Chapter - V

Conclusion
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The oxidation of five reducing sugars viz. glucose, fructose, galactose, maltose and lactose by sodium metaperiodate in presence of RuCl₃ have been studied (Chapter III). The kinetic result and proposed mechanism in presence of the catalyst are summarised as follows:

1. Effect of oxidant on the rate:

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

2. Effect of substrate on the rate:

The reaction was first order in substrate as lower concentrations. However, the order of reaction decreases from unity to zero at higher [substrate].

3. Effect of alkali on the rate:

The order of reaction with respect to alkali was found to be unity at lower [OH⁻]. The order of reaction at higher [OH⁻] decreases from unity to zero.

4. Effect of catalyst on the rate:

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

5. Ionic effect

Negligible effect of ionic strength was observed.

6. Oxidation products

**kinetic conditions**

Under the experimental conditions of the kinetic the reducing sugar oxidised to formaldehyde and corresponding lower aldonic acid. Under the stoichiometric conditions the formaldehyde is further oxidised in presence of excess of the oxidant.

7- **Activation parameter:**

<table>
<thead>
<tr>
<th></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>( E_{\text{act}} ) (kJ mol(^{-1}))</td>
<td>58.80</td>
<td>± 0.50</td>
<td>63.79</td>
<td>69.59</td>
<td>± 0.50</td>
</tr>
<tr>
<td>log ( A )</td>
<td>6.58</td>
<td>9.35</td>
<td>7.35</td>
<td>8.30</td>
<td>10.75</td>
</tr>
<tr>
<td>( \Delta H^# ) (kJ mol(^{-1}))</td>
<td>56.17</td>
<td>± 0.50</td>
<td>61.17</td>
<td>66.96</td>
<td>± 0.50</td>
</tr>
<tr>
<td>( \Delta S^# ) (JK(^{-1}) mol(^{-1}))</td>
<td>-119.17</td>
<td>± 1.0</td>
<td>-104.44</td>
<td>-86.22</td>
<td>± 0.50</td>
</tr>
<tr>
<td>( \Delta G^# ) (kJ mol(^{-1}))</td>
<td>93.77</td>
<td>± 1.0</td>
<td>94.22</td>
<td>94.16</td>
<td>94.87</td>
</tr>
</tbody>
</table>

(203)
8. Reactive species:

(a) Oxidant

In the pH range employed in the present investigations, the reactive species of the oxidant are expected to be \((\text{H}_3\text{IO}_6^{2-})\) and \((\text{H}_2\text{IO}_6^{3-})\) with the following equilibrium

\[
\text{H}_3\text{IO}_6^{2-} + \text{OH}^- \xrightleftharpoons{K} \text{H}_2\text{IO}_6^{3-} + \text{H}_2\text{O}
\]

(b) Substrate

In present investigations, the enediol anion of the sugar has been considered as the reacting species of reducing sugar.

(c) Catalyst

The species \([\text{Ru(H}_2\text{O})_5\text{(OH)}^-]^2+\) has been observed as the reactive species of the catalyst.

9. Complex formation studies

The formation of the \([\text{Ru}^{III} - \text{IO}_4^-]\) complex has been confirmed by spectrophotometric evidence.

10. Proposed mechanistic steps:

\[
\begin{array}{cccccc}
\text{OH} & \text{H} & \text{OH} & \text{OH} & \text{OH} & \text{O} \\
| & | & | & | & |
\end{array}
\]

\[
\begin{array}{c}
\text{R} - \text{C} - \text{C} = \text{O} \Leftrightarrow \text{R} - \text{C} = \text{C} - \text{H} \xrightleftharpoons{K} \text{R} - \text{C} = \text{C} - \text{H} + \text{H}_2\text{O} \ (i) \\
\text{(H)} \\
\text{(S)} \\
\text{(E)} \\
\text{(E^-)}
\end{array}
\]
\[ \text{H}_2\text{IO}_6^{2-} + \text{OH}^- \xrightleftharpoons{K_2} \text{H}_2\text{IO}_6^{3-} + \text{H}_2\text{O} \]  (ii)

\[ \text{(C}_1\text{)} \quad \text{(C}_2\text{)} \]

\[ K_3 \]

\[ [\text{Ru(H}_2\text{O})_5]^{3-} + \text{OH}^- \xrightleftharpoons{K_4} [\text{Ru(H}_2\text{O})_5(\text{OH})]^{2-} + \text{H}_2\text{O} \]  (iii)

\[ \text{(C}_3\text{)} \]

\[ (\text{C}_2)+(\text{C}_4) \xrightleftharpoons{K_4} \]

\[ \begin{array}{c}
\text{O} \\
\text{O}^- \parallel \text{O} - \text{Ru}^{II}(\text{H}_2\text{O})_5 \\
\text{O}^- \\
\text{OH} \\
\text{OH} \\
\end{array} \]

\[ \text{+ OH}^- \]  (iv)

\[ (\text{C}_2)+(\text{C}_4) \xrightleftharpoons{K_5} \]

\[ \begin{array}{c}
\text{OH} \\
\text{R} - \text{C} - \text{O} \parallel \text{O} - \text{Ru}^{II}(\text{H}_2\text{O})_5 \\
\text{H} - \text{C} - \text{O} \\
\text{OH} \\
\text{O}^- \\
\end{array} \]  (v)

