Kinetic and Mechanistic Study of Oxidation of Catechine

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ABSTRACT

A comparative rate study on the oxidation of catechine by quinolinium chlorochromate has been carried out in aqueous solution using spectrophotometric technique. The reaction follows first order kinetics with respect to both [QCC] and [substrate]. The effect of various constraints like solvent effect, reactant effect, oxidant effect and salt effect is also studied. The oxidation is studied in seven organic solvents; the solvent effect has been analyzed by Kamlet and Swain, two different multiparametric equations. On the basis of above study, a mechanism for oxidation of catechine has been purposed.

Keywords: Catechine, Kinetics, Mechanism, Oxidation, Quinolinium Chlorochromate.

INTRODUCTION

Oxidation-reduction reactions are those reactions, which involves transfer of electrons from one atom to another. These involve the use of many oxidizing agents. Commonly used oxidizing agents include potassium permanganate, potassium dichromate, hydrogen peroxide, chromic acid etc [1,2,3]. Kinetics is concerned with the rate of reaction [4], the influence of various conditions on these rates and mechanism by which a reaction occurs. The subject of chemical kinetics cover not only reaction rate but also covers a wide range of studies, which includes empirical studies of the effects of concentration, temperature, pH, solvent etc. on reaction of various types [5]. Quinolinium chlorochromate [6] is a stable reagent originally introduced as an oxidizing agent for alcohol is used in synthetic organic chemistry [7,8,9,10,11,12]. QCC, $C_{9}H_{7}N^{+}HClCrO_{4}^{-}$ is simple to prepare and is not air or moisture sensitive.

Catechine extracted from green-tea has various functions such as antibacterial, deodorization, anti-oxidization and ultraviolet ray cover [13]. Catechine is a powerful, water soluble polyphenol and antioxidant that is easily oxidized.
Hence, we report the oxidation of catechine by chlorochromate (QCC) in aqueous medium using spectrophotometric technique. The rate of oxidation of catechine by quinolinium chlorochromate has been determined by measuring the absorbance of catechine at 355nm. The oxidation of catechine is studied in other organic solvents; hydrogen bond donor (HBD), hydrogen bond accepter (HBA) and solvating property of organic solvent is explained by Kamlet and Swain equation and no free radical formation taken place during oxidation reactions. The rate shows first order dependence on [QCC] and [Catechine].

MATERIALS AND METHODS

2.1 Materials
All chemicals used were AR grade. All the glasswares used were class A. All the solutions were prepared in conductivity water (2-5 ×10^{-6} ohm^{−1} cm^{−1}). Catechine was a commercial product and was obtained from Merck Pvt. Ltd. QCC was prepared by the reported method [14] and its purity was checked by iodometric method. Various solvents like ethanol, methanol, acetone, dioxane, DMF and DMSO used were purified by usual methods [15]. Purity of Catechine was checked by noting its boiling point.

2.2 Kinetic study
Reaction was studied under pseudo first order conditions by keeping excess of catechine over QCC i.e. substrate >> oxidant. The reaction was carried out a constant temperature 30°C and was followed by monitoring decrease in QCC make spectrophotometrically at 355 nm using UV-VIS spectrophotometer 166. Beer’s law was found to be applied in the selected range of concentration. Pseudo first order rate constant, K_{obs} was evaluated from linear plots of 1+log O.D vs time with r^2 > 99%. Duplicate kinetic runs showed that the rate constants are reproducible within ±3%. The second order rate constant, k_2 was determined from reaction k_2=k_{obs}/[catechine].

2.3 Product Analysis
The oxidation of the catechine results in the regeneration of corresponding ketones compound. Oxidation of catechine leads to the formation of corresponding ketones. The quantitative product analysis was carried out under kinetic conditions. In a typical run experiment, catechine = 4.5 × 10^{-3} M and quinolinium chlorochromate [QCC] = 1 × 10^{-3} M were made up to 50 ml with conductivity water and kept in dark for 24 hours to ensure completion of reaction. The amount of ketones was determined by 2, 4-dinitrophenyl hydrazine method reported earlier [16]. According to that method –OH group is hydrolyzed to corresponding hydrazones. The product obtained was 85-87% after crystallization. It is then vacuum dried and weighted.

