Chapter - III

*Ruthenium-III*

*Catalysed Oxidation of Reducing Sugars*
Oxidation of Reducing Sugars by $\text{IO}_4^-$ in Presence of Ruthenium

(III) A. Introduction:

The carbonhydrates (sugars) are important biochemical compounds as they play both a structural role and a mean of energy storage. The interesting as they are, some times, slow to equilibrate and alos oxidise in presence of metal ions. The Kinetics of the oxidation of reducing sugars by various oxidants such as N-bromosuccinimide$^{1-10}$, potassium bromate$^{11-12}$, potassium permanganate$^{13-14}$, hexachloroirridate$^{15}$, cromic acid$^{16}$, hexacyanoferate (III)$^{17-20}$, cerium (IV)$^{21-27}$, iron (III)$^{28}$, copper (II)$^{29-30}$, t-butilhypochlorite$^{31}$, manganese$^{32}$, persulphate ion$^{33}$, chloramine-B$^{34-39}$, bromamine-B$^{40}$, bromamine-T$^{41-43}$, chloramine -T$^{44-49}$, chromium (IV)$^{50}$, N -bromoacetamide$^{51-53}$, sodium metaperiodate$^{54-56}$ have been studied and mechanism of the reactions have been proposed. The effect of various catalysts viz. Thallium (III)$^{57}$, iron (II)$^{58}$] vanadium (V)$^{59-63}$, cobalt (II)$^{64}$, nicketl (II)$^{20}$, osmium (VIII)$^{65}$, palladium (II)$^{5-8,52}$, irriddy (III)$^{1,4,26,50}$, ruthenium (III)$^{2,53,55-56}$ and ruthenium (VIII)$^{54}$ etc. on the rate of oxidation has also been studied. Generally, the reaction proceed via formation of an intermediate complex between the substrate and the catalyst. It has been observed that among the platinum group metal-ions, ruthenium (III) werves as a remarkable effective catalyst. The catalytic role of ruthenium (III) in several redox reactions involving oxidants viz.
cerium (IV), hexacyanoferrate (HI), thallium (III), N-bromosuccinimide, chloramine - B etc. has been reviewed by N.D. Kandpal et al.\textsuperscript{66}.

The kinetics of ruthenium (VIII) catalysed oxidation of some reducing sugars giz. sorbose and maltose by sodium metaperiodate\textsuperscript{54} have been studied in alkaline medium. The reactions followed a first order dependence of rate of oxidation with respect to each [NaIO$_4$], [Ru(VIII)] and [OH$^-$] at their lower concentrations of the reactants, and a zero order dependence of rate with respect to the substrate. Variation of ionic strength of the medium showed a negligible effect of the rate of oxidation.

During the preliminary experiments in the laboratory, it was observed that the kinetic results for the oxidation of reducing sugars by sodium metaperiodate in presence of ruthenium (III) ion were different from those reported by Gupta et al.\textsuperscript{54} for the oxidation of sugars by meaperiodate in presence of ruthenium (VIII) ion. The observed first order dependence of rate with respect to substrate in our experiments clearly indicated the different behaviour of two species of the catalyst, i.e. rethenium (III) and ruthenium (VIII). Therefore, In order to throw the light on the catalytic role of ruthenium (III) during periodate oxidation of reducing sugars, the kinetics of the reactions have been investigated in details and the results are reported in this chapter. The oxidation of five reducing sugars giz. fructose, glucose, galactose, maltose and lactose have been studied. The effect of substrate, oxidant, catalyst, pH,
temperature etc. has been studied on the rate of reaction and a mechanism consistent with kinetic data has been proposed and discussed at the end of the chapter.

**III B. Stoichiometry and Identification of Products:**

The reaction products have been identified in both the conditions i.e. under the kinetic conditions where, [substrate] > [oxidant] and under the stoichiometric conditions where, [oxidant] > [substrate].

**Under kinetic Conditions:**

The reaction mixtures were analysed periodically for identification of products under the kinetic conditions. Several reaction mixtures were prepared keeping (RuCl₃) and [NaOH] at fixed concentration. After the complete reaction, the reaction mixture was taken out from the reaction vessel and product was tested.

The presence of formaldehyde and corresponding lower acid of the reducing sugar was detected by spot test⁶⁷. The presence of formaldehyde was confirmed by formation of 2-4 DNP derivative and comparing its m.p. and TLC with that of the authentic sample. Thus under the kinetic conditions, the reducing sugar oxidised to formaldehyde and corresponding lower acid.

The results may be represented as,

\[
\text{RHC(OH) CHO} \\
\text{Or } \首选 + \text{IO}_4^- + \text{OH}^- \xrightarrow{\text{Catalyst}} \text{RCOO}^- + \text{HCHO} + \text{IO}_3^- + \text{H}_2\text{O} \\
\text{RCO CH}_2 \text{OH}
\]

(39)
where R represents CHOH (CHOH)_{2} CH_{2}OH in case of fructose, glucose and galactose and CHOH\textsubscript{C} (OR') HCHOH CH_{2}OH in case of maltose and lactose where R' is nonreducing glucose and galactose unit of maltose and lactose, respectively.

The formaldehyde as oxidation product of aldoses during periodate oxidation is also reported\textsuperscript{68}.

**Under stoichiometric Conditions:**

The stoichiometry of the reaction was also studied in the presence of excess of oxidant i.e. sodium metaperiodate. Different sets of reaction mixtures containing a known excess of (IO_{4}^{-}) over [Reducing sugar] and at a fixed concentrations of catalyst and OH\textsuperscript{-} were kept at 40^\circ C for 72 hours and then analysed. The unreacted oxidant was determined iodometrically. Estimation of unreacted IO_{4}^{-} showed that one mole of monosaccharide (glucose, galactose and fructose) consumes two moles of IO_{4}^{-} while one mole of disaccharide (maltose and lactose) consumes more than three moles of IO_{4}^{-}.

the qualitative analysis of the product (TLC) indicated the presence of a mixture of formic acid and corresponding lower acid of reducing sugar. These products are indicative for C_{1} – C_{2} splitting.

Thus it seems that the formaldehyde, which is one of the oxidation products under the kinetic conditions, is further oxidised in presence of excess of oxidant. This result in a more than 1:1 stoichiometry between substrate and IO_{4}^{-} in case of monosaccharides. However in case of disaccharide one of the initial
product is a monosaccharide which will be further oxidised in excess of oxidant and thus more than 1:2 stoichiometry between substrate and $\text{IO}_4^-$ is expected which has also been observed experimentally.

**III C. Effect of $\text{IO}_4^-$ on the Rate of Oxidation:**

In order to determine the dependence of reaction rate of $[\text{IO}_4^-]$, the kinetic runs were made for oxidation of various reducing sugars at several initial concentrations of $[\text{IO}_4^-]$. The concentrations of reducing sugar, catalyst and NaOH were kept constant. The amount of hypo required for titration of 5 ml of reaction mixture at different time intervals for various kinetic runs are presented in Tables III-1 to III-5.

It was observed that log ($a-x$) versus time plots were linear upto 80% of the reactions, suggesting a first order dependence of rate with respect to sodium metaperiodate.

The results are represented graphically in Figures III C-1 to III C-5.

The pseudo-first order rate constants in sodium metaperiodate ($k_{\text{obs}}$) evaluated from slopes of the straight lines plotted between log ($a-x$) versus time (Figures III C-1 to III C-5) are summarised in Table III C-1.

