KINETICS AND MECHANISM OF RUTHENIUM (III) CATALYSIS IN THE OXIDATION OF ERYTHRITOL BY CHLORAMINE-T

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ABSTRACT

The kinetic investigations of Ru (III) catalyzed oxidation of erythritol (1, 2, 3, 4-tetrahydroxybutane) by chloramine-T (CAT) in HClO₄ in the presence of Hg (OAc)₂ as scavenger for Cl⁻ have been investigated. The reactions are zero order with respect to alcohol and first order w.r.t of CAT. The reaction rate is first order with respect to [Ru (III)] and zero order is found for perchloric acid, KCl and NaClO₄. Mercuric acetate does not influence the reaction rate. Suitable mechanism in conformity with the observed kinetic data is proposed and thermodynamic parameters are computed.

KEYWORDS: Kinetics, Ru (III) catalyst, oxidation, Erythritol, Chloramine-T, Mercuric acetate.

INTRODUCTION

Ruthenium (III) chloride has been reported as a nontoxic and homogenous catalyst. so far no one has attempted to probe the role of Ruthenium(III) chloride[1,2] in oxidation of polyhydroxy compounds by Chloramine –T (CAT). This is used as a strong oxidizing agent[3,4] for studying the kinetics of oxidation of various organic substances. A number of other oxidants like NBA,[5, 6] NBS,[7, 8] and KBrO₃[9-12] etc., have been used in oxidation of various compounds. Chloramine-T is used as a disinfectant for water because it is less aggressive than chlorine and more stable against light than hypochlorites. Some work has been focused on N-halogen compounds,[14-15] CAT is used as powerful oxidant in acidic as well as basic medium. But surprisingly no reports are available for oxidation of erythritol by Chloramine-T in acidic medium therefore; we selected to do the kinetic and mechanistic study of oxidation of erythritol by CAT in the presence of catalyst Ru (III).
Erythitol\[^{[16,17]}\] is faintly sweet alcohol which is present in small quantities in melons and peaches and currently produced in large quantities for use as a low calorie, tooth friendly bulky sweetener. Extensive toxicological testing has shown that Erythritol is well tolerated & has no toxic effect even after consumption in large quantities. Its antioxidant Properties has been studied.

The use of UV for Chlorine or Chloramines-T removal is an established technology that has been widely accepted in pharmaceutical, beverage, and dialysis applications. Ultraviolet light is also used at aquatic facilities.

**MATERIALS AND METHODS**

All chemicals were of the highest purity and triple distilled water was used. All reagents as Erythitol, Ru (III) Chloride, HClO\(_4\), KCl, NaClO\(_4\), Hg(OAc)\(_2\), Chloramine-T were of A.R grade. All solutions were prepared in triple distilled water. The stock solution of Ru (III) Chloride was prepared by dissolving 1 gm of sample in HCl of known strength (0.018N) and total volume of solution made up 100 ml in black-coated flask to prevent photochemical decompositions. All reaction vessel are also black coated from outside to avoid any photochemical effect.

A thermo stated water bath used to maintain the desired temperature to within ±0.1°C. The reactions were initiated by addition of CAT solution to the other reagents. The progress of the reaction was followed by estimating unconsumed CAT iodometrically in aliquots withdrawn, using starch as an indicator, after suitable time intervals.

**Stoichiometry**

In Stoichiometry, equilibrating the reaction mixture containing an excess of oxidant[CAT] over substrate [Erythritol] in different ratios at room temperature for 48 h and estimation of unconsumed oxidant [CAT] in different sets showed that one mole of erythritol consumed two moles of [CAT]. This resulted showed 1:2 stoichiometry.

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 + 2\text{H}_2\text{O} & \rightarrow 2\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}^- \\
\text{CHOH} + 2\text{H}_2\text{O} & \rightarrow 2\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}^- + \text{COOH} \\
\end{align*}
\]

The oxidation product Erythrinoic acid was detected by different spectral techniques.
Product Analysis

Ultraviolet spectral measurements show that the sharp absorption band was notice at 263 nm for CAT N/400. The intensity of absorption increases due to $\pi-\pi^*$ transition in hyperchromic effect. The peak observed at 246 nm in the presence of HCl in the mixture of oxidant (CAT) and Ru(III) catalyst. While the set of reaction mixture containing reducing Erythritol, Perchloric acid, Mercuric acetate Ruthenium chloride, excess of Chloramines -T were taken in the reaction vessel and kept for two day at room temperature and the spectral data was taken at two different concentrations (Reaction mix1 & 2). The absorbance bands of these solutions were observed at 230nm and 235 nm, indicating complex formation took place between Ru (III) and oxidant. In carbonyl compounds a high energy transition occurs and is quite intense.

