OMH in alkaline medium presents \([\text{OMH}]/[\text{DPC}] = 1:4\) stoichiometry. Since the reaction was enhanced by [OH\(^-\)], added periodate retarded the rate and first order dependency in [DPC] and fractional order in [OMH] and [OH\(^-\)], a plausible reaction mechanism has been proposed which also explains all other experimental observations as shown in Scheme 1.

Lister\(^{31}\) proposed the copper(III) periodate in alkaline medium into three forms as diperiodatocuprate(III) (DPC), monoperiodatocuprate(III) (MPC) and tetrahydroxocuprate(III). The latter is ruled out as its equilibrium constant is \(8.0 \times 10^{-11}\) at 40°C. Hence, in the present study, in view of the negative less
than unit order in periodate on rate of reaction, monoperiodatocuprate(III) MPC is considered to be the active species of copper(III) periodate complex. The results of increase in the rate with increase in alkali concentration and decrease in the rate with increase in periodate concentration suggest that equilibria of different copper(III) periodate complexes are possible as in equations (7) and (8).

Scheme 1
The inverse fractional order in [IO₄⁻] might also be due to this reason. The less than unit order in [OMH] presumably results from formation of a complex (C₁) between the oxidant and DL-ornithine prior to the formation of the products. \( K₃ \) is the composite equilibrium constant comprising the equilibrium to bind OMH to MPC species to form a complex (C₁). Then this complex (C₁) decomposes in a slow step to form a free radical derived from DL-ornithine. This free radical species further reacts with another molecule of MPC species in a fast step to form 4-aminobutaraldehyde intermediate. This 4-aminobutaraldehyde then reacts with two more moles of MPC in a further fast step to form products such as 4-aminobutyric acid, Cu(II) and periodate. All these results may be interpreted in the form of Scheme 1.

Since Scheme 1 is in accordance with the 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 (see infra). This type of radical intermediate has also been observed in earlier work\(^{32,33}\).

Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV - vis spectra of DPC (5.0 × 10⁻⁵ mol dm⁻³), OMH (5.0 × 10⁻⁴ mol dm⁻³), [OH⁻] = 0.08 mol dm⁻³ and a mixture of both. A
bathochromic shift of about 9 nm from 210 to 219 nm in the spectra of DPC to mixture of DPC and OMH was observed (Fig. II (xii) (p. 63). The Michaelis-Menten plot proved the complex formation between oxidant and substrate, which explains less than unit order in \([\text{OMH}]\). Such a complex between an oxidant and substrate has also been observed in other studies \(^{34,35}\).

From Scheme 1, the rate law (14) can be derived as follows,

\[
\text{Rate} = - \frac{d [\text{DPC}]}{dt} = k_1 [C_1] = \frac{k_1 K_1 K_2 K_3 [\text{DPC}][\text{OMH}][\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}]} \tag{9}
\]

The total concentration of \([\text{DPC}]_T\) is given by,

\[
[\text{DPC}]_T = [\text{DPC}]_f + [\text{Cu(H}_2\text{IO}_6)(\text{H}_3\text{IO}_6)^{2-}] + [\text{Cu(H}_2\text{IO}_6\text{H}_2\text{O})_2] + [C_1] \tag{10}
\]

where \(T\) and \(f\) refer to total and free concentrations.

\[
[\text{DPC}]_f = \frac{[\text{DPC}]_T [\text{H}_3\text{IO}_6^{2-}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1 [\text{H}_3\text{IO}_6^{2-}] [\text{OH}^-] + K_1 K_2 [\text{OH}^-] + K_1 K_2 K_3 [\text{OH}^-] [\text{OMH}]} \]

Similarly,

\[
[\text{OMH}]_T = [\text{OMH}]_f + C_1
= [\text{OMH}]_f + \frac{K_1 K_2 K_3 [\text{DPC}][\text{OMH}][\text{OH}^-]_f}{[\text{H}_3\text{IO}_6^{2-}]}
= [\text{OMH}]_f \left[ 1 + \frac{K_1 K_2 K_3 [\text{DPC}][\text{OH}^-]_f}{[\text{H}_3\text{IO}_6^{2-}]} \right]
\]