It is observed from Figures (III C - 1 to III C-5) that during a particular kinetic run, the plot of log ($a-x$) versus time remains linear suggesting first order dependence of the rate with respect of $[\text{IO}_4^-]$. However an increases in initial $[\text{IO}_4^-]$ (Table III C-1), resulted in a decrease in the observed pseudo-first order rate constant.
Effect of $[\text{IO}_3^-]$ oxidation of Fructose;

$k_{\text{obs}} \times 10^4 (\text{s}^{-1})$
- 8.52 for a
- 6.14 for b
- 5.48 for c
- 3.65 for d
- 2.84 for e

Fig. III C - 1: Pseudo-first order plots at 40°C

$[S] = 2.0 \times 10^{-2}$, $[\text{OH}^-] = 0.1$, $[\text{RuCl}_3] = 3.0 \times 10^{-4}$, and $[\text{IO}^-] = 1.0$, 1.5, 2.0, 3.0 and $4.0 \times 10^{-3}$,
in a, b, c, d, and e, respectively.
Concentrations are in mol dm$^{-3}$. 
Effect of $[\text{IO}_4^-]$ oxidation of Glucose;

\[ k_{\text{obs}} \times 10^4 \text{ (s}^{-1}) \]

- $6.67$ for a
- $5.11$ for b
- $4.79$ for c
- $3.26$ for d
- $2.55$ for e

Fig. III C - 2: Pseudo-first order plots at $40^\circ$C

$[S] = 2.0 \times 10^{-2}$, $[\text{OH}^-]$ = 0.1, $[\text{RuCl}_3]$ = $3.0 \times 10^{-4}$, and $[\text{IO}_4^-]$ = 1.0, 1.5, 2.0, 3.0 and $4.0 \times 10^{-3}$, in a, b, c, d, and e, respectively.

Concentrations are in mol dm$^{-3}$. 
Fig. III C - 3: Pseudo-first order plots at 40°C

\[ [S] = 2.0 \times 10^{-2}, [OH^-] = 0.1, [RuCl_3] = 3.0 \times 10^{-4}, \text{ and} \]
\[ [IO^-_4] = 1.0, 1.5, 2.0, 3.0 \text{ and } 4.0 \times 10^{-3}, \]
in a, b, c, d, and e, respectively.

Concentrations are in mol dm\(^{-3}\).
Effect of $[\text{IO}_4^-]$: oxidation of Maltose;

$k_{\text{cat}} \times 10^4$ (s$^{-1}$)

- 7.67 for a
- 5.90 for b
- 5.11 for c
- 3.57 for d
- 2.74 for e

Fig. III C - 4: Pseudo-first order plots at 40°C

$[S] = 2.0 \times 10^{-2}$, $[\text{OH}^-] = 0.1$, $[\text{RuCl}_3] = 3.0 \times 10^{-4}$, and $[\text{IO}_4^-] = 1.0, 1.5, 2.0, 3.0$ and $4.0 \times 10^{-3}$, in a, b, c, d, and e, respectively.

Concentrations are in mol dm$^{-3}$. 
Effect of [IO$_4$]: Oxidation of Lactose;

$k_{obs} \times 10^4 \ (s^{-1})$
- $5.11$ for a
- $4.26$ for b
- $3.83$ for c
- $3.07$ for d
- $2.39$ for e

Fig. III C - 5: Pseudo-first order plots at $40^\circ$C

$[S] = 2.0 \times 10^{-2}, [OH^-] = 0.1, [RuCl_3] = 3.0 \times 10^{-4}$, and $[IO_4^-] = 1.0, 1.5, 2.0, 3.0$ and $4.0 \times 10^{-3}$,
in a, b, c, d, and e, respectively.
Concentrations are in mol dm$^{-3}$.
III.D. Effect of [Substrate] on the rate of Oxidation:

To observe the effect of substrate on the rate of oxidation, the reactions were investigated at several initial concentrations of each reducing substrate. The concentrations of other reactants viz. sodium metaperiodate, ruthenium trichloride (RuCl₃) and sodium hydroxide were kept constant as reported in tables. The amount of hypo (V, in ml) required for titration of 5 ml of reaction mixture at different time intervals for various kinetic runs are presented in Tables - III-6 to III-10. The pseudo-frist order plots i.e. plots of log (a−x) versus time at various initial concentrations of reducing sugars are represented graphically in Figures III D-1 to III D-5.
Table - III C - 1: Effect of [Sodium metaperiodate] on the rate constants at 40°C

<table>
<thead>
<tr>
<th>[IO₄⁻] x 10³</th>
<th>FR (A)</th>
<th>GL (B)</th>
<th>GA (C)</th>
<th>MA (D)</th>
<th>LA (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>8.52</td>
<td>6.67</td>
<td>7.29</td>
<td>7.67</td>
<td>5.11</td>
</tr>
<tr>
<td>1.5</td>
<td>6.14</td>
<td>5.11</td>
<td>6.39</td>
<td>5.90</td>
<td>4.26</td>
</tr>
<tr>
<td>2.0</td>
<td>5.48</td>
<td>4.79</td>
<td>4.98</td>
<td>5.11</td>
<td>3.83</td>
</tr>
<tr>
<td>3.0</td>
<td>3.65</td>
<td>3.26</td>
<td>3.19</td>
<td>3.52</td>
<td>3.07</td>
</tr>
<tr>
<td>4.0</td>
<td>2.84</td>
<td>2.55</td>
<td>2.95</td>
<td>2.74</td>
<td>2.39</td>
</tr>
</tbody>
</table>

[Substrate] = 2.0 x 10⁻²; [OH⁻] = 0.10 for A, B and C; 0.20 for D and E; [RuCl₃] = 3.0 x 10⁻⁴.

The concentration of reactants are in mol Dm⁻³.
The values of \( k_{\text{obs}} \) evaluated from the slopes of linear plots between \( \log(a-x) \) versus time (Figures - III D - 1 to III D - 5) at various initial concentrations of the substrate are summarized in Table - III D - 1.

It is observed from Table - III D - 1 that the \( k_{\text{obs}} \) increases with an increase in [Reducing sugar]. A plot of \( (k_{\text{obs}}) \) versus [Reducing sugar] (Figure - III D - 6) showed a deviation from linearity at higher [Reducing sugar] suggesting that order of reaction in reducing substrate decreases from unity. Further, a plot of \( (1/k_{\text{obs}}) \) versus \( 1/[\text{Reducing sugar}] \) (Figure - III D - 7) was linear with a positive intercept suggesting a Michaelis - Menten type kinetics and confirming that order of reaction in substrate decreases from unity to zero at higher substrate concentration.
Fig. III D - 1: Pseudo-first order plots at 40°C

\([\text{IO}_4^{-}] = 2.0 \times 10^{-2}, [\text{OH}^{-}] = 0.1, [\text{RuCl}_3] = 3.0 \times 10^{-4}, [S] = 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 \text{ and } 5.0 \times 10^{-2}\),
in a, b, c, d, e and f respectively.
Concentrations are in mol dm\(^{-3}\).
Fig. III D - 2: Pseudo-first order plots at 40°C

\([\text{IO}_4^-] = 2.0 \times 10^{-2}, \ [\text{OH}^-] = 0.1, \ [\text{RuCl}_3] = 3.0 \times 10^{-4}, \]

\([\text{S}] = 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 \text{ and } 5.0 \times 10^{-2},\]

in a, b, c, d, e and f respectively.
Concentrations are in mol dm\(^{-3}\).
Effect of [Galactose]: oxidation of Galactose;

\[ k_{\text{obs}} \times 10^4 \ (s^{-1}) = 1.91 \text{ for } a \]
- 3.19 for b
- 4.26 for c
- 4.98 for d
- 6.39 for e
- 7.37 for f
- 7.67 for g

Fig. III D - 3: Pseudo-first order plots at 40°C

\([\text{IO}_4^-] = 2.0 \times 10^{-2}, [\text{OH}^-] = 0.1, [\text{RuCl}_3] = 3.0 \times 10^{-4}, [S] = 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 \text{ and } 5.0 \times 10^{-2},\]

in a, b, c, d, e and f respectively.

Concentrations are in mol dm\(^{-3}\).
Fig. III D - 4: Pseudo-first order plots at 40°C  
\[ [\text{IO}_3^-] = 2.0 \times 10^{-2}, \ [\text{OH}^-] = 0.1, \ [\text{RuCl}_3] = 3.0 \times 10^{-4}, \]  
\[ [\text{S}] = 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 \text{ and } 5.0 \times 10^{-2}, \]  
in a, b, c, d, e and f respectively.  
Concentrations are in mol dm\(^{-3}\).
Fig. III D - 5: Pseudo-first order plots at 40°C

\[
\begin{align*}
[IO_4^-] &= 2.0 \times 10^{-2}, \quad [OH^-] = 0.1, \quad [RuCl_3] = 3.0 \times 10^{-4}, \\
[S] &= 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 \text{ and } 5.0 \times 10^{-2}
\end{align*}
\]

in a, b, c, d, e and f respectively.