2.4 Calculation
Regression analysis was carried out on STATGRAPHIC software. The reaction was studied under pseudo-first order condition, the rate constants were calculated by plotting 1 + logO.D against time. Simple and multivariate correlation analysis was carried out by SPSS software.
RESULTS AND DISCUSSION

3.1 Stoichiometry
Oxidation of catechine results in the formation of corresponding ketones. The QCC undergoes a two electron change. This is in accordance with earlier observations [17]. The reaction is first order and the constant; \( k_{\text{obs}} \) do not depend on the initial concentration of QCC. The reaction increases linearly with increase in concentration of catechine. Thus, reaction is first order with respect to catechine also.

3.2 Rate laws
The plot of log O.D versus time was a straight line. This indicates that the oxidation of catechine followed pseudo first order kinetics with respect to QCC and therefore, the rate constants for this reaction were determined using the expression

\[
K_{\text{obs}} = 2 \cdot 303 \times \text{slope}
\]

\[
K_2 = K_{\text{obs}} / [\text{Catechine}]
\]

\( k_2 \) is the second order rate constant.

3.3 Induced polymerization
Oxidation of catechine in the atmosphere of nitrogen has failed to induce polymerization of acrylonitrile. Further the addition of acrylonitrile did not have any effect on rate. This indicates that one electron oxidation giving rise to free radicals is unlikely in the present reaction.

3.4 Effect of Concentration of Quinolinium Chlorochromate
The effect of concentration of quinolinium chlorochromate (QCC) on the rate of oxidation of catechine has been presented in the Table 1. In general rate constant, \( k_2 \) values increase with decrease in concentration of QCC. The reaction follows first order kinetics for more than 90% reaction. It is observed that the value of \( k_{\text{obs}} \) is independent of initial concentration of QCC.

3.5 Effect of Concentration of Catechine
Rate constant, \( k_2 \) values change with concentration of catechine and results are presented in the Table 2. Plot of 1/\( k_2 \) Vs 1/[Catechine] gave linear line but does not passing through origin suggests that the rate obeys Michaelis-Menten type kinetics with respect to catechine. The overall mechanism therefore, involves the formation of intermediate complex, which is the slowest step and it is the rate determining step. From dependence of reaction rate on concentration of catechine (reductant), the values of K (equilibrium constant) and \( k_2 \) (rate constant) are evaluated from the double reciprocal plots.

3.6 Effect of Salts
The reaction rate is unaffected in presence of salts like KCl, KBr and KI and the results are given in Table 4. The variation in the \( k_2 \) values due to the presence of salt depends on both the mechanism and the structure of the substrate. There is no effect of ionic strength on reaction rate in Debye-Huckle limit. The results are presented in Table 5. It proves that rate determine step is not ion ion-ion type and one of the reactant is neutral type.

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3.7 Effect of Acidity
The reaction is catalyzed by hydrogen ion and results are reported in table 6. Hydrogen ion dependence has the following form:

\[ K_{\text{obs}} = a + b[H^+] \]  

\[ \text{………(1)} \]

The values of ‘a’ and ‘b’ for Catechine is 1.2052 mol dm\(^{-3}\) and 0.0032 mol dm\(^{-3}\) min\(^{-1}\) respectively. \((r^2 = 0.991)\).

