The importance of permanganate is given in the chapter II (p.42 and 43). Oxidation by permanganate ion finds extensive applications in organic syntheses\(^1-7\) especially since the advent of phase transfer catalysis\(^3,4,6\) which permits the use of solvents like methylene chloride and benzene. Kinetic studies are important sources of mechanistic information on the reactions, as demonstrated by results referring to unsaturated acids in both aqueous\(^1,3-7\) and non-aqueous media\(^8\).

The manganese chemistry involved in these multistep redox reactions is an important source of information as the manganese intermediates are relatively easy to identify when they have sufficiently long life time and oxidation states of the intermediates permit useful conclusions as to the possible reaction mechanisms including the nature of intermediates. In strongly alkaline medium, the stable reduction product\(^9\) of permanganate ion is manganate ion, \(\text{MnO}_4^{2-}\) (discussed in detail in Chapter II(p.43)).
Mandelic acid (MA) is used in the form of its salts as a bacteriostatic agent for genitourinary tract infections. It has been oxidized by different oxidants in aqueous alkaline medium\textsuperscript{10}. Its oxidation by permanganate in acid medium is reported\textsuperscript{11}. There are reports\textsuperscript{12} of different oxidation products for mandelic acid. Although, some work on oxidation of organic\textsuperscript{13} and inorganic\textsuperscript{14} substrates by permanganate in aqueous alkaline medium has been carried out, there is no report in literature on the oxidation of mandelic acid in such media. The present study deals with title reaction to understand about the redox chemistry of permanganate and mandelic acid in alkaline medium.

**EXPERIMENTAL**

Stock solution of mandelic acid (Mallin crodt) was prepared by dissolving the appropriate amount of sample in doubly distilled water. The solutions of potassium permanganate and potassium manganate were prepared and standardized as described in chapter II (p.45). All other reagents were of analytical grade and their solutions were prepared by dissolving requisite amounts of the samples in doubly distilled conductivity water. NaOH and NaClO\textsubscript{4} were used to provide the required alkalinity and to maintain ionic
strength respectively.

**Kinetic Measurements**

All kinetic measurements were performed under pseudo-first order conditions where [MA] was at least 10 fold excess over [MnO₄⁻] at a constant ionic strength of 1.0 mol dm⁻³. The reaction was initiated by mixing previously thermostatted solutions of MnO₄⁻ and mandelic acid which also contained required quantities of NaOH and NaClO₄ to maintain required alkalinity and ionic strength respectively. The temperature was uniformly maintained at 26 ± 0.1 °C. The course of reaction was followed by monitoring decrease in the absorbance of MnO₄⁻, in a 1 cm quartz cell of Hitachi 150-20 Spectrophotometer at its absorption maximum 526 nm as a function of time. Earlier, it was verified that there is negligible interference from other species at this wavelength. Beer's law for permanganate at 526 nm had been verified as in previous chapter II (p.46) and the extinction coefficient (ε) was found to be, ε = 2083 ± 50 dm³ mol⁻¹ cm⁻¹ (literature ε = 2200). The first order rate constants, k_{obs} were evaluated by plots of log[MnO₄⁻] versus time. The first order plots in almost all cases were linear up to 80% of the reaction and k_{obs} were reproducible within ± 5%. An example
run is shown in Table III(i) (p.88) and its plot is represented in Fig. III(i) (p.89).

As in chapter II, during the course of measurements the colour of the solution changed from violet to blue and further to green. The spectrum of green solution was identical to that of $\text{MnO}_4^{2-}$. It is empirical that blue colour is originated from violet of permanganate and green from manganate, excluding the accumulation of hypomanganate.

The effect of dissolved oxygen on the rate of reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results obtained under the nitrogen and in presence of air was observed. In view of the ubiquitous contamination of carbonate in basic solutions, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. However, fresh solutions were used while conducting the experiments.
Table III(i)
Oxidation of mandelic acid by aqueous alkaline permanganate at 26 °C.