Concentrations are in mol dm\(^{-3}\).
III. E. Effect of [Alkali] on the Rate of Oxidation:

In order to determine the dependence of the rate of oxidation on the alkali concentration, the reactions were studied at different initial concentrations of the sodium hydroxide keeping at fixed ionic strength (as mentioned in tables III-11 to III-15) maintained by the addition of sodium perchlorate ($\text{NaClO}_4$). The amount of NaOH required to neutralise HCl already present in the catalyst was taken into account. The concentrations of other reactants viz. sodium metaperiodate, reducing sugars and catalyst were kept constant.

The amount of hypo required for titration of 5 ml of reaction mixtures at different time intervals for various kinetic runs are reported in Tables III-11 to III-15.

The plots of log $(a-x)$ versus time i.e. pseudo first order plots for various kinetic runs in case of each reducing sugar are represented graphically in Figures — III E-1 to III E-5.
Table - III D - 1: Effect of [Substrate] on the rate constants at 40°C

<table>
<thead>
<tr>
<th>[IO₄⁻] x 10²</th>
<th>FR (A)</th>
<th>GL (B)</th>
<th>GA (C)</th>
<th>MA (D)</th>
<th>LA (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.29</td>
<td>1.66</td>
<td>1.91</td>
<td>1.70</td>
<td>0.66</td>
</tr>
<tr>
<td>1.0</td>
<td>3.41</td>
<td>2.55</td>
<td>3.19</td>
<td>2.84</td>
<td>1.82</td>
</tr>
<tr>
<td>1.5</td>
<td>4.38</td>
<td>3.65</td>
<td>4.26</td>
<td>3.83</td>
<td>2.95</td>
</tr>
<tr>
<td>2.0</td>
<td>5.48</td>
<td>4.79</td>
<td>4.98</td>
<td>5.11</td>
<td>3.73</td>
</tr>
<tr>
<td>3.0</td>
<td>6.39</td>
<td>5.90</td>
<td>6.39</td>
<td>6.14</td>
<td>4.79</td>
</tr>
<tr>
<td>4.0</td>
<td>7.31</td>
<td>6.97</td>
<td>7.37</td>
<td>7.31</td>
<td>5.48</td>
</tr>
<tr>
<td>5.0</td>
<td>7.83</td>
<td>7.32</td>
<td>7.67</td>
<td>7.56</td>
<td>5.54</td>
</tr>
</tbody>
</table>

[IO₄⁻] = 2.0 x 10⁻³; [OH⁻] = 0.10 for A, B and C; 0.20 for D and E; [RuCl₃] = 3.0 x 10⁻⁴.

The concentration of reactants are in mol Dm⁻³.
Fig. III D-6: Pseudo $k_{ob}$ vs [S] at 40°C
$[\text{IO}_4^-] = 2.0 \times 10^{-3}$, $[\text{OH}^-] = 0.10$ for A, B and C;
0.20 for D and E; $[\text{RuCl}_3]$ = 3.0x $10^{-4}$,
Concentrations are in mol dm$^{-3}$. 

(57)
Fig. III D-6: Pseudo of $(k_{obs})$ Vs $[S]$ at 40°C

$[IO_4^-] = 2.0 \times 10^{-3}$, $[OH^-] = 0.10$ for A, B and C;
$0.20$ for D and E; $[RuCl_3] = 3.0 \times 10^{-4}$,

Concentrations are in mol dm$^{-3}$.

(58)
The observed rate constant \((k_{\text{obs}})\) evaluated from the slopes of the linear plots between \(\log (a - x)\) versus time (Figures III E-1 to III E-5) are summarised in Table — III E-1.

It is observed that on increasing \([\text{OH}^-]\) at fixed ionic strength, the \(k_{\text{obs}}\) increases and a plot of \((k_{\text{obs}})\) versus \([\text{OH}^-]\) showed a deviation from linearity (Figures III E—6). However, a plot of \((1/k_{\text{obs}})\) versus \((1/\text{[OH}^-]\) was linear with a positive intercept (Figure III E—7). Therefore, it is clear, that order of reaction in \(\text{OH}^-\) decreases from unity to zero at higher \([\text{OH}^-]\). The results are similar to that of substrate effect on the rate.
Fig. III E-1: Pseudo-first order plots at 40°C

\([\text{IO}_3^-] = 2.0 \times 10^{-3}, [S] = 0.2 \times 10^{-2}, [\text{RuCl}_3] = 3.0 \times 10^{-4}, [\text{OH}^-] = 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 \text{ and } 5.0 \times 10^{-1},\]
in a, b, c, d, e, f and g respectively, \(\mu = 4.0\)

Concentrations are in mol dm\(^{-3}\).
Effect of $[\text{OH}^-]$: oxidation of Glucose

$k_{obs} \times 10^4 \text{ (s}^{-1}) = 2.64 \text{ for a}$
$k_{obs} \times 10^4 \text{ (s}^{-1}) = 4.51 \text{ for b}$
$k_{obs} \times 10^4 \text{ (s}^{-1}) = 5.68 \text{ for c}$
$k_{obs} \times 10^4 \text{ (s}^{-1}) = 6.67 \text{ for d}$
$k_{obs} \times 10^4 \text{ (s}^{-1}) = 7.31 \text{ for e}$
$k_{obs} \times 10^4 \text{ (s}^{-1}) = 7.67 \text{ for f}$
$k_{obs} \times 10^4 \text{ (s}^{-1}) = 8.01 \text{ for g}$

Fig. III E-2: Pseudo-first order plots at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$, $[\text{S}] = 0.2 \times 10^{-2}$, $[\text{RuCl}_3] = 3.0 \times 10^{-4}$, $[\text{OH}^-] = 0.5, 1.0, 1.5, 2.0, 3.0, 4.0$ and $5.0 \times 10^{-1}$, in a, b, c, d, e, f and g respectively, $\mu = 4.0$

Concentrations are in mol dm$^{-3}$. 

(61)
Fig. III E-3: Pseudo-first order plots at 40°C

\[ [\text{IO}_4^-] = 2.0 \times 10^{-3}, \ [\text{S}] = 0.2 \times 10^{-2}, \ [\text{RuCl}_3] = 3.0 \times 10^{-4}, \]

\[ [\text{OH}^-] = 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 \text{ and } 5.0 \times 10^{-1}, \]

in a, b, c, d, e, f and g respectively, \( \mu = 4.0 \)

Concentrations are in mol dm\(^{-3}\).
Fig. III E-4: Pseudo-first order plots at 40°C  
$[\text{IO}_4^-] = 2.0 \times 10^{-3}$, $[S] = 0.2 \times 10^{-2}$, $[\text{RuCl}_3] = 3.0 \times 10^{-4}$,  
$[\text{OH}^-] = 1.0, 2.0, 3.0, 4.0, 6.0, 8.0$ and $10.0 \times 10^{-1}$,  
in a, b, c, d, e, f and g respectively, $\mu = 4.0$  
Concentrations are in mol dm$^{-3}$.  

\[ k_{\text{obs}} \times 10^4 \text{(s}^{-1}) = 2.84 \text{ for a} \]  
= 4.79 for b  
= 5.90 for c  
= 6.97 for d  
= 7.67 for e  
= 8.32 for f  
= 8.56 for g
Fig. III E -4 : Pseudo- first order plots at 40°C

\[
[\text{IO}_4^-] = 2.0 \times 10^{-3}, \ [S] = 0.2 \times 10^{-2}, \ [\text{RuCl}_3] = 3.0 \times 10^{-4}, \\
[\text{OH}^-] = 1.0, 2.0, 3.0, 4.0, 6.0, 8.0 \text{ and } 10.0 \times 10^{-1},
\]
in a, b, c, d, e, f and g respectively, \( \mu = 4.0 \)
Concentrations are in mol dm\(^{-3} \).
III F. Effect of [RuCl$_3$] on the Rate of Oxidation:

In order to investigate the effect of catalyst i.e. ruthenium trichloride, on the rate of reaction, the kinetics of oxidation of all the reducing sugars under investigations were studied at several initial concentrations of ruthenium-trichloride, keeping the concentrations of all the other reactants at constant.