In view of low concentration of \([\text{DPC}]\) and \([\text{H}_3\text{IO}_6^{2-}]\), second term can be neglected.

\[
[\text{OMH}]_T = [\text{OMH}]_f \tag{11}
\]
Spectroscopic evidence for the complex formation between DPC and OMH (a) UV-vis spectra of DPC complex (415, 258 and 210 nm); (b) UV-vis spectra of mixture of DPC and OMH; (c) UV-vis spectra of OMH
Similarly

\[
[\text{OH}^-]_T = [\text{OH}^-]_f + [\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_3\text{IO}_6)]^{2-} + [\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2] \\
= [\text{OH}^-]_f + K_1[\text{OH}^-][\text{DPC}] + \frac{K_1K_2[\text{DPC}][\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}]}
\]

In view of low concentration of [DPC] and [H$_3$IO$_6^{2-}$] used,

\[
[\text{OH}^-]_f = [\text{OH}^-]_f
\]

Substituting the values of [DPC]$_f$, [OMH]$_f$ and [OH$^-$]$_f$ in equation (9) and omitting subscripts, we have,

\[
\text{Rate} = \frac{d[DPC]}{dt} = \frac{k_1K_1K_2K_3[\text{DPC}][\text{OMH}][\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{OMH}]}
\]

(13)

\[
k_U = \frac{\text{Rate}}{[\text{DPC}]} = \frac{k_1K_1K_2K_3[\text{OMH}][\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{OMH}]}
\]

(14)

which explains all the observed kinetic orders of different species. The rate law (14) can be rearranged into the following form which is suitable for verification.

\[
\frac{1}{k_U} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{k_1K_1K_2K_3[\text{OH}^-][\text{OMH}]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{k_1K_2K_3[\text{OMH}]} + \frac{1}{k_1K_3[\text{OMH}]} + \frac{1}{k_1}
\]

(15)

According to equation (15), other conditions being constant, plots of 1/$k_U$ versus 1/[OMH], 1/$k_U$ versus 1/[OH$^-$] and 1/$k_U$ versus [H$_3$IO$_6^{2-}$] should be linear and are found to be so (Fig. II (xiii) (p. 66, 67)). The slopes and
intercepts of such plots lead to the values of $k_1$ (Table II (vi a) (p. 52), $K_1$, $K_2$ and $K_3$ (Table II (ix a) (p. 68)). The values of $K_1$ and $K_2$ are in good agreement with the literature. Using these constants, the rate constants were calculated over different experimental conditions, and there is a reasonable agreement between the calculated and the experimental values (Table II (ii) (p. 38) and (iv) (p. 43)), which fortifies the proposed mechanism (Scheme 1). The equilibrium constant $K_1$ is far greater than $K_2$ which may be attributed to the greater tendency of DPC to undergo hydrolysis compared to the dissociation of hydrolyzed species in alkaline medium.

The negligible effect of ionic strength and dielectric constant of medium on the rate explains qualitatively the reaction between neutral and negatively charged ions, as seen in Scheme 1. The thermodynamic quantities for the different equilibrium steps, in Scheme 1 can be evaluated as follows. The $[\text{OMH}]$, $[\text{OH}^-]$, and $[\text{H}_3\text{IO}_6^{2-}]$ (Table II (ii) (p. 38) and (iv) (p. 43)) were varied at four different temperatures. The plots of $1/k_U$ versus $1/[\text{OMH}]$, $1/k_U$ versus $1/[\text{OH}^-]$ and $1/k_U$ versus $[\text{H}_3\text{IO}_6^{2-}]$ should be linear and are found to be so. From the slopes and intercepts, the values of $K_1$, $K_2$ and $K_3$ were calculated at different temperatures. A vant Hoff’s plot was made for the variation of $K_1$, $K_2$ and $K_3$ with temperature ($\log K_1$ versus $1/T$, $\log K_2$ versus $1/T$ and $\log K_3$ versus $1/T$). The values of enthalpy of reaction $\Delta H$, entropy of reaction $\Delta S$ and free energy of reaction $\Delta G$ were calculated for the first, second and third equilibrium steps. These values are given in Table II (ix b) (p. 68).
Verification of rate law (14) for the oxidation of DL-ornithine by diperiodatocuprate(III). Plots of (A) $1/k_U$ versus $1/[\text{OMH}]$, (B) $1/k_U$ versus $1/[\text{OH}^-]$, (C) $1/k_U$ versus $[\text{H}_3\text{IO}_6]^{2-}$, at four different temperatures