(205)
\[ k \]
\[ \xrightarrow{\text{RCOO}^- + \text{HCHO} + [\text{Ru(OH}^-) (\text{H}_2\text{O})_5]^2^- + \text{IO}_3^- + \text{OH}^-} \]  

11. Derived rate law on the basis of proposed mechanism:

The rate law which explains all the experimental results in presence of ruthenium (III) has been derived as follows:

\[
\frac{-d [\text{IO}_4^-]}{dt} = \frac{kK'[\text{OH}^-][S][\text{CAT}]_T[\text{IO}_4^-]_T}{(K_2 + K_3) + K_2K_3[\text{OH}^-] + K'[\text{OH}^-][S][\text{IO}_4^-]_T}
\]

The rate law also indicate that the order of reaction with respect to catalyst is always unity. On the basis of the above results and mechanism it may be concluded that retuenium (III) works as the catalyst in above reactions.
The oxidation of four amino alcohols viz. 2—amino ethanol, 3—amino proponol, diethanolamine and trithanolamine by sodium meta periodate in presence of ruthenium (III) catalyst in acidic medium have also been studied (Chapter IV).

The kinetic results and proposed mechanism in presence of the RuCl$_3$ are summarised as follows:

1. **Effect of variation in sodium metaperiodate concentration**

   The kinetic results suggest that observed rate constants remained nearly identical at various initial concentration of [IO$_4^-$] in case of each amino alcohol, which further confirmed first order dependence of rate with respect to [IO$_4^-$].

2. **Effect of variation in ruthenium (III) concentration**

   The results of the effect of ruthenium (III) concentration suggest that an increase in RuCl$_3$ concentration proportionally increases the observed pseudo first rate constant with respect to [IO$_4^-$].

   The plots of ($K_{obs}$) versus RuCl$_3$ figure (IV E—5) represent straight lines passing through origin. The reaction is, therefore, of first order with respect to RuCl$_3$ concentration.
3. **Effect of variation in amino alcohol concentrations:**

The results suggest that an increase in the initial concentration of amino alcohols resulted in a negligible effect on the rate constants. It therefore appears that the order of reaction in amino alcohol is zero.

4. **Effect of variation in perchloric acid concentrations**

The plots of \((k_{obs})\) versus \((HClO_4)\) figure IV F-5 showed a deviation from linearity while that plots of \(1/(k_{obs})\) versus \(1/[HClO_4]\) figure IV F-6, were linear with intercepts. It therefore suggests that order of reaction in acid decreases from unity to zero at higher acid concentrations.

5. **Effect of Cl\(^-\) on the rate of reaction**

The results of effect of NaCl table IV H-1 show that on addition of sodium chloride in the reaction mixture increases the rate of reaction.

6. **Reactive species.**

   (i) **Oxidant**

In the pH range employed in the present investigations, the reactive species of the oxidant are expected to be \(H_5IO_6^+\) or \([I(OH)_6]^+\).

\[
HIO_4 + 2H_2O \rightleftharpoons H_5IO_6
\]
\[ K \]
\[ H_3IO_6^- + H^+ \overset{\text{equilibrium}}{\rightarrow} H_6IO_6^{\text{+}} \]

(ii) **Substrate**

In the present investigations primary, secondary and tertiary amino alcohols have been considered as the reacting species.

(iii) **Catalyst**

A positive effect of Cl\(^{-}\) on the rate of reaction has been observed in the present investigation.

This suggests that the neutral species i.e. RuCl\(_3\) is the reacting species of the catalyst.

7. **Effect of variation in temperature**

In the present investigation the reaction were carried out at a for different temperature viz. 35, 40, 45 and 50\(^\circ\)C. The reactant concentration as have been kept constant table IV-I-1 and Figure IV-I-1. The values of energy of activation were as 57.5 ± 0.5, 48.8 ± 0.5, 29.9 ± 0.5 and 25.5 ± 0.5 kJ mol\(^{-1}\) for the oxidation of 2—amino ethanol, 3—amino propanol diethanolamine and triethanolamine respectively.

8. **Oxidation products**

*kinetic conditions*

Under the experimental conditions of the kinetic, the amino
alcohols oxidised to formaldehyde and corresponding carboxylic acids.

On the basis of these findings and the proposed mechanism the rate law which explains all the experimental results in presence of ruthenium (III) has been derived as follows:

\[
\frac{-d(CAT)}{dt} = \frac{K_{15}K_1(CAT)_1[H^+][Ru(III)]}{1 + K_1(H^+)} \quad \ldots (18)
\]

It is evident from rate law equation (18), that for the double reciprocal plot (Figure IV F - 6) both intercept and slope should be independent of the aminoalcohol. However figure (IV F - 6) indicates that the intercepts and gradients for four different aminoalcohols are quite clearly at variance with one another. Therefore, the results are not consistent with the mechanism involving the adduct between sodium meta periodate and RuCl₃.