Example run

\[
\begin{align*}
[MnO_4^-] &= 3.0 \times 10^{-4}; \\
[MA] &= 3.0 \times 10^{-3}; \\
[OH^-] &= 0.50; \\
I &= 1.0/mol\ dm^3.
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density</th>
<th>([MnO_4^-] \times 10^4) mol dm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.619</td>
<td>2.97</td>
</tr>
<tr>
<td>1.0</td>
<td>0.522</td>
<td>2.50</td>
</tr>
<tr>
<td>2.0</td>
<td>0.437</td>
<td>2.09</td>
</tr>
<tr>
<td>3.0</td>
<td>0.370</td>
<td>1.77</td>
</tr>
<tr>
<td>4.0</td>
<td>0.318</td>
<td>1.52</td>
</tr>
<tr>
<td>5.0</td>
<td>0.276</td>
<td>1.32</td>
</tr>
<tr>
<td>6.0</td>
<td>0.242</td>
<td>1.16</td>
</tr>
<tr>
<td>7.0</td>
<td>0.215</td>
<td>1.03</td>
</tr>
<tr>
<td>8.0</td>
<td>0.194</td>
<td>0.93</td>
</tr>
<tr>
<td>9.0</td>
<td>0.177</td>
<td>0.84</td>
</tr>
<tr>
<td>10.0</td>
<td>0.162</td>
<td>0.77</td>
</tr>
<tr>
<td>11.0</td>
<td>0.151</td>
<td>0.72</td>
</tr>
<tr>
<td>12.0</td>
<td>0.142</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Figure III(i)

Pseudo-first order plots of alkaline permanganate oxidation of mandelic acid at 26 °C.

(Conditions as in Table III(iii) (p.93))
RESULTS

Stoichiometry and Product Analysis

Different sets of reaction mixture containing the excess permanganate concentration over mandelic acid in presence of 0.50 mol dm\(^{-3}\) NaOH adjusted to a constant ionic strength of 1.0 mol dm\(^{-3}\) were kept to react. After completion of the reaction, the remaining permanganate was assayed as described in chapter II (p.52). The results indicated that two moles of MnO\(_4^-\) consumed one mole of mandelic acid as given by equation (1). The results are represented in Table III(ii) (p.91). The main oxidation products were identified as aldehyde\(^{15}\) by spot test and manganate. The formation of benzaldehyde as a product of oxidation was also confirmed by preparing its 2,4-DNP derivative and comparing its M.P. with that of an authentic sample. Such products were also obtained in previous work\(^{16}\).

It was further observed that the aldehyde does not undergo further oxidation under the present kinetic conditions.

\[
\begin{align*}
C_6H_5-CH-COOH + 2MnO_4^- + 2OH^- &\rightarrow C_6H_5CHO + CO_2 + 2MnO_4^{2-} + 2H_2O \\
\text{OH} &
\end{align*}
\]

(1)
Table III(ii)

Stoichiometry of oxidation of mandelic acid by aqueous alkaline permanganate.

\[ [\text{OH}^-] = 0.50 \text{ mol dm}^{-3}; \quad I = 1.0 \text{ mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>Taken</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>[MnO$_4^-$] x 10$^4$</td>
<td>[MA] x 10$^4$</td>
</tr>
<tr>
<td>mol dm$^{-3}$</td>
<td>mol dm$^{-3}$</td>
</tr>
<tr>
<td>4.0</td>
<td>2.0</td>
</tr>
<tr>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>6.0</td>
<td>2.0</td>
</tr>
<tr>
<td>8.0</td>
<td>3.0</td>
</tr>
<tr>
<td>8.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Error ± 5%.
Reaction Order

The reaction order was determined from the slopes of log $k_{\text{obs}}$ versus log(concentration) plots by varying the concentration of reductant and alkali in turn, while keeping others constant.

Effect of [Oxidant]

In order to study the effect of oxidant, potassium permanganate concentration on the reaction, its concentration was varied in the range of $9.0 \times 10^{-5}$ to $9.0 \times 10^{-4}$ mol dm$^{-3}$ as shown in Table III(iii) (p.93). The linearity of plots of log[MnO$_4^-$] versus time indicates the order in [MnO$_4^-$] as unity as shown in Fig. III(i) (p.89). This was also confirmed by varying [MnO$_4^-$] which did not show any change in pseudo-first order constants ($k_{\text{obs}}$) values (Table III(iii) (p.93)).