(Conditions as in Table II (ii) (p. 38) and (iv) (p. 43))
(B)

![Graph showing the relationship between 1/k_U x 10^{-3}s and 1/[OH^-] x 10^{-1}dm^3 mol^{-1} at different temperatures.]

(C)

![Graph showing the relationship between 1/k_U x 10^{-3}s and [H_3IO_6^{2-}] x 10^4 mol dm^{-3} at different temperatures.]

Chapter – II
(a) Effect of temperature on $K_1$, $K_2$ and $K_3$ of Scheme 1 for the oxidation of OMH by diperiodatocuprate(III) in aqueous alkaline medium

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_1 \times 10^1$ (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>288</td>
<td>0.87</td>
<td>1.25</td>
<td>4.70</td>
</tr>
<tr>
<td>298</td>
<td>1.24</td>
<td>1.01</td>
<td>3.66</td>
</tr>
<tr>
<td>308</td>
<td>2.22</td>
<td>0.85</td>
<td>2.48</td>
</tr>
<tr>
<td>318</td>
<td>4.33</td>
<td>0.69</td>
<td>1.68</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>40.6</td>
<td>-14.7</td>
<td>-26.3</td>
</tr>
<tr>
<td>$\Delta S$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>120</td>
<td>-126</td>
<td>-1.68</td>
</tr>
<tr>
<td>$\Delta G_{298}$ (kJ mol$^{-1}$)</td>
<td>5.15</td>
<td>22.8</td>
<td>-26.0</td>
</tr>
</tbody>
</table>
comparison of the $\Delta H$ value (40.6 kJ mol$^{-1}$) from $K_1$ with that of $\Delta H^\#$ (50.2 kJ mol$^{-1}$) of rate-limiting step supports that the reaction before the rate determining step is fairly fast as it involves low activation energy$^{37, 38}$. A high negative value of $\Delta S^\#$ (-121 JK$^{-1}$ mol$^{-1}$) suggests that intermediate complex (C$_1$) is more ordered than the reactants$^{39}$.

2.4.2. Mechanism for Ru(III) catalyzed reaction

Ru(III) chloride acts as an efficient catalyst in many redox reactions, particularly in an alkaline medium$^{24, 40}$. In the present study it is quite probable that the [Ru(H$_2$O)$_5$OH]$^{2+}$ species might assume the general form [Ru(III)(OH)$_x$]$^{3-x}$. The $x$ value would always be less than six because there are no definite reports of any hexahydroxy ruthenium species. The remainder of the coordination sphere would be filled by water molecules. Hence, under the conditions employed, e.g., [OH$^-$] >> [Ru(III)], ruthenium(III) is mostly present as the hydroxylated species, [Ru(H$_2$O)$_5$OH]$^{2+}$$^{41}$.

In the earlier reports of Ru(III) catalyzed oxidation, it was observed that$^{42}$, if there exists a fractional order dependence with respect to [substrate] and [Ru(III)], and unit order with respect to [oxidant], it leads to the formation of Ru(III)–substrate complex. This complex is further oxidized by the oxidant to Ru(IV)–substrate complex followed by the rapid redox decomposition with regeneration of Ru(III) catalyst. In case$^{43}$, if the process involves a zeroth order dependence with respect to [oxidant], first order with respect to [Ru(III)] and a fractional order with respect to [substrate], it leads to the formation of Ru(III)–
substrate complex and further cleaves to Ru(I) species which is rapidly oxidized by the oxidant to regenerate Ru(III) catalyst.