3.8 Thermodynamic parametric study
From effect of temperature on reaction rate, the enthalpy of activation \(\Delta H^*\), the energy of activation \(\Delta S^*\) and the free energy of activation \(\Delta G^*\) are computed. Various thermodynamic parameters \(E_a, \Delta H^*, \Delta S^*, \text{ and } \Delta G^*\) are presented in the Table 7, 8 and 9. The enthalpy of activation \(\Delta H^*\), values is 32.87\(\pm\)0.865 K Cal mol\(^{-1}\).The entropies of activation \(\Delta S^*\) are all negative indicating extensive and solvation of transition state over the reactants. It has been observed that \(\Delta G\) is positive (+), \(\Delta S\) is negative (-) and \(\Delta H\) is positive. These are as expected for bimolecular reaction. Calculation of activation energy parameter shows that these reactions are not enthalpy control.

3.9 Effect of solvent composition
To study the effect of solvent composition on oxidation rate of catechine 1,4 Dioxane is used as solvent. At a particular ionic strength, the rate oxidation of catechine with QCC increases with decreasing polarity of solvent. In other words, decrease in polarity with increase of dielectric constant of solvent mixture (1,4 dioxane - water) is observed and increase in oxidation of catechine.

According Scatchared [18], the plot of \(\log k_{\text{obs}}\) versus 1/D is found as linear. This explains that ion dipole type of interaction is involved in rate determined step. Tabular and graphical presentation of these result are given in Table 10 and figure 2 and 3 respectively.

3.10 Solvent Effect
The oxidation of catechine was studied in seven different solvents. The choice was limited because of solubility of catechine and QCC. There was no reaction with solvent chosen. The kinetics is similar in all the solvents which have been recorded in Table 5.

3.11 Correlation Analysis of Reactivity
The rate constant, \(k_2\) of oxidation of catechine in seven solvents showed significant correlation in terms of linear solvation energy correlation analysis equation of Kamlet [19].

\[ \log K_2 = A_0 + C\pi^* + b\beta + a\alpha \]  

\[ \text{……… (2)} \]

In the equation, \(\pi^*\) represents the solvent polarity, \(\beta\) the hydrogen acceptor basicity and \(\alpha\) is hydrogen bond donor acidity. \(A_0\) is the intercept term. The results of correlation analysis in terms of eq. (2); a biparametric equation involving \(\pi^*\) and \(\beta\) are given in below equations.
Here ‘n’ is the no. of data points and ‘Ψ’ is the Exner’s statistical parameter. Kamlet’s triparametric equation explains calculated 83% of the effect of solvent on oxidation. However by Exner’s criterian [20], the correlation is not even satisfactory (eq. 2). The minor contribution is of solvent polarity is observed. It alone accounted for ca. 55%. Both β and α are playing relatively minor role.

Swain equation [21] was also applied to analyze the data to explain solvent effect. The equation is given as under:

\[
\log K_2 = aA + bB + C
\]

In the above equation, ‘A’ is anion solvating power and ‘B’ is the cation solvating power. ‘C’ is the intercept term. ‘A+B’ represents solvent polarity. The rates in different solvents were analyzed in terms of equation (9) with A, B and with (A+B).

\[
\begin{align*}
\log K_2 &= 3.755 + 2.631(\pm 1.212)\alpha - 2.750(\pm 2.084)\pi^+ - 0.606(\pm 1.503)\beta \\
r^2 &= 0.832, \text{ sd } = 0.930, n = 7, \Psi = 0.111
\end{align*}
\]

\[
\begin{align*}
\log K_2 &= 5.768 - 5.3227(\pm 2.379)\pi^- - 0.794(\pm 0.885)\beta \\
r^2 &= 0.567, \text{ sd } = 1.29, n = 7, \Psi = 0.188
\end{align*}
\]

\[
\begin{align*}
\log K_2 &= -3.65 + 2.421(\pm 0.973)\alpha - 2.944(\pm 1.803)\pi^- \\
r^2 &= 0.822, \text{ sd } = 0.826 n =7, \Psi = 0.032
\end{align*}
\]

\[
\begin{align*}
\log K_2 &= 6.189 - 5.345(\pm 2.174)\pi^- \\
r^2 &= 0.547, \text{ sd } = 1.180, n = 7, \Psi = 0.057
\end{align*}
\]

