INTRODUCTION

A survey of literature shows that reports on kinetics of oxidation of Phenyl acetic acid and DL-Mandelic acid by various oxidants are well documented. But it clearly indicates that there is no comparative studies on oxidation of Phenyl acetic acid and DL-Mandelic acid under similar conditions by Mn(VII). Hence to establish the differential reactivity of the above substrates oxidation by Mn(VII) in acidic medium has been investigated. This was also useful in understanding the differential mechanistic pathways in these oxidations, nature of valence states and role of solvent.

MATERIAL AND METHODS

Potassium permanganate – BDH (AR) was prepared in doubly distilled water and used as stock solution. Phenyl acetic acid – BDH (AR) was used without further purification. DL-mandelic acid – BDH (AR) was used without further purification. All other chemicals, acids and solvents used in
these investigations were of analytical reagent grade.

**Kinetic method**

The method employed by Tompkins\(^22\) was used: 5.0 ml aliquots of the reaction solution to 5% KI solution acidified with 2N H\(_2\)SO\(_4\) and the liberated iodine was titrated with standard thiosulphate solution. To reduce aerial oxidation of the acidified iodide solution, the acid concentration was kept low. When possible, the aliquot was titrated immediately after the withdrawal. In fast runs they were titrated in random order. In all the cases the titrations were completed within 10 minutes of the liberation of iodine. The low concentration of the thiosulphate employed necessitated its standardization frequently with standard dichromate.

**Product analysis**

Both substrates like Phenyl acetic acid and DL-Mandelic acid are oxidised to give benzaldehyde as the major product. This was identified by 2,4-DNP test and its melting point was found to be 234\(^0\)C which matches with known value.

**RESULTS AND DISCUSSION**

Kinetics and mechanism of oxidation of phenyl acetic acid and DL mandelic acid by Mn(VII) in aqueous acetic acid medium in the presence of perchloric acid have been investigated. The kinetics results are given below.

**Phenyl acetic acid**

**Effect of varying concentration of oxidant on reaction rate**

The reactions are found to be first order with respect to the oxidant. The first order nature with respect to oxidant is confirmed from the constancy in the rate constants at different initial concentrations of oxidant. Moreover a plot of log(a-x) vs time is linear confirming the first order dependence on oxidant (Table-I).

**Effect of varying concentration of substrate on reaction rate**

The dependence on the substrate has been found to be zero order as the first order rate constants do not change with increase in concentration of substrate (Table-I).

**DL- Mandelic acid**

**Effect of varying concentration of oxidant on reaction rate**

The reactions are found to be first order with respect to the oxidant. The first order nature
with respect to oxidant is confirmed from the constancy in the rate constants at different initial concentrations of oxidant. Moreover a plot of log (a-x) vs time is linear confirming the first order dependence on oxidant (Table-II).

**Effect of varying concentration of substrate on reaction rate**

The dependence on the substrate appears to be zero order at all concentrations of substrate as forty fold increase in concentration of the substrate results in 3-fold increase only in reaction rate. This points out that the reaction is apparently of zero order in substrate as found with phenyl acetic acid (Table-II).

**Effect of varying concentrations of acid on reaction rate**

The effect of variation of H+ in this oxidation could not be studied due to the enormous fastness of reaction with increasing acidity.

**Nature of oxidation states of manganese**

Manganese exhibits a variable oxidation number. Oxidation states of manganese i.e. +2, +4 and +7 are stable over wide range of acidity. In basic solution Mn(VI) and Mn(IV) are the main species of manganese.

The redox potentials are given below to give a comparative account of valency changes of manganese. However, the overall potential of Mn(VII) to Mn(II) change is 1.51V.

Mn(VII)-Mn(VI) e + MnO₄⁻ → MnO₅²⁻ + 0.558 ± 0.002

Mn(VI) − Mn(V) e + MnO₂⁻ → MnO⁺ + 0.285 ± 0.001

Mn(III) − Mn(II) e + Mn → Mn + 1.51

In the present investigation it appears that the two electron change in the rate determining step is important followed by fast changes of Mn(V) leading to finally Mn(II) in acid medium.

**Mechanistic pathway of oxidation of Phenyl acetic acid**

The kinetic orders observed are first order in oxidant, first order in H⁺ and zero order in substrate. The initial reaction appears to be intermediate formation of mandelic acid which decomposes to give benzenaldehyde in fast step.