The amount of hypo required for titration of 5 ml. of the reaction mixture at different time intervals for various kinetic runs are presented in Table III-16 to III-20

The Pseudo-first order plots i.e. log (a$-x$) versus time plots at different initial (RuCl$_3$) are represented graphically in Figures III F-1 to III F-5.
Table - III E - 1: Effect of [OH⁻] on the rate constants at 40°C

<table>
<thead>
<tr>
<th>[IO₄⁻] x 10²</th>
<th>FR (A)</th>
<th>GL (B)</th>
<th>GA (C)</th>
<th>MA (D)</th>
<th>LA (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.0</td>
<td>2.64</td>
<td>3.19</td>
<td>1.0</td>
<td>2.84</td>
</tr>
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<td>1.0</td>
<td>5.98</td>
<td>4.51</td>
<td>4.60</td>
<td>2.0</td>
<td>4.79</td>
</tr>
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<td>1.5</td>
<td>8.48</td>
<td>5.68</td>
<td>6.39</td>
<td>3.0</td>
<td>5.90</td>
</tr>
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<td>2.0</td>
<td>10.24</td>
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<td>7.67</td>
<td>4.0</td>
<td>6.97</td>
</tr>
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<td>6.0</td>
<td>7.67</td>
</tr>
<tr>
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<td>10.00</td>
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<tr>
<td>5.0</td>
<td>18.00</td>
<td>8.01</td>
<td>10.04</td>
<td>10.0</td>
<td>8.56</td>
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</tbody>
</table>

[IO₄⁻] = 2.0 x 10⁻³; [Substrate] = 2.0 x 10⁻²; [RuCl₃] = 3.0 x 10⁻⁴; μ = 0.4 for A, B and C; 0.8 for D and E;

The concentration of reactants are in mol Dm⁻³.
Fig. III E-6: Pseudo of $k_{obs}$ Vs $[\text{OH}^-]$ at 40°C

$[\text{IO}_3^-] = 2.0 \times 10^{-3}$, $[S] = 2.0 \times 10^{-2}$

$[\text{RuCl}_3] = 3.0 \times 10^{-4}$, $\mu = 0.4$ for A, B and C;
0.8 for D and E

Concentrations are in mol dm$^{-3}$. 

(67)
Fig. III E-6: Pseudo of \( k_{obs} \) Vs \([\text{OH}^-] \) at 40°C

\[
[\text{IO}_4^-] = 2.0 \times 10^{-3}, [S] = 2.0 \times 10^{-2}
\]

\[
[\text{RuCl}_3] = 3.0 \times 10^{-4}, \mu = 0.4 \text{ for A, B and C;}
0.8 \text{ for D and E}
\]

Concentrations are in mol dm\(^{-3}\).
The pseudo-first order rate constant obtained from the slopes of log (a − x) versus time plots (Figures III F−1 to III F−5) at various initial concentrations of (RuCl₃) are summarized in Table- III F−1. The rate constants (k_{obs}) were also evaluated for uncatalysed path i.e. when [RuCl₃] = 0.

The plot of (k_{obs}) versus [RuCl₃] (Figure III F-6) was linear with an intercept suggesting that rate constant increases on increasing [RuCl₃] in case of each reducing sugar and also reveals that, rate is proportional to \(k' + k'' [\text{RuCl}_3]\) where \(k'\) and \(k''\) are rate constant for uncatalysed and catalysed path, respectively. The reactions proceed in absence of the catalyst. However, in absence of the catalyst, the reactions were found to be extremely slow. The observed rate constant for uncatalysed path (k') i.e. k_{obs} at [RuCl₃] = 0, was matching with the value of intercept of the plot of (k_{obs}) versus [RuCl₃] in case of each reducing sugar.
Fig. III F-1: Pseudo-first order plots at 40°C

\[ [\text{IO}_4^-] = 2.0 \times 10^{-3}, \ [S] = 0.2\times10^{-2}, \ [\text{OH}^-] = 1.0 \text{ and} \]

\[ [\text{RuCl}_3] = \text{Nil, 1.5, 3.0, 4.5, 6.0 and 9.0} \times 10^{-4}, \]

in a, b, c, d, e and f respectively, \( \mu = 4.0 \)
Concentrations are in mol dm\(^{-3}\).
Effect of [RuCl₃]; oxidation of Glucose;

\[ k_{\text{cat}} \times 10^4 \text{ (s}^{-1}) = 1.80 \text{ for } a \]
\[ = 2.95 \text{ for } b \]
\[ = 4.79 \text{ for } c \]
\[ = 5.40 \text{ for } d \]
\[ = 6.97 \text{ for } e \]
\[ = 9.03 \text{ for } f \]

**Fig. III F-2**: Pseudo-first order plots at 40°C

\([\text{IO}_3^-] = 2.0 \times 10^{-3}, [S] = 0.2 \times 10^{-2}, [\text{OH}^-] = 1.0\) and

\([\text{RuCl}_3] = \text{Nil}, 1.5, 3.0, 4.5, 6.0\) and \(9.0 \times 10^{-4}\),

in a, b, c, d, e and f respectively, \(\mu = 4.0\).

Concentrations are in mol dm\(^{-3}\).
Fig. III F-3: Pseudo-first order plots at 40°C

\[ \text{[IO}_4^-\text{]} = 2.0 \times 10^{-3}, \text{[S]} = 0.2 \times 10^{-2}, \text{[OH}^-\text{]} = 1.0 \text{ and} \]

\[ \text{[RuCl}_3\text{]} = \text{Nil, 1.5, 3.0, 4.5, 6.0 and 9.0 \times 10^{-4},} \]

in a, b, c, d, e and f respectively, \( \mu = 4.0 \)

Concentrations are in mol dm\(^{-3}\).
Effect of \([\text{RuCl}_3]\); oxidation of Maltose;

\[ k_{\text{obs}} \times 10^4 \text{ (s}^{-1}) \]
- 1.40 for a
- 3.19 for b
- 5.11 for c
- 6.39 for d
- 8.52 for e
- 11.81 for f

Fig. III F-4: Pseudo- first order plots at 40°C

\([\text{IO}_4^{-}] = 2.0 \times 10^{-3}, \ [\text{S}] = 0.2\times10^{-3}, \ [\text{OH}^{-}] = 1.0 \text{ and}
\ [\text{RuCl}_3] = \text{Nil, 1.5, 3.0, 4.5, 6.0 and 9.0} \times 10^{-4},
\]
in a, b, c, d, e and f respectively, \( \mu = 4.0 \)

Concentrations are in mol dm\(^{-3}\).
Fig. III F-5: Pseudo-first order plots at 40°C

\[ [\text{IO}_4^-] = 2.0 \times 10^{-3}, [S] = 0.2 \times 10^{-2}, [\text{OH}^-] = 1.0 \text{ and} \]

\[ [\text{RuCl}_3] = \text{Nil, 1.5, 3.0, 4.5, 6.0 and 9.0} \times 10^{-4}, \]

in a, b, c, d, e and f respectively, \( \mu = 4.0 \)

Concentrations are in mol dm\(^{-3}\).
III G. Effect of temperature on the Rate of Oxidation:

To investigate the effect of temperature on the reaction rate and to determine activation parameters, the kinetic runs were made at four different temperatures viz. 35, 40, 45 and 50°C. The concentrations of all the reactants were kept constant as mentioned in corresponding Tables III-21 to III-25.

