Ruthenium (III) Catalyzed Oxidation of Sugar Alcohols by N-chlorophthalimide

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Abstract: Ru(III) catalysed oxidation of sugar alcohols (sorbitol and xylitol) have been studied by N-chlorophthalimide (NCP) in aqueous acetic acid medium in presence of hydrochloric acid at 303 K. The reactions obeyed first-order in [NCP] and fractional-order each in [sugarol] and [H⁺]. The reactions under investigation follow $k_{obs} = c + d [H^+]$ i.e. Bunnett-Olson model. The enhancement in rate was observed in the 10% to 40% (v/v) range of acetic acid. Ru(III) catalyses the reaction at low concentration showing first-order kinetic but declined to follow zero-order at its higher concentration. Michales-Menten equation was verified at transition state for complex. The plausible mechanism was proposed involving HOC1 reacting species of oxidant stoichiometrically (1:1) in slow step to yield aldehydes as main products. The thermodynamic parameters and derived rate expression support the mechanism.

Key words: Sorbitol, Xylitol, N-chlorophthalimide, Ruthenium(III) chloride, Kinetics.

1. INTRODUCTION

Sugar alcohols are extracted from the products (fruits and berries). These are often used in food industry, bio-diesel, oleochemical industries, pharmacology and beverage etc. Common sugar alcohols are sorbitol (6-carbon) xylitol (5-carbon). Sorbitol can be dehydrated to isosorbide.[¹] They are distinguished by their stereochemistry, that is, the relative orientation of the –OH groups attached to the C-H atom. There are innumerable reports show that kinetics of oxidation of sugar alcohols have been studied extensively using variety of two electron oxidizing agents in various media such as QCC,[²] alkaline hexacyanoferrate(III),[³] V(V),[⁴] etc. N-chlorophthalimide (NCP) is a mild, inexpensive reagent, has been reported to generate a source of positive Cl⁺ ion. This is very effective oxidant[⁵] used successfully as an oxidant for catalytic and non-catalytic oxidation studies. In presence of mineral acid, it produces HOC1 and protonated H₂O⁺Cl reacting species. However, in many cases over oxidation hampered the selectivity at these reactions. Recently involving NCP the protocol of the mechanism was explained through oxidation via a concerted symmetrical transition state elaborately studied the alcohols[⁶,⁷] (aliphatic/ aromatic/ cyclic) hydroxyacids,[⁸] carbohydrates,[⁹] and amino acids[¹⁰] etc. Ru(III) catalyst in very effective oxidant gives an excellent results in acidic medium. It belongs to transition metal ion provide promising results as a highly efficient catalyst.[¹¹] Its species facilitates the oxidation at highly pH dependent that exists in acidic medium. A number of reports of oxidation involving Ru(III) with different oxidants for organic substrates are available, such as carbohydrates,[¹²-¹⁵] acids,[¹⁶] alcohols,[¹⁷-¹⁹] etc. However, the study with sugar alcohols appeared to be scanty. In this article, we want to elaborate the kinetics and mechanism of hexitol (sorbitol) and xylitol catalysed by Ru(III) using NCP in aqueous acetic acid and HCl media.

2. EXPERIMENTAL

The sugars such as sorbitol and xylitol undertaken for investigation belongs to Sigma-Aldrich India and used as such received. Ru(III) chloride was of A.R. grade (Johnson-Matthey), its sample solution was prepared in concentrated HCl of known strength (0.018 N), and stored in black coated bottle to avoid from photochemical reaction. NCP (Across, AG) solution was prepared in 100% acetic acid frequently standardized by iodometric procedure, before its use for each set of the experiment. Other Miscellaneous solutions pertaining to present experiments were prepared in bulk.

Kinetic Procedure

Thermostat was set to desired temperature. The flask containing known volume of NCP in aqueous acetic acid whereas in another flask contains substrate and required amount of Ru(III) and acid alongwith other additives were clamped in a thermostatic both. The reaction was commenced by mixing requisite amount of NCP to the other contents of the reaction. The entire reaction mixture was mixed thoroughly and the progress of the reaction was monitored by estimating for unreacted [NCP] iodometrically at regular intervals of time. Finally, the rate was determined using integrated and graphical methods. The results was reproducible with a precision of ±4% error.