In the present investigation, the reaction was enhanced by [OH\(^-\)], added periodate retarded the rate, first order dependency in [DPC] and catalyst [Ru(III)] and fractional order in [OMH] and [OH\(^-\)] was observed. To explain the observed orders the following Scheme 2 has been proposed for ruthenium(III) catalyzed reaction considering its OMH as anionic form of OMH in alkaline medium. In this study, in view of the negative less than unit order of periodate on the rate of reaction, monoperiodatocuprate(III) MPC is considered to be the active species of copper(III) periodate complex. The results of increase in the rate with increase in alkali concentration and decrease in the rate with increase in periodate concentration suggest that equilibria of different copper(III) periodate complexes are possible as already shown in equations (7) and (8). Anionic species of OMH reacts with ruthenium(III) active species to form a complex (C\(_2\)) which further reacts with one mole of MPC in a slow step to give the free radical species of OMH, Cu(II) with regeneration of catalyst, ruthenium(III). Further this free radical species of OMH reacts with one more molecule of MPC species in a fast step to form 4-aminobutaraldehyde intermediate. This 4-aminobutaraldehyde then reacts with two more moles of MPC in a further fast step to form products such as 4-aminobutyric acid, Cu(II) and periodate. All these results may be interpreted in the form of Scheme 2. Similar type of key steps, in the mechanism, has been proposed for the catalyzed reaction in the earlier studies\(^{36}\).
Spectroscopic evidence for the complex formation between Ru(III) and OMH was obtained from UV-vis spectra of OMH (5.0 \times 10^{-4} \text{ mol dm}^{-3}), Ru(III) (8.0 \times 10^{-7} \text{ mol dm}^{-3}), [OH^-] = 0.08 \text{ mol dm}^{-3} and a mixture of both. A hypsochromic shift of about 5 nm from 276.9 to 271.9 nm in the spectra of Ru(III) to the mixture of Ru(III) and OMH was observed (Fig. II (xiv) p. 72). The Michaelis-Menten plot proved the complex formation between catalyst and substrate, which explains less than unit order in [OMH]. Such a complex
Figure II (xiv)

Spectroscopic evidence for the complex formation between Ru(III) and OMH
(a) UV-vis spectra of Ru(III) (229.1, 276.9 and 326 nm); (b) UV-vis spectra of mixture of Ru(III) and OMH (229.1, 271.9, 326); (c) UV-vis spectra of OMH
between a catalyst and substrate has also been observed in other studies.\textsuperscript{44}

From Scheme 2, the rate law (22) can be derived as follows,

$$\text{Rate} = -\frac{d[DPC]}{dt} = k_2 [C_2][MPC] = \frac{k_2 K_1 K_3 [DPC]_f [OMH]_f [OH^-]_f [Ru(III)]_f}{[H_3IO_6^{2-}]}$$  \hspace{1cm} (16)

The total concentration of [DPC]_T is given by,

$$[DPC]_T = [DPC]_f + [Cu(H_2IO_6)(H_3IO_6)]^{2-} + [Cu(H_2IO_6)(H_2O)_2]$$  \hspace{1cm} (17)

where T and f refer to total and free concentrations

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

Similarly,

$$[OMH]_f = \frac{[OMH]_T}{1 + K_3 [Ru(III)]}$$

In view of low concentrations of Ruthenium(III) used,

$$[OMH]_f = [OMH]_T$$  \hspace{1cm} (18)

Similarly,

$$[Ru(III)]_f = [Ru(III)]_T$$  \hspace{1cm} (19)

$$[OH^-]_T = [OH^-]_f + [Cu(H_2IO_6)(H_3IO_6)]^{2-} + [Cu(H_2IO_6)(H_2O)_2]$$

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

In view of low concentration of [DPC] and [H_3IO_6^{2-}] used,

$$[OH^-]_T = [OH^-]_f$$  \hspace{1cm} (20)
Substituting equations (17), (18), (19) and (20) in equation (16), and omitting subscripts, the final form of the equation obtained is,

\[
\begin{align*}
\text{Rate} = \frac{-d[DPC]}{dt} &= \frac{k_2 K_1 K_2 K_4 [DPC][OMH][OH^-][Ru(III)]}{[H_3IO_6^{2-}] + K_1 [OH^-][H_3IO_6^{2-}] + K_1 K_2 [OH^-] + K_1 K_2 K_4 [OH^-][OMH]}
\end{align*}
\]