Effect of [Substrate]

The substrate, mandelic acid was varied in the concentration range of $9.0 \times 10^{-4}$ to $9.0 \times 10^{-3}$ mol dm$^{-3}$ at 26°C as in Table III(iv) (p.94), keeping all other conditions constant. From the plot of log $k_{\text{obs}}$ versus log[MA] the order in [MA] was found to be less than unity (Fig. III(ii) (p.95)).
Table III(iii)

Effect of variation of $[\text{MnO}_4^-]$ on the oxidation of mandelic acid by permanganate in aqueous alkaline medium at 26°C.

$[\text{MA}] = 3.0 \times 10^{-3}$; $[\text{OH}^-] = 0.50$; $I = 1.0/\text{mol dm}^{-3}$.

<table>
<thead>
<tr>
<th>$[\text{MnO}_4^-] \times 10^4$ (mol dm$^{-3}$)</th>
<th>$k_{\text{obs}} \times 10^3$ s$^{-1}$</th>
<th>Expt.*</th>
<th>calcd.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>2.20</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>2.25</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>2.23</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>2.26</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>9.0</td>
<td>2.22</td>
<td>2.34</td>
<td></td>
</tr>
</tbody>
</table>

* Experimental and calculated.
Table III(iv)

Effect of variation of [MA] and [OH\textsuperscript{-}] on the oxidation of mandelic acid by permanganate in aqueous alkaline medium at 26°C.

\[ [\text{MnO}_4^-] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}; \quad I = 1.0 \text{ mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>[MA] x 10\textsuperscript{3}</th>
<th>[OH\textsuperscript{-}]</th>
<th>( k_{\text{obs}} \times 10^3 \text{ s}^{-1} )</th>
<th>Expt.*</th>
<th>calcd.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>0.5</td>
<td>0.90</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.5</td>
<td>1.74</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.5</td>
<td>2.25</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>0.5</td>
<td>3.24</td>
<td>3.33</td>
<td></td>
</tr>
<tr>
<td>9.0</td>
<td>0.5</td>
<td>5.81</td>
<td>5.63</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.1</td>
<td>0.85</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.3</td>
<td>1.70</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.5</td>
<td>2.25</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.7</td>
<td>2.70</td>
<td>2.66</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>1.0</td>
<td>3.15</td>
<td>2.85</td>
<td></td>
</tr>
</tbody>
</table>

* Experimental and calculated
Figure III(ii)

Order of reaction with respect to [MA] and [OH\textsuperscript{-}] in the oxidation of mandelic acid by alkaline permanganate.

(Conditions as in Table III(iv) (p. 94))

\begin{align*}
\log[\text{OH}^-] &= -2.0, -2.2, -2.4, -2.6, -2.8, -3.0, -3.0, -2.8, -2.6, -2.4, -2.2, -2.0 \\
\log[\text{MA}] &= -3.0, -2.8, -2.6, -2.4, -2.2, -2.0 \\
\log k_{\text{obs}} &= -3.0, -2.8, -2.6, -2.4, -2.2, -2.0 
\end{align*}
Effect of [Alkali]

To determine the order of the reaction with respect to [OH\(^-\)], the [OH\(^-\)] was varied from 0.1 to 1.0 mol dm\(^{-3}\) at fixed concentration of mandelic acid and MnO\(_4^-\), keeping constant ionic strength of 1.0 mol dm\(^{-3}\) as in Table III(iv) (p.94). It was found from the slope of log \(k_{\text{obs}}\) versus log[OH\(^-\)] plot, the order with respect to [OH\(^-\)] is less than unity [Fig. III(ii) (p.95)].

Effect of Ionic Strength

The effect of ionic strength on the reaction was studied by varying the sodium perchlorate concentration from 0.50 to 2.0 mol dm\(^{-3}\) at constant concentrations of permanganate, mandelic acid and alkali as given in Table III(v) (p.97). It was found that the rate constant enhanced with increasing concentration of NaClO\(_4\) and the plot of log \(k_{\text{obs}}\) versus \(I^{1/2}\) was linear with positive slope which is given in Fig. III(iii) (p.98).
Table III(v)

Effect of variation of ionic strength (I) and solvent polarity (D) on the oxidation of mandelic acid by alkaline permanganate at 26 °C.