![UV SPECTRA Fig.](image_url)
Fig: 2 FT-IR Spectrum of Erythrnoic acid

FT-IR is one of the important spectroscopy from which identification of the functional groups have been observed. The studied compound contains 4 carbon atoms. The symmetric stretching vibration of V-OH observes at 3600cm\(^{-1}\) in the experiment. The C=O vibration observes at 1700 cm\(^{-1}\) ascribed to the C=O stretching vibration. The C-O-H in plane bending appears at 1150cm\(^{-1}\) confirms the presence of – OH group to the carbon frame. The C-C
stretches vibration appears at 1010 cm\(^{-1}\). The C-H stretching vibration of V(C-H) appears at 2900 cm\(^{-1}\). The bending vibration observes at 770.97 cm\(^{-1}\).

**KINETIC RESULT AND DISCUSSION**

Kinetic of the oxidation of Erythritol by Chloramine-T in the presence of Ru (III) chloride as homogenous catalyst have been studied at constant temp 40\(^{0}\)C.

**Effect the oxidant concentration on the rate**

The kinetic data are reported in (table-1). The reaction followed first order dependence in Chloramine-T at all concentration of the reactant. This was confirmed by plotting a graph between (-dc/dt) vs [CAT]. First order kinetics was found in the case Ru (III) and graph was plotted between (-dc/dt) and [Ru (III)] gave straight line. Erythitol variation showed zero order.

**Table-1: Effect of variation of Oxidant, Ru(III) and Erythitol at 40\(^{0}\)C**

<table>
<thead>
<tr>
<th>[CAT] x10(^{-3}) mol dm(^{-3})</th>
<th>Ru(III) x10(^{6}) Mol dm(^{-3}) S(^{-1})</th>
<th>[Substrate]x10(^{3}) Mol dm(^{-3})</th>
<th>(-dc/dt) x10(^{-7})</th>
<th>K(_1)x10(^{5}) S(^{-1})</th>
</tr>
</thead>
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<td>1.0</td>
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<td>0.83</td>
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<td>1.0</td>
<td>1.0</td>
<td>0.90</td>
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<td>1.25</td>
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<td>1.4</td>
<td>0.84</td>
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<td>1.67</td>
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<td>1.0</td>
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<td>0.84</td>
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<td>2.50</td>
<td>1.0</td>
<td>1.0</td>
<td>4.0</td>
<td>0.84</td>
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<tr>
<td>5.0</td>
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<td>1.0</td>
<td>17.5</td>
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<td>1.0</td>
<td>1.0</td>
<td>1.4</td>
<td>0.21</td>
</tr>
<tr>
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<td>1.5</td>
<td>1.0</td>
<td>2.3</td>
<td>0.21</td>
</tr>
<tr>
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<td>2.0</td>
<td>1.0</td>
<td>3.0</td>
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<td>1.0</td>
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<td>3.0</td>
<td>1.0</td>
<td>4.4</td>
<td>0.20</td>
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<td>3.5</td>
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<td>5.0</td>
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The negligible effect of Hg(OAc)$_2$ excluded the possibility of its involvement either as a catalyst or as an oxidant. Experimental data showed negligible effect of ionic strength of medium on the rate. Effect of variation of [KCl] concentration showed no effect on the rate of reaction in (table-2).

**Effect of temperature on the rate**

The kinetic reaction were performed at different temperatures 30$^0$C, 35$^0$C, 45$^0$C & 50$^0$C and specific rate constants (table-3) were calculated and a plot was drawn between log k versus 1/T (Fig-3) which was linear. The Calculated value of activation parameter for various sets of reaction is show in the table-3. The activation energy ($\Delta E^*$) is calculated. With help of rate of constant K$^r$, value of the other activation parameters such as log A where (A) is Arrhenius factor, entropy of activation ($\Delta S^*$), Free energy of activation ($\Delta G^*$) were calculated.