The volume of hypo required for titration of 5 ml of reaction mixture at different time intervals for each kinetic run was determined. With the help of these data, the log \((a-x)\) versus time plots i.e. pseudo-first order plots in metaperiodate have been obtained. The results are represented in Figures III G-1 to III-G-5.
<table>
<thead>
<tr>
<th>[RuCl₃] x 10⁴</th>
<th>FR (A)</th>
<th>GL (B)</th>
<th>GA (C)</th>
<th>MA (D)</th>
<th>LA (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>1.20</td>
<td>1.80</td>
<td>1.91</td>
<td>1.40</td>
<td>1.80</td>
</tr>
<tr>
<td>1.5</td>
<td>3.30</td>
<td>2.95</td>
<td>3.45</td>
<td>3.19</td>
<td>3.07</td>
</tr>
<tr>
<td>3.0</td>
<td>5.48</td>
<td>4.79</td>
<td>4.98</td>
<td>5.11</td>
<td>3.83</td>
</tr>
<tr>
<td>4.5</td>
<td>8.08</td>
<td>5.40</td>
<td>5.75</td>
<td>6.39</td>
<td>4.26</td>
</tr>
<tr>
<td>6.0</td>
<td>9.59</td>
<td>6.97</td>
<td>7.29</td>
<td>8.52</td>
<td>5.11</td>
</tr>
<tr>
<td>9.0</td>
<td>13.95</td>
<td>9.03</td>
<td>9.59</td>
<td>11.81</td>
<td>6.97</td>
</tr>
</tbody>
</table>

[IO₄⁻] = 2.0 x 10⁻³; [Substrate] = 2.0 x 10⁻²; (OH⁻) = 0.10 for A, B and C; 0.20 for D and E;
The concentration of reactants are in mol Dm⁻³.
Fig. III F-6 : Pseudo of $k_{\text{obs}}$ Vs $[\text{RuCl}_3]$ at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$, $[\text{S}] = 2.0 \times 10^{-2}$

$[\text{OH}^-] = 0.1$ for A, B and C; 0.2 for D and E

Concentrations are in mol dm$^{-3}$. 

(77)
The pseudo-first order rate constant ($K_{obs}$) obtained from log $(a-x)$ versus time plots at different temperatures in case of various reducing sugars are summarized in Table—III G.1.

It is observed from the Table III G-1 that ($K_{obs}$) increases on increasing temperature with a temperature coefficient = 2.12, 2.96, 2.42, 2.86, 2.63 in case of fructose, glucose, galactose, maltose and lactose, respectively.

In order to determine the energy of activation of the reaction ($E_{act}$), the Arrhenius plot i.e. plot of log ($K_{obs}$) versus $1/T$ was plotted in each case. (Figure—III G-6). From the slope of the Arrhenius plot the value of $E_{act}$ ($E_{act} = 2.303 \times R \times$ slope) has been evaluated.

The other activation parameters have also been evaluated using the following relations:

$$\Delta H^* = E_{act} - RT \quad \text{(i)}$$

$$K_{obs} = \frac{K_b T}{h} \ e^{\frac{\Delta S^*}{R}} \ e^{-\frac{E_{act}}{RT}} \quad \text{(ii)}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad \text{(iii)}$$

Where, $R$ = Gas constant

$h$ = Planck's Constant

$k_b$ = Boltzmann constant

$\Delta S^*$ = Entropy change

$\Delta H^*$ = Enthalpy change

$\Delta G^*$ = Gibb's free energy change

(78)
Fig. III G-1: Pseudo first order plots

\[ [\text{IO}_4^-] = 2.0 \times 10^{-3}, \quad [\text{OH}^-] = 1.0, \quad [\text{RuCl}_3] = 3.0 \times 10^{-4} \]

Nil, 1.5, 3.0, 4.5, 6.0 and 9.0 \( \times 10^{-4} \),

\[ [S] = 0.2 \times 10^{-2}, \quad \text{and temp.} = 35, 40, 45 \text{ and } 50^\circ \text{C} \]

in a, b, c, and d respectively

Concentrations are in mol dm\(^{-3}\).
Fig. III G-2: Pseudo first order plots

\[ [\text{IO}_4^-] = 2.0 \times 10^{-3}, [\text{OH}^-] = 1.0, \ [\text{RuCl}_3] = 3.0 \times 10^{-4} \]
Nil, 1.5, 3.0, 4.5, 6.0 and 9.0 \( \times 10^{-4} \),
\[ [\text{S}] = 0.2 \times 10^{-2}, \text{ and temp.} = 35, 40, 45 \text{ and } 50^\circ \text{C} \]
in a, b, c, and d respectively.
Concentrations are in mol dm\(^{-3}\).
Fig. III G-3 : Pseudo first order plots

\[ [\text{IO}_4^-] = 2.0 \times 10^{-3}, \ [\text{OH}^-] = 1.0, \ [\text{RuCl}_3] = 3.0 \times 10^{-4} \]

Nil, 1.5, 3.0, 4.5, 6.0 and 9.0 \( \times 10^{-4} \),
\[ [\text{S}] = 0.2 \times 10^{-2}, \ \text{and temp.} = 35, 40, 45 \text{ and } 50^\circ \text{C} \]
in a, b, c, and d respectively
Concentrations are in mol dm\(^{-3}\).
Fig. III G-4: Pseudo first order plots

\[ [\text{IO}_4^-] = 2.0 \times 10^{-3}, \quad [\text{OH}^-] = 1.0, \quad [\text{RuCl}_3] = 3.0 \times 10^{-4} \]

Nil, 1.5, 3.0, 4.5, 6.0 and 9.0 \( \times \) 10\(^{-4}\),

\[ [\text{S}] = 0.2 \times 10^{-2}, \quad \text{and temp.} = 35, 40, 45 \text{ and } 50^\circ C \]
in a, b, c, and d respectively

Concentrations are in mol dm\(^{-3}\).
Fig. III G-5: Pseudo first order plots

\[ [\text{IO}_4^-] = 2.0 \times 10^{-3}, \ [\text{OH}^-] = 1.0, \ [\text{RuCl}_3] = 3.0 \times 10^{-4} \]

Nil, 1.5, 3.0, 4.5, 6.0 and 9.0 \times 10^{-4},

\[ [S] = 0.2 \times 10^{-2}, \ \text{and temp.} = 35, 40, 45 \text{ and } 50^\circ C \]

in a, b, c, and d respectively

Concentrations are in mol dm\(^{-3}\).
The activation parameters are summarized in Table III-G-2. It is observed from Table III G-2 that $\Delta G^\#$ is almost same ($\sim 94.34^\circ \pm 1.0$ kJmol$^{-1}$) for all reducing sugars suggesting that the oxidation of reducing sugars follow almost a common mechanism.
III H. Influence of Ionic Strength:

The effect of ionic strength on the rate of oxidation of each reducing sugars has also been investigated by adding different amount of sodium perchlorate (NaClO₄) in the reaction mixture. The reactants concentrations were kept constant as mentioned in Table-III-26 to III-30 in which result of effect of NaClO₄ are presented.

The observed pseudo-first order rate constants is metaperiodate ($k_{obs}$) at different initial concentrations of sodium perchlorate obtained from the slopes of straight lines plotted between log (a−x) versus times are summarized in Table — III H—1.
### Table - III G-1: Effect of Temperature on the rate constants.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>FR (A)</th>
<th>GL (B)</th>
<th>GA (C)</th>
<th>MA (D)</th>
<th>LA (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>4.38</td>
<td>1.91</td>
<td>3.19</td>
<td>2.55</td>
<td>2.13</td>
</tr>
<tr>
<td>40</td>
<td>5.48</td>
<td>4.79</td>
<td>4.98</td>
<td>5.11</td>
<td>3.83</td>
</tr>
<tr>
<td>45</td>
<td>8.52</td>
<td>6.97</td>
<td>7.29</td>
<td>7.67</td>
<td>5.90</td>
</tr>
<tr>
<td>50</td>
<td>12.70</td>
<td>10.96</td>
<td>12.79</td>
<td>13.95</td>
<td>9.59</td>
</tr>
<tr>
<td>(Temp coefficient) average</td>
<td>2.12</td>
<td>2.96</td>
<td>2.42</td>
<td>2.86</td>
<td>2.63</td>
</tr>
</tbody>
</table>

\[ [\text{IO}_4^{-}] = 2.0 \times 10^{-3};  [\text{Substrate}] = 2.0 \times 10^{-2};  [\text{OH}^-] = 0.10 \text{ for A, B and C};  0.20 \text{ for D and E};  [\text{RuCl}_3] = 3.0 \times 10^{-4}. \]