4. RESULTS AND DISCUSSION

The stoichiometry of the NCP- sugarol reaction catalysed by Ru(III) chloride was determined. The [NCP] was taken in excess of [sugar alcohol] in aqueous acetic acid medium in presence of H⁺ ions. The reaction was allowed to proceed till it is completed. The
estimated results showed that one mole of NCP was needed to oxidized one mole of sugar alcohol. The general reaction may be formulated as

\[ R = \text{CH}_2\text{OH} - (\text{CHOH})_x \text{ (sorbitol)} \quad \text{and} \quad \text{CH}_2\text{OH}(\text{CHOH})_3 \text{ (xylitol)} \]

where, R = CH₂OH-(CHOH)₄ (sorbitol) and CH₂OH(CHOH)₃ for xylitol respectively.

The corresponding products obtained as respective aldehydes were identified by TLC and also by forming their 2,4-DNP derivatives. Further, the study was performed to detect free radicals present in the reaction mixture. The addition of scavenger acrylonitrile 10% to reaction mixture in an nitrogen atmosphere failed to produce polymerisation in the system hence based on one electron mechanism is unlikely.

A series of experiment with varying concentration of NCP were conducted at pre-set conditions. The linear plots of ln [NCP] vs. time with derived unit slope in each reaction showed that first-order kinetics prevail with respect to [NCP].

The study was made for different concentrations (5X) of variant (sugar alcohols) (Table 1). The study showed that plots of k against [polyols] (Fig.1) bear a curve bending towards X-axis at their higher concentration of [sugar alcohol] under investigation thus verifying Michaelis-Menten types kinetics operative in them. The second order (k₂) value afforded not consistency i.e. complex is formed at the top of the barrier of activated transition state.

**Table 1: Variation of [sugar alcohol] on rate**

<table>
<thead>
<tr>
<th>10² [sugarol] (mol dm⁻³)</th>
<th>10⁴ k (s⁻¹)</th>
<th>Sorbitol (1)</th>
<th></th>
<th>Xylitol (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.49</td>
<td>1.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>1.68</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>2.25</td>
<td>1.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>3.21</td>
<td>1.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>3.66</td>
<td>2.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.33</td>
<td>4.81</td>
<td>3.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.00</td>
<td>5.95</td>
<td>4.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td></td>
<td>4.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The dependence on [H⁺] has been investigated by 5 X concentration of acid. It is found that reaction is somewhat little sensitized apparently to acidity in two ways (i) acid dependent and (ii) acid independent of [H⁺]. Thus, reaction under investigation follow \( k_{obs} = c+d[H^+] \). The reaction is of fractional order in nature satisfying Bunnet-Olson criteria.\(^{20}\)
The effect of solvent polarity shows positive trend in rate. Thus, ion dipole involved in the rate determining step. The solvent does not react with the reactant and causes solvation in transition state. Primary salt and ionic strength of the medium show inert effect in the rate of oxidation whereas added phthalimide shows negligible effect discarding its claim to act as a reacting species to participate in the mechanism.

Ru(III) chloride in concentrated HCl acid was employed in the present investigation has shown fractional order kinetic at its optimum concentration (Table 2). The plots of log k vs. log [Ru(III)] (Fig.2) giverise slope less then one showing ability to form complexes with the substrate. It is presumed that Ru(III) might be forming a distorted tetrahedral complex during the reaction in conjunction with oxidant NCP. In presence of acid HCl, Ru(III) has been recognized as a reacting species in catalysed oxidation after considering a lot of foregoing kinetic results and HOCl (unprotonated) and H₂O⁺Cl⁻ (protonated) formulated as prime reacting species of NCP.

Table 2: Dependence of rate on variation in [Ru(III) chloride]

<table>
<thead>
<tr>
<th>[Ru(III)] (mol dm⁻³)</th>
<th>10⁴ k (s⁻¹) Sorbitol</th>
<th>10⁴ k (s⁻¹) Xylitol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.66</td>
<td>1.34</td>
</tr>
<tr>
<td>1.25</td>
<td>2.04</td>
<td>-</td>
</tr>
<tr>
<td>1.50</td>
<td>2.39</td>
<td>1.90</td>
</tr>
<tr>
<td>2.00</td>
<td>3.21</td>
<td>2.56</td>
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<td>2.50</td>
<td>3.91</td>
<td>3.01</td>
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<tr>
<td>3.33</td>
<td>6.23</td>
<td>4.34</td>
</tr>
<tr>
<td>5.00</td>
<td>6.95</td>
<td>4.89</td>
</tr>
<tr>
<td>6.25</td>
<td>-</td>
<td>5.18</td>
</tr>
</tbody>
</table>