Table-2: Effect of variation HClO$_4$, KCl, Hg(OAc)$_2$, NaClO$_4$ at 40$^0$C

<table>
<thead>
<tr>
<th>[HClO$_4$]x10$^3$ mol</th>
<th>[KCl]x10$^4$ Mol</th>
<th>[Hg(OAc)$_2$]x10$^4$ Mol</th>
<th>[NaClO$_4$] X 10$^4$ mol</th>
<th>(-dc/dt) x10$^7$</th>
</tr>
</thead>
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<td>1.67</td>
<td>1.0</td>
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<td>1.3</td>
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Table 3: Effect of the temperature on the Reaction Rate

<table>
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<th>T°C</th>
<th>dc/dt</th>
<th>Kr x 10^2</th>
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<td>30°C</td>
<td>1.4</td>
<td>0.17</td>
</tr>
<tr>
<td>35°C</td>
<td>2.7</td>
<td>0.33</td>
</tr>
<tr>
<td>40°C</td>
<td>3.2</td>
<td>0.40</td>
</tr>
<tr>
<td>45°C</td>
<td>4.4</td>
<td>0.55</td>
</tr>
<tr>
<td>50°C</td>
<td>5.2</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Table 4: Values of Activation Parameter

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ea(KJmol⁻¹)</th>
<th>log A</th>
<th>ΔH*(KJmol⁻¹)</th>
<th>ΔS*(KJmol⁻¹)</th>
<th>ΔG*(KJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erythritol</td>
<td>12.04</td>
<td>3.99</td>
<td>17.88</td>
<td>-182.90</td>
<td>78.91</td>
</tr>
</tbody>
</table>

**DISCUSSION AND MECHANISM**

Chloramine-T acts as mild oxidant in both acid and alkali solutions with a two electron change to give reduced products.

\[ \text{RNClNa} \rightarrow \text{RNCl}^- + \text{Na}^+ \quad \text{(1)} \]
Step (4) is slow and rate determine step rate of reaction. The rate of reaction is term of consumption of concentration of \([RNCl^-]\) ions may be written as equation (1).

\[
-\frac{d[RNCl^-]}{dt} = K_2[X][S] \quad \text{(1)}
\]

Concentration of the complex i.e. [X] May be determined by applying steady state treatment to [X]

Hence,

\[
\frac{d[X]}{dt} = K_1[RNHCl][Y] - K_{1}[X] - K_2[X][S] = 0
\]

\[
K_1[RNHCl][Y] = [X]\left\{K_{1}+K_{2}[S]\right\}
\]

\[
[X] = \frac{K_1[RNHCl][Y]}{K_{1}+K_{2}[S]} \quad \text{(2)}
\]

\[
-\frac{d[RNCl^-]}{dt} = \frac{K_2 K_1 [RNHCl] [Y][S]}{K_{1}+K_{2}[S]} \quad \text{(3)}
\]

The total concentration of Ru(III) chloride , i.e. \([\text{Ru(III)}]_T\) may be written by equation (4)
Putting value from equation (2) to equation (4), we get

\[
[Ru(III)]_T = [Y] + \frac{K_1[RNHCl][Y]}{K_1 + K_2[S]}
\]

\[
= [Y] \left\{ 1 + \frac{K_1[RNHCl]}{K_1 + K_2[S]} \right\}
\]

\[
= [Y] \left\{ \frac{K_1 + K_2[S] + K_1[RNHCl]}{K_1 + K_2[S]} \right\}
\]

\[
[Y] = [Ru(III)]_T \left\{ \frac{K_1 + K_2[S]}{K_1 + K_2[S] + K_1[RNHCl]} \right\}
\]

On comparing ion equation (3) and (5)

\[
\frac{-d[RNCl^-]}{dt} = \frac{K_2K_1[RNHCl][Ru(III)]_T}{K_1 + K_2[S]} \frac{K_1 + K_2[S]}{K_1 + K_1[RNHCl] + K_2[S]}
\]

\[
= \frac{K_1[RNHCl][Ru(III)]_T[S]}{K_1 + K_1[RNHCl] + K_2[S]}
\]

On assuming, \( K_2[S] \gg K_1 + K_1[RNHCl] \) and on neglecting the second term in the denomination of equation (6)

We get,

\[
\frac{-d[RNCl^-]}{dt} = \frac{K_2K_1[RNHCl][Ru(III)]_T[S]}{K_2S}
\]

\[
= K_2[RNHCl][Ru(III)]_T
\]

**CONCLUSION**

The CAT redox reaction has been carried out in HClO_4 medium. A 1:2 (equation 1) reaction stoichiometry involving the oxidation by CAT has been observed. The products of oxidation are Erythroic acid. The thermodynamic parameters, \( E_a, \Delta H^*, \Delta S^* \) and \( \Delta G^* \), have been computed from Arrhenius plots. A mechanism consistent with observed parameters has been proposed and rate law is derived.
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REFERENCES