\[
\begin{align*}
\log K_2 &= 1.622 + 3.542(\pm 1.084)\alpha - 1.063(\pm 1.592)\beta \\
r^2 &= 0.734, \text{ sd } = 1.01, n = 7 \Psi = 0.71
\end{align*}
\]

\[
\begin{align*}
\log K_2 &= 1.555 + 3.27(\pm 0.949)\alpha \\
r^2 &= 0.704, \text{ sd } = 0.955, n = 7 \Psi = 0.018
\end{align*}
\]
log \( K_2 \) = 3.963 − 1.466(± 1.859)\( A + B \) 
\[ r^2 = 0.111, \text{sd} = 1.65, n = 7, \Psi = 0.466 \] 

The rate of oxidation of catechine in seven different solvents showed correlation in Swain equation (eq. 9) with calculated 80% contributions. Effect of cation solvating and anion solvating power was poor. An attempt was made to correlate permittivity of solvent. The plot of log(rate) against inverse of relative permittivity is not linear. \( (r^2 = 0.4103, \text{sd} = 0.43, \Psi = 0.79) \).

We have used coefficient of determination (\( r^2 \)), standard deviation (sd) and Exner’s parameter (\( \Psi \)) as the measures of goodness of fit.

3.12 Mechanism

The rate of oxidation increases on increasing the concentration of catechine. Plot of \( \frac{1}{k_2} \) vs. \( \frac{1}{\text{Substrate}} \) is linear and has slope 1.4097. The rate of reaction increases with increasing [H\(^+\)] concentration. Plot of \( 1/k_2 \) vs. \( 1/\text{[Substrate]} \) gave linear line but does not pass through origin suggest that the rate obeys Michaelis-Menten type kinetics. Plot of \( K_2 \) vs [H\(^+\)] is a straight line with slope 1.359. It supports the idea that QCC may be protonated and the rate of oxidation increase. The overall mechanism therefore, involves the formation of intermediate complex in the slowest step and it is the rate determining step. There is no effect of ionic strength on the oxidation reaction giving the idea that in the rate determining step, no ions are involved. Increase in percentage of 1,4 dioxane increase the rate suggesting that medium of low dielectric constant favored the reaction. Linear plot of \( k_2 \) vs. \( 1/D \) confirms the ion-dipole type of interaction in the rate determining step. If \( k_2 \) vs. \( \frac{D - 1}{2D + 1} \) is a straight line with negative slope indicates that activated state is less polar, while positive indicates more polar activated state. In present study positive slope indicates that activated state is polar. Therefore, by increasing percentage of 1, 4 dioxane rates should increase, which is observed here.

Rate of reaction has increased by increasing temperature. Energy of activation is 41.47 ± 0.853 K Cal mol\(^{-1}\). This energy is less and does not correspond to C-C bond fission in decomposition of catechine by Cr(VI) in rate-determining step. On the basis of above study following mechanism has been proposed for oxidation of catechine.

Calculation of activating parameters showed that these reactions are not enthalpy controlled. Lowest energy of activation is not associated with highest rate or vice versa. The observed enthalpy of activation also supports this. As the charge separation takes place, the charged ends become highly solvated. This results in an immobilization ion by a large number of solvent molecules; it is reflected by entropy values.
On the basis of Michaelis-Menten concept, following overall mechanism and rate law is proposed.

\[
\text{Catechine} + \text{QCC} \xrightarrow{\kappa} \text{[Complex]} \\
\text{[Complex]} \xrightarrow{k_2} \text{Product}
\]

\[
\text{Rate} = - \frac{d[\text{QCC}]}{dt} = \frac{k_2 \times K_{\text{Catechine}} [\text{QCC}]}{1 + K_{\text{Catechine}}}
\]