The concentration of reactants are in mol Dm\(^{-3}\).
Fig. III G-6: Arrhenius plots of log ($k_{obs}$) Vs 1/T

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$, $[S] = 2.0 \times 10^{-2}$
$[\text{OH}^-] = 0.10$ for A, B and C; 0.20 for D and E
$[\text{RuCl}_3] = 3.0 \times 10^{-4}$

Concentrations are in mol dm$^{-3}$.
Table - III G-2: Activation parameters for the oxidation of reducing sugars in presence of RuCl₃.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( E_{act} ) ( \text{(KJ mol}^{-1}\text{)} )</th>
<th>( \text{log A} ) ( \text{(KJ mol}^{-1}\text{)} )</th>
<th>( \Delta H^# ) ( \text{(KJ mol}^{-1}\text{)} )</th>
<th>( \Delta S^# ) ( \text{(KJ mol}^{-1}\text{)} )</th>
<th>( \Delta G^# ) ( \text{(KJ mol}^{-1}\text{)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, Fructose</td>
<td>58.80 ± 0.50</td>
<td>6.58 ± 0.02</td>
<td>56.17 ± 0.50</td>
<td>-119.17 ± 1.0</td>
<td>93.77 ± 1.0</td>
</tr>
<tr>
<td>B, Glucose</td>
<td>76.50 ± 0.50</td>
<td>9.35 ± 0.02</td>
<td>73.84 ± 0.50</td>
<td>-66.09 ± 0.50</td>
<td>94.72 ± 1.0</td>
</tr>
<tr>
<td>C, Galactose</td>
<td>63.79 ± 0.50</td>
<td>7.35 ± 0.02</td>
<td>61.17 ± 0.50</td>
<td>-104.44 ± 0.50</td>
<td>94.22 ± 1.0</td>
</tr>
<tr>
<td>D, Maltose</td>
<td>69.59 ± 0.50</td>
<td>8.30 ± 0.02</td>
<td>66.96 ± 0.50</td>
<td>-86.22 ± 1.0</td>
<td>94.16 ± 1.0</td>
</tr>
<tr>
<td>E, Lactose</td>
<td>85.05 ± 0.50</td>
<td>10.75 ± 0.03</td>
<td>82.42 ± 0.50</td>
<td>-39.45 ± 0.50</td>
<td>94.87 ± 1.0</td>
</tr>
</tbody>
</table>

\[ [IO_4^{-}] = 2.0 \times 10^{-3}; \text{[Substrate]} = 2.0 \times 10^{-2}; \text{[OH}^{-}] = 0.10 \text{ for A, B and C; 0.20 for D and E;} \text{[RuCl}_3] = 3.0 \times 10^{-4}. \]

The concentration of reactants are in mol Dm\(^{-3}\).
It is evident from Table III H−1 that an addition of sodium perchlorate (NaClO₄) up to 0.2 M for fructose, glucose, galactose and 0.4 M for maltose and lactose) in the reaction mixture resulted an insignificant effect of the ionic strength on the observed pseudo-first order rate constant. Therefore, it may be concluded that at least one neutral species in involved (as one of the reactant) in the rate determining step of the mechanism.
Table - III H - 1: Effect of addition of [Sodium perchlorate] on the rate constants at 40°C

<table>
<thead>
<tr>
<th>[Sodium perchlorate]</th>
<th>FR (A)</th>
<th>GL (B)</th>
<th>GA (C)</th>
<th>[Sodium perchlorate]</th>
<th>MA (D)</th>
<th>LA (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>5.48</td>
<td>4.98</td>
<td>Nil</td>
<td>5.11</td>
<td>3.83</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>5.48</td>
<td>4.98</td>
<td>4.98</td>
<td>10</td>
<td>5.11</td>
<td>3.83</td>
</tr>
<tr>
<td>10.0</td>
<td>5.94</td>
<td>4.98</td>
<td>5.18</td>
<td>20</td>
<td>5.56</td>
<td>4.03</td>
</tr>
<tr>
<td>15.0</td>
<td>6.14</td>
<td>5.37</td>
<td>5.18</td>
<td>30</td>
<td>5.75</td>
<td>4.22</td>
</tr>
<tr>
<td>20.0</td>
<td>6.14</td>
<td>5.56</td>
<td>5.37</td>
<td>40</td>
<td>5.94</td>
<td>4.41</td>
</tr>
</tbody>
</table>

[IO₄⁻] = 2.0 × 10⁻³; [Substrate] = 2.0 × 10⁻²; (OH⁻) = 0.10 for A, B and C; 0.20 for D and E; [RuCl₃] = 3.0×10⁻⁴.

The concentration of reactants are in mol Dm⁻³.
III. I. Evidence for complex Formation:

The ability of platinum group metal-ions to form complexes with organic substances in well reported in the literature 69-71. Spectrophotometric evidence for the formation of ruthenium (III) complex of metaperiodate and reducing sugars has been obtained in alkaline medium. All the studies have been made on spectronic-20 spectrophotometer (MILTON ROY & COMP.)

It was observed that ruthenium (III) chloride in the present oc NaOH and sodium metaperiodate absorbs maximum at 390 nm. The absorbance of sodium metaperiodate at 390 nm was negligible. A series of solutions were prepared containing a fixed amount of RuCl₃ (3.80x10⁻⁴ mol dm⁻³), NaOH (0.1 mol dm⁻³) and varying amounts of sodium metaperiodate. The absorbance of these solutions were measured at 390 nm at room temperature. The absorbance at different [IO₄⁻] are recorded in Table — III I -1. The plot of (absorbance) versus [IO₄⁻] 390 nm is represented in Figure. III I -1 (a). It is observed from the Figure (III I -1a) that the absorbance of mixture decreases linearly until the ratio of [Ru³⁺]/[[IO₄⁻]] nearly becomes unity, after that the absorbance of the mixtures slightly increases. The results indicate the formation of 1:1 complex between ruthenium (III) and IO₄⁻ that is the [Ru³⁺—IO₄⁻] complex.

The possibility of the formation of complex between ruthenium (III) and reducing sugars was also tested in the similar manner by replacing sodium metaperiodate by reducing sugar in above solutions. No complex formation was observed at room temperature.
(there was no change in absorbance.) However, when these solutions were heated at ~60°C for about 15 minutes, allowed to cool at room temperature and then the absorbance were obtained at 390 nm, a change in absorbance of the solutions was observed. The results are given in Table—III I—1, and represented graphically in form of plot between (Absorbance) and [Reducing sugar] [Figure. III I—1 (b)]. The formation of 1:1 complex between ruthenium (III) and reducing sugar is also indicated from Figure. III I-1 (b). However, the complex between ruthenium (III) and reducing sugar under the similar conditions is observed only at high temperature (~60°C) while that between ruthenium (III) and IO⁻⁴ has been observed at low temperature (~35°C). The formation of 1:1 complex between ruthenium (III) and various oxidants i.e. \{RU^{III}—Bromide ion\} Complex ⁷² and \{Ru^{III}—IO⁻⁴\}⁷³⁻⁷⁴ complex is also reported in the literature.
III. J. Kinetic Results at a Glance:

The kinetics of ruthenium (III) catalysed oxidation of reducing sugars viz. D(+)-glucose, D(+)-galactose, D(-)-fructose, maltose and lactose by sodium metaperiodate have been studied in alkaline medium. The reaction followed almost a similar kinetics. The results may be summarised as follows:

- The order of reaction with respect of sodium metaperiodate was found to be unity during a particular kinetic run. However, the observed rate constant ($K_{obs}$) was found to decrease with an increase in [IO$^{-}_4$].

- The results of effect of substrate and OH$^-$ on the rate of oxidation was similar. The reaction was first order in substrate of OH$^-$ at lower concentrations. However the order of reaction decreases from unity to zero at higher (Substrate) or [OH$^-$].