\>[\text{MnO}_4^-] = 3.0 \times 10^{-4}; \quad [\text{HA}] = 3.0 \times 10^{-3}; \quad I = 1.0/\text{mol dm}^{-3}.

<table>
<thead>
<tr>
<th>I (mol dm(^{-3}))</th>
<th>(k_{\text{obs}} \times 10^3) (s(^{-1}))</th>
<th>% t-butanol</th>
<th>D (v/v)</th>
<th>(k_{\text{obs}} \times 10^3) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.50</td>
<td>1.0</td>
<td>77.82</td>
<td>1.51</td>
</tr>
<tr>
<td>0.7</td>
<td>1.85</td>
<td>2.0</td>
<td>77.14</td>
<td>2.02</td>
</tr>
<tr>
<td>1.0</td>
<td>2.25</td>
<td>3.0</td>
<td>76.47</td>
<td>2.74</td>
</tr>
<tr>
<td>1.5</td>
<td>4.30</td>
<td>4.0</td>
<td>75.79</td>
<td>5.72</td>
</tr>
<tr>
<td>2.0</td>
<td>4.90</td>
<td>5.0</td>
<td>75.12</td>
<td>8.03</td>
</tr>
</tbody>
</table>

Error ± 5%
Figure III(iii)

Effect of variation of ionic strength (I) and solvent polarity (D) on the oxidation of mandelic acid by alkaline permanganate at 26°C.

(Conditions as in Table III(v) (p.97))

\[ \frac{1}{D} \times 10^2 \]

![Graph showing log_10(kobs) vs. \( \sqrt{I} \) for the oxidation of mandelic acid by alkaline permanganate.](image)
Effect of Solvent Polarity

The relative permittivity (D) effect was studied by varying t-butanol-water content (Table III(v) (p.97)) in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivity were failed. However, they were computed from the values of pure liquids as in earlier work. There was no reaction of solvent with oxidant under experimental conditions used. The rate constant, \( k_{\text{obs}} \), increased with decrease in dielectric constant of the medium. The plot of \( \log k_{\text{obs}} \) versus 1/D was linear which is shown in Fig. III(iii) (p.98).

Effect of Initially Added Products

At a constant concentrations of permanganate, mandelic acid and alkali and at fixed ionic strength, some kinetic runs were carried out by adding benzaldehyde and \( \text{MnO}_4^2- \) in the concentration range of \( 1.0 \times 10^{-4} \) to \( 1.0 \times 10^{-3} \) and \( 2.0 \times 10^{-5} \) to \( 2.0 \times 10^{-4} \) mol dm\(^{-3} \) respectively as given in Table III(vi) (p.100). The non-variation of rate constants indicated that the initially added products did not affect the rate of the reaction to any significant extent [Table III(vi) (p.100)].
Table III(vi)

The effect of initial addition of products on the oxidation of mandelic acid by alkaline permanganate at 26 °C.

\[
\begin{align*}
[MnO_4^{-}] &= 3.0 \times 10^{-4}; \\
[MA] &= 3.0 \times 10^{-3}; \\
[OH^{-}] &= 0.50; \\
I &= 1.0/mol \text{ dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>([C_6H_5CHO] \times 10^3) mol dm(^{-3})</th>
<th>([MnO_4^{2-}] \times 10^4) mol dm(^{-3})</th>
<th>(k_{obs} \times 10^3) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-</td>
<td>2.25</td>
</tr>
<tr>
<td>0.2</td>
<td>-</td>
<td>2.30</td>
</tr>
<tr>
<td>0.4</td>
<td>-</td>
<td>2.35</td>
</tr>
<tr>
<td>0.7</td>
<td>-</td>
<td>2.30</td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>2.32</td>
</tr>
<tr>
<td>-</td>
<td>0.2</td>
<td>2.26</td>
</tr>
<tr>
<td>-</td>
<td>0.4</td>
<td>2.30</td>
</tr>
<tr>
<td>-</td>
<td>0.8</td>
<td>2.34</td>
</tr>
<tr>
<td>-</td>
<td>1.2</td>
<td>2.32</td>
</tr>
<tr>
<td>-</td>
<td>2.0</td>
<td>2.22</td>
</tr>
</tbody>
</table>

Error ± 5%
Test for Free Radicals

The reaction mixture was kept for an hour with acrylonitrile scavenger in an inert atmosphere. Diluting by methanol, the formation of precipitate indicates the free radical intervention in the reaction.