(21)

\[
\begin{align*}
\frac{\text{Rate}}{[DPC]} &= k_c = k_T - k_U = \frac{k_2 K_1 K_2 K_4 [OMH][OH^-][Ru(III)]}{[H_3IO_6^{2-}] + K_1 [OH^-][H_3IO_6^{2-}] + K_1 K_2 [OH^-] + K_1 K_2 K_4 [OH^-][OMH]}
\end{align*}
\]

(22)

The rate law (22) can be rearranged into the following form which is suitable for verification.

\[
\begin{align*}
\frac{[Ru(III)]}{k_c} &= \frac{[H_3IO_6^{2-}]}{k_2 K_1 K_2 K_4 [OH^-][OMH]} + \frac{[H_3IO_6^{2-}]}{k_2 K_2 K_4 [OMH]} + \frac{1}{k_2 K_4 [OMH]} + \frac{1}{k_2}
\end{align*}
\]

(23)

According to equation (23), other conditions being constant, plots of \([Ru(III)]/k_c\) versus \(1/[OMH]\), \(1/[OH^-]\) and \([H_3IO_6^{2-}]\) should be linear and are found to be so (Fig. II (xv) (p. 75, 76)). The slopes and intercepts of such plots lead to the values of \(k_2\) (Table II (vii a) (p. 55), \(K_1\), \(K_2\) and \(K_4\) (Table II (x a) (p. 77)). The value of \(K_1\) and \(K_2\) are in good agreement with the literature\(^{36}\). Using these constants, the rate constants were calculated and compared with the experimental \(k_c\) values. There was a reasonable agreement with each other (Table II (iii) (p. 39) and (v) (44)), which fortifies the proposed mechanism (Scheme 2).

The negligible effect of ionic strength and dielectric constant of medium...
Figure II (xv)

Verification of rate law (22) for the Ru(III) catalysed oxidation of DL-ornithine by diperiodatocuprate(III). Plots of (A): \( \frac{[\text{Ru}(\text{III})]}{k_C} \) versus \( 1/\text{[OMH]} \), (B): \( \frac{[\text{Ru}(\text{III})]}{k_C} \) versus \( 1/\text{[OH}^-] \) and (C): \( \frac{[\text{Ru}(\text{III})]}{k_C} \) versus \( [\text{H}_3\text{IO}_6]^{2-} \) at four different temperatures

(Conditions as in (Table II (iii) (p. 39) and (v) (44)).
(B)  

![Graph showing the relationship between \( [\text{OH}^-] \times 10^{-1} \text{dm}^3 \text{mol}^{-1} \) and \( [\text{Ru(III)}]/kC \times 10^4 \text{mol dm}^{-3} \text{s} \) at different temperatures (288K, 298K, 308K, 318K).]

(C)  

![Graph showing the relationship between \( [\text{H}_3\text{IO}_6^{2-}] \times 10^4 \text{mol dm}^{-3} \) and \( [\text{Ru(III)}]/kC \times 10^4 \text{mol dm}^{-3} \text{s} \) at different temperatures (288K, 298K, 308K, 318K).]
(a) Effect of temperature on $K_1$, $K_2$ and $K_3$ of Scheme 2 for the ruthenium(III) catalysed oxidation of OMH by diperiodatocuprate(III) in aqueous alkaline medium

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_1 \times 10^1$ (dm$^3$ mol$^{-1}$)</th>
<th>$K_2 \times 10^4$ (mol dm$^{-3}$)</th>
<th>$K_4 \times 10^{-4}$ (dm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>0.60</td>
<td>7.23</td>
<td>0.76</td>
</tr>
<tr>
<td>298</td>
<td>1.35</td>
<td>2.54</td>
<td>1.29</td>
</tr>
<tr>
<td>308</td>
<td>2.60</td>
<td>0.94</td>
<td>2.02</td>
</tr>
<tr>
<td>318</td>
<td>5.98</td>
<td>0.36</td>
<td>2.82</td>
</tr>
</tbody>
</table>

