Kinetic Study of Oxidation of Some Diols by Isoquinolinium Chlorochromate in Aqueous Acetic acid Medium

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Abstract- This paper reports the kinetics of oxidation of diols such as pentane-1,5-diol, hexane 1,6-diol by Isoquinolinium chlorochromate in aqueous acetic acid medium under first-order kinetic conditions with respect to oxidant. The study reveals the existence of complex formation between substrate and oxidant at the transition point. The study determined the ionic strength of the medium. The substrates follow the sequence hexane-1,6-diol > Pentane1,5-diol for all the alcohols studied. The thermodynamic parameters have been interpreted in terms of the molecular dynamics and reaction mechanism suggested for the proton abstraction in the oxidation process.

Key words: Isoquinolinium chlorochromate, hexane-1,6-diol, pentane 1,5-diol, oxidation, kinetics.

1. INTRODUCTION
The quantitative conversion of pentane-1,5-diol and hexane-1,6-diol to their corresponding aldehydes have been exhaustively reported in literature,[1-7] which has received the attention over years in search of versatile and selective reagent for this purpose. There are few reports of the kinetic studies of oxidation of diols using a variety of oxidants. Well known halochromates[8] have been used as a moderate oxidising agent in synthetic organic chemistry among them, isoquinolinium chlorochromate[9] (IQCC) is a new chromium containing compound has been employed as an oxidant for the oxidation of a large number of compounds.[10-12] The literature survey reveals that IQCC presented different kinetic picture for the oxidation of some industrially[13] important diols with halochromates herein. We have considered IQCC worthwhile to report the kinetic and thermodynamic aspects of the mechanism of oxidation of the diols in aqueous acetic acid and H⁺ ion medium. The sequence of the oxidation rate has also been interpreted as a prime aim in terms of structural and characteristic of alcohols.

2. EXPERIMENTAL
All the chemicals and reagents employed were either of AnalaR or guaranteed reagent grade and were used as such received. The diols-pentane 1,5-diol and hexane 1,6-diol of BDH brand were distilled over and used in standard form. Doubly distilled water was used both for kinetics as well as reagents solutions in an all glass assembly. IQCC was synthesized[14] and its solution was prepared in water and mineral acid (HCl), and also was checked by iodometric process.

3. Kinetic measurements
The oxidation of diols was studied under pseudo first-order kinetic conditions with respect to IQCC i.e. maintaining a large excess ( X 10 or greater) of the diols over IQCC.

The solutions of diol and oxidant IQCC in required amounts were allowed to equilibrate in a thermostat at experimental temperature (accuracy ± 0.1°C), after the temperature equilibrium was reached, the solutions were mixed together to initiate the reaction.

Aliquots of the reaction mixture were withdrawn at regular time interval, and the unreacted oxidant (IQCC) left was estimated iodometrically.

The rate constants (k) were determined from the slopes of linear plots of unreacted log [IQCC] versus time using integrated and graphical methods. Duplicate runs showed that the kobs were reproducible within ±3%.

4. Results and Discussion
The stoichiometry of IQCC– diol system can be determined iodometrically without any interference from diol or its products. Thus, the above reactions were allowed to occur in a thermostated water bath at 30°C for 12 h. The excess of IQCC was measured iodometrically which reveals a mole of diol is consumed by a mole of IQCC corresponding to stoichiometry represented by equation (1).
\[
R \text{CH}_2 \text{OH} + O_2 \xrightarrow{H^+} \text{R} \text{CHO} + H_2O + O \text{Cr} \text{ClO} \text{QH}^+ 
\]

\[
\ldots \ldots (1)
\]

where, \( R = \text{HO (CH}_2\text{)}_4 \) and \( \text{HO(CH}_2\text{)}_5 \) for 1,5-pentane diol and 1,6-hexane diol respectively.

The oxidation products i.e. aldehydes were identified by 2,4-dinitrophenyl hydrazone also characterised by their m.ps. (76°C and 104°C) and further confirmed by TLC method.