- The rate is proportional to $[k' + k'' [RuCl_3]]$ where $k'$ and $k''$ are rate constant for uncatalysed and catalysed path, respectively. The reactions were also proceeding in absence of the catalyst. However, in absence of the catalyst, the reactions were found to be extremely slow. The observed rate constant for uncatalysed path ($k'$) i.e. $k_{obs}$ at (RuCl$_3$) = 0 was matching with the value of intercept of the plot of ($k_{obs}$) versus (RuCL$_3$) in case of each reducing sugar.

- Effect of temperature has been studied at four different temperatures (35, 40, 45 and 50°C) and activation parameters
Table III I-1: Absorbance of reaction mixture at 390 nm.

<table>
<thead>
<tr>
<th>[IO₄⁻] x 10⁴</th>
<th>[RuCl₃] = 3.0x10⁻⁴ M (OH⁻) = 0.10 M, at room temperature</th>
<th>[Fructose] x 10⁴</th>
<th>[RuCl₃] = 3.0x10⁻⁴ M (OH⁻) = 0.10 M, after heating the solutions at 60°C for 15 min then cooling at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>Absorbance</td>
<td>M</td>
<td>Absorbance</td>
</tr>
<tr>
<td>Nil</td>
<td>0.94</td>
<td>Nil</td>
<td>1.20</td>
</tr>
<tr>
<td>1.0</td>
<td>0.80</td>
<td>1.0</td>
<td>1.15</td>
</tr>
<tr>
<td>2.0</td>
<td>0.66</td>
<td>2.0</td>
<td>1.05</td>
</tr>
<tr>
<td>3.0</td>
<td>0.50</td>
<td>4.0</td>
<td>0.91</td>
</tr>
<tr>
<td>4.0</td>
<td>0.38</td>
<td>6.0</td>
<td>0.93</td>
</tr>
<tr>
<td>5.0</td>
<td>0.14</td>
<td>8.0</td>
<td>0.96</td>
</tr>
<tr>
<td>6.0</td>
<td>0.45</td>
<td>10.0</td>
<td>0.98</td>
</tr>
<tr>
<td>8.0</td>
<td>0.51</td>
<td>12.0</td>
<td>1.00</td>
</tr>
<tr>
<td>10.0</td>
<td>0.58</td>
<td>16.0</td>
<td>1.10</td>
</tr>
<tr>
<td>12.0</td>
<td>0.60</td>
<td>18.0</td>
<td>1.10</td>
</tr>
<tr>
<td>16.0</td>
<td>0.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.0</td>
<td>0.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. III I-1 :  (a) Plot of Absorbance Vs $[\text{IO}_4^-]$ at room temperature  
(b) Plot of Absorbance Vs [Fructose] at 60°C
have been evaluated (Table — III G—2). The same value of \( \Delta G^\# \) (94.34± 1.0 kJ mol\(^{-1}\)) suggests the operation of a common mechanism for the oxidation process.

- The negligible effect of ionic strength was observed on the rate of reaction in case of each reducing sugars, suggesting involvement of at least one neutral species in rate determining step.

- At room temperature, the formation of \([\text{Ru}^{III} – \text{IO}_4^-]\) complex has been confirmed by spectrophotometric evidence. It has also been observed that the complex between ruthenium (III) and reducing sugar under the similar conditions is also formed but at very high temperature.

- The reaction products were identified in both the conditions i.e. under the kinetic conditions and under stoichiometric condition. Under the kinetic conditions the formaldehyde and corresponding lower-acid was detected as the oxidation products of the reducing sugars. Under the stoichiometric condition, the formaldehyde is further oxidised in presence of excess of oxidant.
III. K. Reacting species:

Reactive species of catalysts:

The electronic spectrum of ruthenium trichloride has shown\(^{75-77}\) that exists in the hydrated form as \([\text{Ru(H}_2\text{O)}_6]^{3+}\). In alkaline medium the metal ions \([\text{Ru(H}_2\text{O)}_6]^{3+}\) are known\(^{78}\) to exist as \([\text{Ru(OH}^-)(\text{H}_2\text{O})_5]^{2+}\).

A general formula \([\text{Ru(OH)}_x(\text{H}_2\text{O})_{6-x}]^{(3-x)+}\) where \(x < 6\) in place of \([\text{Ru(OH)(H}_2\text{O})_5]^{2+}\) has also been considered in some case, yet there is no evidence for existence of the hexahydroxo species of ruthenium (III). Connick and Find\(^{77}\) showed that the aqueous solution of \(\text{RuCl}_3\) contains the species \(\text{RuCl}_2^+\) which exists as the cis and trns-hydrated complexes, \((\text{RUCl}_2(\text{H}_2\text{O})_4)^{2+}\), \([\text{RuCl}_2(\text{H}_2\text{O})_4]^{2+}\) and \([\text{RuCl}_4(\text{H}_2\text{O})_2]^{-}\) have not been given importance. In alkaline medium generally \([\text{Ru(H}_2\text{O)}_5(\text{OH}^-)]^{2+}\) has been considered\(^{79}\) as the reactive species of the catalyst according to the following equilibrium,

\[
[\text{Ru(H}_2\text{O)}_6]^{3+} + \text{OH}^- \rightleftharpoons [\text{Ru(H}_2\text{O)}_5(\text{OH}^\text{I})]^{2+} + \text{H}_2\text{O}
\]

\([\text{Ru(H}_2\text{O)}_5(\text{OH}^-)]^{2+}\) can undergo further substitution by hydroxide ion in higher alkali concentration. In the present investigations, therefore, the species \([\text{Ru(H}_2\text{O)}_5(\text{OH}^-)]^{2+}\) has been considered as the reactive species of the catalyst i.e. ruthenium (III).

Reactive species of periodate:

\(\text{IO}_4^-\) is a powerful oxidising agent both in acidic and basic
media. Crouthamel et al.\textsuperscript{80} suggested the following equilibria in aqueous solutions of periodate, which are pH controlled,

\[
\begin{align*}
\text{H}_5\text{IO}_6^- & \rightleftharpoons K_a \text{H}_4\text{IO}_6^- + \text{H}^+ \quad (a) \\
\text{H}_4\text{IO}_6^- & \rightleftharpoons K_b \text{H}_3\text{IO}_6^{2^-} + \text{H}^+ \quad (b) \\
\text{H}_3\text{IO}_6^{2^-} & \rightleftharpoons K_c \text{H}_4\text{IO}_6^{3^-} + \text{H}^+ \quad (c)
\end{align*}
\]

The dissociation constants $K_a$, $K_b$ and $K_c$ at 25°C are reported\textsuperscript{81} to be $2.3 \times 10^{-2}$, $4.35 \times 10^{-9}$ and $1.5 \times 10^{-15}$, respectively.

Amount the above species the periodic acid $\text{H}_5\text{IO}_6^-$ exist in acidic media and $\text{H}_4\text{IO}_6^-$ near pH $-7$.\textsuperscript{82} The UV and Raman spectral studies\textsuperscript{83–86} indicate that in aqueous acid media (>5M), periodate mainly exists in the form of tetrahedral ($\text{IO}_4^-$) and the octahedral ($\text{H}_4\text{IO}_6^-$ and $\text{H}_5\text{IO}_6^-$). At higher acidities protonated species $\text{H}_6\text{IO}_6^+$ or I(OH)$_6^+$ exists. Galliford et al.\textsuperscript{85} reported that at pH <2 the dilute periodate solutions are mainly in the form of $\text{H}_5\text{IO}_6^-$ and IO$_4^-$. However, in the alkaline medium the solubility of sodium metaperiodate decreases with increase in [alkali]. The literature recorded and insolation of many species of periodate viz. IO$_4^-$, [O$_4$I−O−IO$_4$]$^{4-}$, [H$_3$IO$_6$]$^{2-}$ and (H$_4$IO$_6$)$^-$ . In alkaline medium the monoanion H$_4$IO$_6^-$ species as reactive species of IO$_4^-$ has been considered by several workers\textsuperscript{87–88}. However, in the pH range employed in the present investigations, the reactive species of the oxidant are expected to be (H$_3$IO$_6^{2-}$) and (H$_2$IO$_6^{3-}$) with the following equilibrium,
\[ H_3IO_6^- + OH^- \quad \text{H}_2\text{IO}_6^3^- + H_2O \] (d)