**RATE LAW**

\[
[MnO⁺] + [H⁺] \rightarrow HMnO₄
\]

\[
HMnO₄ + [S] \rightarrow \text{Complex}
\]

\[
\text{Complex} \xrightleftharpoons[k_{\text{eq}}]{k} \text{Products}
\]

\[
\text{Rate} = k \times [c]
\]

\[
[H MnO₄] = \left[HMnO₄\right] + [C]
\]

\[
[H MnO₄] = \left[HMnO₄\right] + K_i[H MnO₄][S]
\]

\[
[H MnO₄] = \frac{[HMnO₄]+[S]}{1+K_i[S]}
\]

Substitute equation (2) in equation (1), we get

\[
= \frac{k \times K_i[H MnO₄][S]}{1 + K_i[S]}
\]

The reaction sequence can be represented as follows

\[
[MnO] + [H⁺] \xrightarrow{K} \text{HMnO₄}
\]

\[
\text{HMnO₄} + [S] \xrightarrow{K_1} \text{Complex}
\]

The final product is benzaldehyde

The sequence given above indicates that the rate determining step involves a two electron loss leading to a carbonium ion which rapidly reacts with water to give mandelic acid initially. Mandelic
Table 1: Effect of variation of various constituents on reaction rate of Phenyl acetic acid

<table>
<thead>
<tr>
<th>Variant</th>
<th>Concentration of Non variant</th>
<th>Concentration of Variant</th>
<th>$k \times 10^3$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KMnO$_4$</td>
<td>[Phenyl acetic acid] = 0.01M</td>
<td>0.000125M</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>[HClO$_4$] = 0.01M</td>
<td>0.00025M</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>AcOH = 20%</td>
<td>0.00025M</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>Temp. = 40°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenyl acetic acid</td>
<td>[KMnO$_4$] = 0.00025M</td>
<td>0.0025M</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>[HClO$_4$] = 0.01M</td>
<td>0.005M</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>AcOH = 20%</td>
<td>0.01M</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>Temp. = 40°C</td>
<td>0.02M</td>
<td>1.09</td>
</tr>
<tr>
<td>HClO$_4$</td>
<td>[Phenyl acetic acid] = 0.01M</td>
<td>0.0025M</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>[KMnO$_4$] = 0.00025M</td>
<td>0.0050M</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>AcOH = 20%</td>
<td>0.01M</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>Temp. = 40°C</td>
<td>0.02M</td>
<td>1.80</td>
</tr>
<tr>
<td>AcOH</td>
<td>[Phenyl acetic acid] = 0.01M</td>
<td>10%</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>[KMnO$_4$] = 0.00025M</td>
<td>20%</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>[HClO$_4$] = 0.01M</td>
<td>30%</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>Temp. = 40°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Effect of variation of various constituents on reaction rate of DL-Mandelic acid

<table>
<thead>
<tr>
<th>Variant</th>
<th>Concentration of Non variant</th>
<th>Concentration of Variant</th>
<th>$k \times 10^3$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KMnO$_4$</td>
<td>[DL-Mandelic acid] = 0.01M</td>
<td>0.000125M</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>[HClO$_4$] = 0.01M</td>
<td>0.00025M</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>AcOH = 20%</td>
<td>0.00025M</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>Temp. = 40°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DL-Mandelic acid</td>
<td>[KMnO$_4$] = 0.00025M</td>
<td>0.00025M</td>
<td>3.65</td>
</tr>
<tr>
<td></td>
<td>[HClO$_4$] = 0.01M</td>
<td>0.0005M</td>
<td>5.23</td>
</tr>
<tr>
<td></td>
<td>AcOH = 20%</td>
<td>0.01M</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>Temp. = 40°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
acid is rapidly oxidised to give benzaldehyde which is the final product.

**Mechanistic pathway of oxidation of DL-Mandelic acid**

In the present investigation mandelic acid undergoes oxidative decarboxylation to give benzaldehyde. In acid medium permanganate functions as a two electron oxidant. Hence the ionic pathway through ester formation is preferred. In this connection a comment on the oxidation of mandelic acid by acid permanganate at pH 4.3 by earlier workers is necessary. At pH 4.3 the authors postulated a mechanism involving one electron loss leading to radical formation. It is suggested that acid permanganate essentially reacts through a two electron transfer leading to an ionic pathway. It is only in alkaline medium a one electron loss is postulated in permanganate oxidations. It is difficult to arrive at any of the three types of decarboxylation with ionic path way on the basis of kinetic data alone. In the present investigation the pathway is as follows.

\[
\text{Oxidant} + S \xrightleftharpoons{} \text{Ester} \\
\text{Ester} \rightarrow \text{Products}
\]

The above reactions are represented as follows:

![Chemical reaction diagram]

**Comparison of oxidation of phenyl acetic acid and Mandelic acid**

Mandelic acid reacts much faster than phenyl acetic acid. The presence of hydroxy group helps in simultaneous oxidation and decarboxylation leading to faster rate. Phenyl acetic acid undergoes initial slow oxidation to mandelic acid which later is oxidized rapidly to benzaldehyde. The corresponding rate constants are \(1.08 \times 10^3\) sec\(^{-1}\) and \(10.22 \times 10^3\) sec\(^{-1}\) for phenyl acetic acid and mandelic acid respectively. The high reactivity of mandelic acid over phenyl acetic acid may be due to different mechanisms operating with the two substrates. The former may be passing through a rate determining O – H bond cleavage through ester formation and the latter by C – H bond fission.

**REFERENCES**