The free radicals was tested qualitatively by adding 2 ml acrylonitrile in reaction mixture by trapping method in an atmosphere of nitrogen. The added radical scavenger acrylonitrile has no effect on the rate.

The effect of ionic strength (\( \mu \)) and salt on the oxidation rate of diol was determined and had no effect on the rate.

The reaction is formed to be first-order in IQCC. The individual kinetic run obeyed strictly first-order in IQCC and remains independent on the initial concentration of oxidant. (The linear plots of log [IQCC] vs. time, with unit slope). The rate of oxidation increases linearly but further an enhancement in the concentration of diol (Table 1) shows little nature of curvature. The plots of \( k \) vs. [diol] (Fig. 1) yields straight line with slope less than one indicates that order with respect to diols is unity. The second-order rate constant (\( k_s \)) values are found not constant.

### Table 1: Dependence of rate on [diols]

<table>
<thead>
<tr>
<th>[diol] ( \times 10^2 ) (mol dm(^{-3} ))</th>
<th>( 10^3 k ) (s(^{-1} ))</th>
<th>pentane 1,5-diol (1)</th>
<th>hexane 1,6-diol (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>1.33</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>1.64</td>
<td>2.15</td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>-</td>
<td>2.82</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>2.54</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>3.35</td>
<td>4.08</td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>4.21</td>
<td>5.22</td>
<td></td>
</tr>
<tr>
<td>3.33</td>
<td>5.53</td>
<td>6.66</td>
<td></td>
</tr>
<tr>
<td>4.00</td>
<td>6.25</td>
<td>7.71</td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td>7.08</td>
<td>8.80</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1 Plot of \( k \) vs. [substrate]

\[
10^3 \times [\text{IQCC}] \text{ (mol dm}^{-3}) = 3.33 \ (1, 2); \ [H^+] \text{ (mol dm}^{-3}) = 0.10 \ (1, 2); \ [\text{CH}_3\text{COOH-H}_2\text{O \%}, (v/v) = 25 \ (2), 30 \ (1); \ Temperature K = 303 \ (1, 2),
\]

The reaction is catalysed by hydrogen ion (Table 2). The hydrogen ion dependence has the following form: \( k_{obs} = a+b[H^+] \). The graphic plots of log \( k \) vs. log \( [H^+] \) (Fig. 2) gave almost unit slope for both the cases indicating first-order dependence on \( [H^+] \).

### Table 2: Dependence of rate on [H\(^+\)]

<table>
<thead>
<tr>
<th>[H(^+)]</th>
<th>( 10^3 k ) (s(^{-1} ))</th>
</tr>
</thead>
</table>
| \( 10^3 \times [\text{IQCC}] \text{ (mol dm}^{-3}) = 3.33 \ (1, 2); \ [\text{CH}_3\text{COOH-H}_2\text{O \%}, (v/v) = 25 \ (2), 30 \ (1); \ Temperature K = 303 \ (1, 2),
\]

The reaction is catalysed by hydrogen ion (Table 2). The hydrogen ion dependence has the following form: \( k_{obs} = a+b[H^+] \). The graphic plots of log \( k \) vs. log \( [H^+] \) (Fig. 2) gave almost unit slope for both the cases indicating first-order dependence on \( [H^+] \).
The study reveals the rate of oxidation of diols with IQCC increases with decrease in polarity of the solvent. The plots of \( \log k_{\text{obs}} \) vs. \( 1/D \) is linear with positive slope indicating ion-dipole type of the reaction.