**Reactive species of sugars:**

In alkaline solution, sugars undergo enolization to form the enediolate\(^{89}\) anion as,

\[
\begin{array}{c}
\text{RCH(OH)}\text{CHO} \\
\text{Reducing sugar} \\
\uparrow \quad \downarrow \\
\text{R(OH)C} = \text{CH(OH)} \\
\text{Enediol} \\
\uparrow \quad \downarrow \\
\text{OH}^- \quad \text{H}_2\text{O} \\
\text{R(OH)C} = \text{CHO} \\
\text{Enediol anion (E}^-\text{)}
\end{array}
\] (e)

In absence of other reactants these enediol undergo epimerisation and insomersation (Lobry de—Bruyun Alberda Van Ekenstein transformation) to form a mixture of aldoses and ketoses\(^{89}\). Isbell and coworkers\(^{90}\) Proposed that aldoses and ketoses generally yield mixture of \(Z\)— and \(E\)—enediols, the proportionality of which differ from sugar to sugar and experimental conditions viz. strength, nature of alkali and temperature etc. However, the enediol anion reacts with oxidant to form an intermediate\(^{30,36,38-40,91}\) which in turn
undergoes cleavage to form products. Therefore, in present investigations the enediol anion of the sugar has been considered as the reacting species of the reducing sugar.
III L. Mechanism for Oxidation process:

On the basis of the reported literature, experimental results and evidence for the complex formation between ruthernium (III) and IO₄⁻, a common mechanism for the oxidation of reducing sugars by IO₄⁻ in presence of ruthernium (III) may be summarised as given in Scheme—I

Scheme—I

\[ \text{(S)} \quad \text{(E)} \quad \text{(E')} \]

(i)

\[ R - C - C = O \rightleftharpoons R - C = C - H \quad \text{K}_1 \quad \text{OH}^- \quad \text{OH} \quad \text{O}^- \]

(ii)

\[ \text{H}_3\text{IO}_6^- + \text{OH}^- \xrightarrow{\text{K}_2} \text{H}_2\text{IO}_5^+ + \text{H}_2\text{O} \]

(iii)

\[ \text{C}_1 \quad \text{C}_2 \quad \text{C}_3 \]

\[ \text{[Ru(H}_2\text{O})_6]^{3+} + \text{OH}^- \xrightarrow{\text{K}_3} \text{[Ru(H}_2\text{O})_5(\text{OH}^-)]^{2+} + \text{H}_2\text{O} \]

(iv)

\[ \text{C}_2 + \text{C}_4 \xrightarrow{\text{K}_4} \]

\[ \left[ \begin{array}{c} \text{O} \\ \\ \text{O} \\ \\ \text{O} \end{array} \right] \text{Ru}^{II}(\text{H}_2\text{O})_3 \quad \text{+ OH}^- \]

(v)

\[ \text{C}_3 + \text{E'} \xrightarrow{\text{K}_5} \]

\[ \left[ \begin{array}{c} \text{OH} \\ \\ \text{R} - \text{C} - \text{O} \\ \\ \text{H} - \text{C} - \text{O} \end{array} \right] \text{Ru}^{II}(\text{H}_2\text{O})_3 \quad \text{O} \quad \text{OH} \quad \text{OH} \quad \text{OH} \\
\]

\[ \text{X} \xrightarrow{\text{k}} \text{RCOO}^- + \text{HCHO} + \text{[Ru(OH)}^- \text{(H}_2\text{O})_3]^{2+} + \text{IO}_3^- + \text{OH}^- \]

(101)
III M. Derivation of Rate Law:

According to scheme I, the rate of disappearance of $[\text{IO}_4^-]$ may be obtained as,

$$-\frac{D[\text{IO}_4^-]}{dt} = k [X]$$  \hspace{1cm} (1)

considering the total concentration of $\text{IO}_4^-$ may be obtained as,

$$[\text{IO}_4^-] = [C_1] + [C_2]$$  \hspace{1cm} (2)

Where $[C_2] = K_2 \cdot [\text{OH}^-] \cdot [C_1]$  

($K_2$ also includes water molecule)

$[C_2]$ in terms of $[\text{IO}_4^-]$, may be obtained as,

$$[C_2] = \frac{K_2 [\text{IO}_4^-] [\text{OH}^-]}{\{1 + K_2 [\text{OH}^-]\}}$$  \hspace{1cm} (3)

Again the total concentration of the catalyst at any time in given by,

$$[\text{Cat}]_t = [C_3] + [C_4] + [C_5] + (X)$$  \hspace{1cm} (4)

where,

$$[C_4] = K_3 \cdot [C_3] \cdot [\text{OH}^-]$$  \hspace{1cm} (5)

($K_3$ also includes water molecule)

$$[C_5] = \frac{K_4 [C_2] C_4}{[\text{OH}^-]}$$

$$= \frac{K_2 K_3 K_4 [\text{OH}^-] [\text{IO}_4^-] [C_3]}{\{1 + K_2 [\text{OH}^-]\}}$$  \hspace{1cm} (6)

and
\[(X) = K_5 [C_3][E^-]
\]

(where \([E^-] = K_1 [S] [OH^-]\) from step (i))

or,

\[\begin{align*}
[X] &= \frac{K_1 K_2 K_3 K_4 K_5 [OH^-]^2 [IO^-_4][S][C_3]}{[1 + K_2 [OH^-]]} \\
&= \frac{kK_1 K_2 K_3 K_4 K_5 [OH^-]^2 [S][Cat]_t [IO^-_4]_t}{[1 + K_2 [OH^-]] ([1 + K_2 [OH^-]] + K_2 K_3 [OH^-] [IO^-_4]_t [1 + K_1 K_3 [S] [OH^-]])}
\end{align*}\]  

(7)

Thus, finding the value of \([X]\) in terms of \([Cat]_t\), the rate of disappearance of \([IO^-_4]\) has been obtained as,

\[- \frac{d[IO^-_4]}{dt} = \frac{kK_1 K_2 K_3 K_4 K_5 [OH^-]^2 [S][Cat]_t [IO^-_4]_t}{[1 + K_2 [OH^-]] ([1 + K_2 [OH^-]] + K_2 K_3 [OH^-] [IO^-_4]_t [1 + K_1 K_3 [S] [OH^-]])}\]  

(8)

taking \((K_2 + K_3 [OH^-]) + K_2 K_3 [OH^-] >> 1\)

and \(K_1 K_3 [S] [OH^-] >> 1\), as suitable approximations in denominator of eq (8), the rate law (8) reduces to,

\[- \frac{d[IO^-_4]}{dt} = \frac{kK_1 K_2 K_3 K_4 K_5 [OH^-]^2 [S][Cat]_t [IO^-_4]_t}{(K_2 + K_3) + K_2 K_3 [OH^-] + K_1 K_2 K_3 K_4 K_5 [S] [OH^-] [IO^-_4]_t}\]  

(9)

or

\[- \frac{d[IO^-_4]}{dt} = \frac{kK' [OH^-] [S][Cat]_t [IO^-_4]_t}{(K_2 + K_3) + K_2 K_3 [OH^-] + K' [S] [OH^-] [IO^-_4]_t}\]  

(10)

where, \(K' = K_1 K_2 K_3 K_4 K_5\).
III N. Rate Law and experimental Results:

The rate law (10) is in agreement with the experimental results, i.e. first order dependence of rate with respect to each, i.e. substrate, OH\(^{-}\) and oxidant at lower concentrations. The decrease in the observed rate constant (\(k_{obs}\)) with an increase [IO\(^{-}\)] and a decrease in the order of reaction with respect to OH\(^{-}\) and substrate at higher [OH\(^{-}\)] and [substrate], respectively. The rate law is also indicates that the order of reaction with respect to catalyst is always unity. Thus the proposed mechanism and corresponding rate law explain all the experimental results.