(b) Thermodynamic quantities using $K_1$, $K_2$ and $K_4$

<table>
<thead>
<tr>
<th>Thermodynamic quantities</th>
<th>Values from $K_1$</th>
<th>Values from $K_2$</th>
<th>Values from $K_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (kJ mol$^{-1}$)</td>
<td>54.4</td>
<td>-75.8</td>
<td>33.3</td>
</tr>
<tr>
<td>$\Delta S$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>166</td>
<td>-323</td>
<td>190</td>
</tr>
<tr>
<td>$\Delta G_{298}$ (kJ mol$^{-1}$)</td>
<td>4.95</td>
<td>20.5</td>
<td>-23.4</td>
</tr>
</tbody>
</table>
on the rate explains qualitatively the reaction between neutral and positively charged ions, as seen in Scheme 2. The thermodynamic quantities for the different equilibrium steps, in Scheme 2 can be evaluated as follows. The [OMH], [OH⁻] and [H₃IO₆²⁻] (Table II (iii) (p. 39) and (v) (44)) were varied at four different temperatures. The plots of [Ru(III)]/k_C versus 1/[OMH], [Ru(III)]/k_C versus 1/[OH⁻] and [Ru(III)]/k_C versus [H₃IO₆²⁻] should be linear and are found to be so. From the slopes and intercepts, the values of K₁, K₂ and K₄ were calculated at four different temperatures. A vant Hoff’s plot was made for the variation of K₁, K₂ and K₄ with temperature (log K₁ versus 1/T, log K₂ versus 1/T and log K₄ versus 1/T). The values of enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG were calculated for the first, second and third equilibrium steps. These values are given in Table (x b) (p. 77). The negative value of ΔS° (-11.5 JK⁻¹ mol⁻¹) suggests that intermediate complex is more ordered than the reactants³⁹. The observed modest enthalpy of activation and higher rate constant for the slow step indicate that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observation⁴⁵, ⁴⁶. The activation parameters evaluated for the catalyzed and uncatalyzed reactions explain the catalytic effect on the reaction. The catalyst Ru(III) forms the complex (C₂) with substrate, which enhances the reducing property of substrate than that without catalyst. Further, the catalyst Ru(III) modifies the reaction path by lowering the energy of activation.
Chapter – II

It is also interesting to note that the transient species involved in both the uncatalyzed and Ru(III) catalyzed reactions is different but leads to the formation of same products. The uncatalyzed reaction in alkaline medium has been shown to proceed via a MPC - OMH complex which decomposes slowly in a rate determining step to give the products via free radical in the further fast steps, whereas, in the catalyzed reaction, it has been shown to proceed via Ru(III) - OMH complex which further reacts with one mole of MPC in the rate determining step to give the products via free radical in the further fast steps. Since MPC was involved in the mechanisms as the active species of Cu(III) in both the cases, the products obtained were same.

2.5. IMPORTANCE OF CHAPTER II

A comparative study of uncatalyzed and Ru(III) catalyzed oxidation of DL-ornithine by diperiodatocuprate(III) was studied. Among the various species of copper(III) in alkaline medium, [Cu(H₂IO₆)(H₂O)₂] was considered to be the active species for the title reaction. The active species of Ru(III) was found to be [Ru(H₂O)₅OH]²⁺. The reaction rates revealed that Ru(III) catalyzed reaction was about eight-fold faster than the uncatalyzed reaction. It becomes apparent that, in carrying out this reaction, the role of reaction medium is crucial. Activation parameters were evaluated for both catalyzed and uncatalyzed reactions. Catalytic constants and the activation parameters with reference to catalyst were also computed. The overall sequence described here is consistent with all the experimental evidences including the product, spectral, mechanistic and kinetic studies.
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