**General Mechanism**

Considering the kinetic results and involving protonated form of IQCC, a plausible mechanism is proposed as:

\[
\begin{align*}
\text{RCH}_2\text{OH} + \text{O}_\text{HCrOQH}_\text{Cl} & \rightleftharpoons K_1 \text{RCHO} + \text{H}_2\text{O} + \text{HO CrClOQH}^+ \quad \text{(unstable)} \\
\text{R} & \text{C} = \text{O} \text{CrOQH}_\text{OH} & \text{R} \text{C} = \text{O} \text{CrOQH}_\text{OH} & \text{R} \text{C} = \text{O} \text{CrOQH}_\text{OH} & \text{R} \text{C} = \text{O} \text{CrOQH}_\text{OH} \\
\text{slow process} & \quad k \quad \text{RCHO} + \text{H}_2\text{O} + \text{HO CrClOQH}^+ & \quad \text{RCHO} + \text{H}_2\text{O} + \text{HO CrClOQH}^+ & \quad \text{RCHO} + \text{H}_2\text{O} + \text{HO CrClOQH}^+ & \quad \text{RCHO} + \text{H}_2\text{O} + \text{HO CrClOQH}^+ \\
\text{R} & \text{C} = \text{O} \text{CrOQH}_\text{OH} & \text{R} & \text{C} = \text{O} \text{CrOQH}_\text{OH} & \text{R} & \text{C} = \text{O} \text{CrOQH}_\text{OH} \\
\end{align*}
\]

The present study reports the order of reactivity of the oxidation of diols as:

**hexane 1,6-diol > pentane 1,5-diol**

which is explained on the basis of length of carbon skeleton, alkyl group linked to hydroxyl group and positive inductive effect.

+I effect produces more for long size of CH\(_3\) group of diols make the oxidative process feasible. The thermodynamic activation parameters evaluated (Table 3) also support the above order of reactivity besides rate of oxidation measurements. The value of Ea (energy of activation) for hexane 1,6-diol is less than that of pentane 1,5-diol. The values (Ea) of the reaction under investigation were observed in accordance with the order of mentioned sequence. The
reactivity was observed in terms of $\Delta H^*$ and $\Delta S^*$ as hexane 1,6-diol is $>$ pentane 1,5-diol, it is also supported by highly solvated molecules.

The high negative values of $\Delta S^*$ show inhibition in the rotational and vibrational degree of freedom of the reactants when they form a transitory / momentary complex.

This leads that reaction are both enthalpy and entropy controlled. The values of free energy of activation reaction almost similar, thus in light of these values trends also support the identical paths of the reaction mechanism. Similar type of reaction mechanism have also been reported by eminent authors.\cite{15,16}

**Table 3. Thermodynamic and activation parameters for the reaction between diols and IQCC**

<table>
<thead>
<tr>
<th>Diols</th>
<th>$E_a$ (kJ/mol$^{-1}$)</th>
<th>$A$ (s$^{-1}$)</th>
<th>$\Delta H^*$ (kJ mol$^{-1}$)</th>
<th>$\Delta G^*$ (kJ mol$^{-1}$)</th>
<th>$-\Delta S^*$ (JK$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pentane-1,5-diol</td>
<td>51.72</td>
<td>1.55x10$^5$</td>
<td>48.46</td>
<td>84.87</td>
<td>119.12</td>
</tr>
<tr>
<td>hexane-1,6-diol</td>
<td>47.03</td>
<td>4.38x10$^4$</td>
<td>44.49</td>
<td>84.40</td>
<td>130.62</td>
</tr>
</tbody>
</table>

**Conclusion**

The oxidation rates of diols follow the sequence hexane 1,6-diol $>$ pentane 1,5-diol. The oxidation of two diols by IQCC in aqueous acetic acid medium in presence of H$^+$ leads to the formation of corresponding aldehydes. The reaction is first-order with respect to IQCC and shows Michaelis-Menten types kinetics with respect to diols and is catalysed by H$^+$ ion. The hydrogen ion dependence has the form $k_{obs} = a + b [H^+]$. A hydrogen abstraction mechanism has been proposed. The oxidation is accompanied by losing entropy of activation.

**Acknowledgement**

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**Conflict of Interest**

The research scholar declare no conflict interest.

**REFERENCES:**