Where ‘K’ is the formation constant (equilibrium constant) and ‘k_2’ is the rate constant of the reaction.
Table 1 Effect of Concentration of Quinolinium Chlorochromate (QCC) on the Rate at [Catechine] = 4.5×10^{-3} M

<table>
<thead>
<tr>
<th>QCC ×10^{-3} M</th>
<th>k_2, dm^3 m^{-1} min^{-1}</th>
<th>Regression(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 (Typical Run)</td>
<td>1.4097</td>
<td>0.993</td>
</tr>
<tr>
<td>0.50</td>
<td>15.0800</td>
<td>0.294</td>
</tr>
<tr>
<td>0.25</td>
<td>33.7300</td>
<td>0.940</td>
</tr>
<tr>
<td>0.13</td>
<td>73.7300</td>
<td>0.973</td>
</tr>
</tbody>
</table>

Table 2 Effect of Concentration of Catechine on the Rate at [QCC] = 1×10^{-3} M

<table>
<thead>
<tr>
<th>Catechine × 10^{-3} M</th>
<th>k_2, dm^3 m^{-1} min^{-1}</th>
<th>Regression(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.6667</td>
<td>0.914</td>
</tr>
<tr>
<td>1.5</td>
<td>1.1000</td>
<td>0.967</td>
</tr>
<tr>
<td>2.5</td>
<td>1.3155</td>
<td>0.990</td>
</tr>
<tr>
<td>3.5</td>
<td>1.3245</td>
<td>0.993</td>
</tr>
<tr>
<td>4.5</td>
<td>1.4097</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Table 3 Variation of Rate with Catechine Concentration

<table>
<thead>
<tr>
<th>1/[Catechine]</th>
<th>1/k_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>1.5022</td>
</tr>
<tr>
<td>0.667</td>
<td>0.9939</td>
</tr>
<tr>
<td>0.400</td>
<td>0.8799</td>
</tr>
<tr>
<td>0.286</td>
<td>0.7579</td>
</tr>
<tr>
<td>0.222</td>
<td>0.7094</td>
</tr>
</tbody>
</table>

Table 4 Effect of Some Salts on the Rates of Oxidation of Catechine by QCC at [Catechine] = 4×10^{-3} M

<table>
<thead>
<tr>
<th>Salts, 4.5×10^{-3} M</th>
<th>k_2, dm^3 m^{-1} min^{-1}</th>
<th>Regression(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Run</td>
<td>1.4097</td>
<td>0.993</td>
</tr>
<tr>
<td>KCl</td>
<td>1.4194</td>
<td>0.972</td>
</tr>
<tr>
<td>KBr</td>
<td>1.4616</td>
<td>0.912</td>
</tr>
<tr>
<td>KI</td>
<td>1.4152</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 5 Effect of Ionic strength on the Rates of Oxidation of Catechine [Catechine] = 4×10^{-3} M, [QCC] =1×10^{-3} M

<table>
<thead>
<tr>
<th>Ionic Strength</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_2, dm^3 m^{-1} min^{-1}</td>
<td>1.4097</td>
<td>1.4142</td>
<td>1.4256</td>
<td>1.4303</td>
<td>1.4081</td>
</tr>
</tbody>
</table>

Table 6 Effect of Acidity on the Rates of Oxidation of Catechine by QCC

<table>
<thead>
<tr>
<th>H^+ ×10^{-3} M</th>
<th>k_2, dm^3 m^{-1} min^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Run</td>
<td>1.4097</td>
</tr>
<tr>
<td>1.5</td>
<td>1.4103</td>
</tr>
<tr>
<td>2.5</td>
<td>1.4425</td>
</tr>
<tr>
<td>3.5</td>
<td>1.4669</td>
</tr>
<tr>
<td>4.0</td>
<td>1.4795</td>
</tr>
<tr>
<td>4.5</td>
<td>1.4943</td>
</tr>
</tbody>
</table>
Table 7  Formation Constant (K) for Oxidation of Catechine by QCC