Mechanism

Utilizing HOCl and H₂O⁺Cl⁻ active species of oxidant, stoichiometric ratio and considering slower reaction facilitation of complex formation, the pathways of mechanism is postulated as per following mode of Scheme-1

\[
\begin{align*}
\text{HOCI} + \text{H}^+ &\rightleftharpoons \text{H}_2\text{O}^+ \text{Cl} \\
\text{K}_2 &
\end{align*}
\]

\[
\begin{align*}
\text{NCl} + \text{HOH} &\rightleftharpoons \text{HOCI} + \text{N-H} \\
\text{K}_1 &
\end{align*}
\]

\[
\begin{align*}
\text{R} + \text{Ru(III)} &\rightleftharpoons \text{R} + \text{Ru(III)} \text{Complex (C₁)} \\
\text{K}_3 &
\end{align*}
\]
The reaction can be represented as:

\[
\begin{align*}
  \text{Ru(III)} + \text{C} = \text{O} + \text{HCl} & \rightleftharpoons K_4 \left( \text{Complex (C)} \right) \\
  \text{Ru(III)} + \text{Cl}^- + \text{Ru(III)} & \rightarrow \text{H}_2\text{O} + \text{H}_+ + \text{Cl}^- + \text{Ru(III)} \quad \text{..... (4)}
\end{align*}
\]

The observed rate law can be expressed as:

\[
k_{\text{obs}} = \frac{k_1K_2[A][\text{Ru(III)}]}{[\text{Phthalimide}] + K_1 + K_2K_3[A][\text{Ru(III)}]}
\]

Equation (10) explains satisfactorily all the kinetic features of the reaction verifying Michaelis-Menten type of kinetics.

The sequence of reactivity order in the present investigation is observed as:

Sorbitol > Xylitol

This order is probably due to cumulative effects like polar, steric, hydrophobic, interactions, and chain length, which mainly controls the rate and dominate in the reactivity order. Sorbitol is oxidized faster than to xylitol. This is attributed due to increase in chain length (sorbitol) that decreases the rate in case of xylitol. Moreover xylitol has lowest alcoholic percentage that of sorbitol which has the highest.

The large negative value of entropy of activation (\(\Delta S^a\)) probably suggest a systematic arrangement of atom in the transition state due to solvation being activated complex polar. There is a loss in transitional energy which shows compactness of transition state that restricts on transitional and rotational freedom, thus reducing \(\Delta S^a\).

The review of thermodynamic parameters, especially fastest reaction has lowest value of \(\Delta E_a\) and vice versa (Table 3). The value of \(\Delta G^a\) (Gibbs free energy) appears to be constant indicating that similar mechanism is operative in the present investigation. Over all the assessment indicates that reaction is enthalpy controlled.

Table 3. Thermodynamic and activation parameters for the [Ru(III)] catalysed reaction between Sugar alcohols and NCP

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>(E_a) [kJ mol(^{-1})]</th>
<th>(\Delta H^a) [kJ mol(^{-1})]</th>
<th>(\Delta G^a) [kJ mol(^{-1})]</th>
<th>(-\Delta S^a) [JK(^{-1})mol(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbitol</td>
<td>36.34</td>
<td>34.11</td>
<td>85.11</td>
<td>166.94</td>
</tr>
<tr>
<td>Xylitol</td>
<td>38.48</td>
<td>35.87</td>
<td>86.24</td>
<td>164.87</td>
</tr>
</tbody>
</table>

Conclusion

Ru(III) catalysed and NCP mediated oxidation of sorbitol and xylitol have been investigated in aqueous acetic acid medium in presence of mineral acid HCl under the kinetic conditions, [sugarols] > [NCP]. Ru(III) catalyst shows the capability of forming ternary complex when used in microquantity. HOCl and H\(_2\)O\(^+\)Cl\(-\) was postulated as reacting species of oxidant. Overall reaction observed first-order dependence on [NCP] and fractional-order to polyols. The reaction is not much of sensitized to acidity followed \(k_{\text{obs}} = c + d[H^+]\) showing acid dependent and acid independent paths. The stoichiometry was found (1:1) and the order of reactivity observed as sorbitol > xylitol. The proposed mechanism supported by physical and thermodynamic parameters was discussed.
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Conflict of Interest
The authors declare conflict of no interest whatsoever.

REFERENCES