<table>
<thead>
<tr>
<th>Temperature, Kelvin</th>
<th>298k</th>
<th>303k</th>
<th>308k</th>
<th>313k</th>
<th>318k</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_2$, dm$^3$mol$^{-1}$min$^{-1}$</td>
<td>2.7319</td>
<td>2.6114</td>
<td>2.5001</td>
<td>2.4131</td>
<td>2.2803</td>
</tr>
</tbody>
</table>

Table 8  Rate Constant ($k_2$) for Oxidation of Catechine by QCC

<table>
<thead>
<tr>
<th>Temperature, Kelvin(K)</th>
<th>298k</th>
<th>303k</th>
<th>308k</th>
<th>313k</th>
<th>318k</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_2$, dm$^3$mol$^{-1}$min$^{-1}$</td>
<td>2.2727</td>
<td>2.4913</td>
<td>2.7513</td>
<td>2.9103</td>
<td>3.0150</td>
</tr>
</tbody>
</table>

Table 9  Thermodynamic Parameters for Oxidation of Catechine

<table>
<thead>
<tr>
<th>Thermodynamic Parameters</th>
<th>$E_a$, K Cal mol$^{-1}$</th>
<th>$\Delta H^*$, K Cal mol$^{-1}$</th>
<th>$\Delta S^*$, K Cal mol$^{-1}$</th>
<th>$\Delta G^*$, K Cal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_2$, dm$^3$mol$^{-1}$min$^{-1}$</td>
<td>32.87±0.865</td>
<td>55.86±0.357</td>
<td>27.05±1.007</td>
<td>93.717</td>
</tr>
</tbody>
</table>

Figure 1 Variation of Rate with Catechine Concentration

Table 10 Variation of Rate with Solvent Composition

<table>
<thead>
<tr>
<th>% Dioxane (v/v)</th>
<th>Dielectric Constant (D)</th>
<th>$k_2$, dm$^3$min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>78.30</td>
<td>1.4097</td>
</tr>
<tr>
<td>10</td>
<td>69.69</td>
<td>2.6119</td>
</tr>
<tr>
<td>20</td>
<td>60.79</td>
<td>4.2311</td>
</tr>
<tr>
<td>30</td>
<td>51.90</td>
<td>7.1401</td>
</tr>
<tr>
<td>40</td>
<td>42.98</td>
<td>9.0010</td>
</tr>
<tr>
<td>50</td>
<td>34.26</td>
<td>11.4320</td>
</tr>
<tr>
<td>60</td>
<td>25.85</td>
<td>13.1700</td>
</tr>
</tbody>
</table>
Figure 2 Variation of Rate with Solvent Composition

Figure 3 Variation of Rate with Solvent Composition of Dioxane
Table 11 Effect of Solvent on Oxidation of Catechine by QCC

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$k_2$, dm$^3$ m$^{-3}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.4097</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>3.8350</td>
</tr>
<tr>
<td>N-propyl alcohol</td>
<td>4.1741</td>
</tr>
<tr>
<td>Acetone</td>
<td>3.1083</td>
</tr>
<tr>
<td>Dioxane</td>
<td>1.5954</td>
</tr>
<tr>
<td>Dioxane</td>
<td>0.4516</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.2877</td>
</tr>
</tbody>
</table>

CONCLUSION

Oxidation of Catechine follows first order reaction kinetics with QCC. Reaction is affected by various constraints like acidity, addition of salts, primary salt effect and concentration change in substrates. The rate obeys Michal-Menton type of kinetics. Oxidation does not take place by via free radical and activated state is more polar than reactant. The energy of activation is $32.87 \pm 0.865$ K Cal mol$^{-1}$, it does not correspond to C-C bond fission in decomposition of Catechine by Cr(VI) in the rate determining step. Solvent polarity plays a major role in activated state and it is experiment by both swain equation and multiparametric equation.

REFERENCES