Effect of Temperature

The rate constants, k, of the slow step of scheme 1 were obtained from the intercepts of the plots of $1/k_{obs}$ versus $1/[MA]$ at different temperatures. The values of $k \text{ (s}^{-1})$ were $0.90 \pm 0.04 \times 10^{-2}$, $1.67 \pm 0.08 \times 10^{-2}$ and $2.85 \pm 0.14 \times 10^{-2}$ at 26, 31 and 36 °C respectively. These data were subjected to least square analysis as in chapter II and are tabulated in Table III(vii) (p.102). From the plot of log k versus 1/T (Fig. III(iv) (p.103)), the activation parameters have been calculated as in chapter II(p.62-66) and are tabulated (Table III(viii) (p.104)).
Table II(vii)

Effect of temperature on the slow step of the mechanism of oxidation of mandelic acid by alkaline permanganate.

\[ [\text{MnO}_4^-] = 3.0 \times 10^{-4}; \quad [\text{OH}^-] = 0.50; \quad I = 1.0/\text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>T*K</th>
<th>k</th>
<th>1/T(X)</th>
<th>logk(Y)</th>
<th>Y_{cal}**</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>s^{-1}</td>
<td>K^{-1}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
<td>--------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>299</td>
<td>0.009</td>
<td>0.003344</td>
<td>-2.04576</td>
<td>-2.04115</td>
</tr>
<tr>
<td>304</td>
<td>0.0167</td>
<td>0.003289</td>
<td>-1.77728</td>
<td>-1.78665</td>
</tr>
<tr>
<td>309</td>
<td>0.0285</td>
<td>0.003236</td>
<td>-1.54516</td>
<td>-1.54039</td>
</tr>
</tbody>
</table>

*T = Temperature

**Cal = Calculated.
Figure III(iv)

Effect of temperature on the slow step of the mechanism of oxidation of mandelic acid by alkaline permanganate.

(Conditions as in Table III(vii) (p.102))

\[
\frac{1}{T} \times 10^3
\]

\[3.1 \quad 3.2 \quad 3.3 \quad 3.4 \quad 3.5\]

\[\log k\]

\[\begin{array}{c}
3.1 \\
3.2 \\
3.3 \\
3.4 \\
3.5
\end{array}
\]

\[\begin{array}{c}
-1.2 \\
-1.4 \\
-1.6 \\
-1.8 \\
-2.0
\end{array}
\]
Table III(viii)

Thermodynamic activation parameters for the oxidation of mandelic acid by alkaline permanganate.

---

Activation parameters with respect to slow step of scheme 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$</td>
<td>$65 \pm 2 \text{ k J mol}^{-1}$</td>
</tr>
<tr>
<td>$\log A$</td>
<td>$9.5 \pm 0.5$</td>
</tr>
<tr>
<td>$\Delta S^#$</td>
<td>$-72 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>$\Delta H^#$</td>
<td>$63 \pm 3 \text{ k J mol}^{-1}$</td>
</tr>
<tr>
<td>$\Delta G^#$</td>
<td>$85 \pm 4 \text{ k J mol}^{-1}$</td>
</tr>
</tbody>
</table>
DISCUSSION

The permanganate ion, MnO$_4^-$, is a powerful oxidant in aqueous alkaline medium. As it exhibits multitude oxidation states, the stoichiometric results and pH of the reaction media play an important role. Under the present experimental condition at pH $> 12$, the reduction product of Mn(VII) being Mn(VI) is stable and further reduction of Mn(VI) might be stopped$^{14}$. The Diode Array Rapid Scan Spectrophotometer (DARSS) studies have shown that at pH $> 12$, the product of Mn(VII) is Mn(VI) and no further reduction was observed as reported$^{14}$ by Simandi et al. However, on long standing Mn(VI) is reduced to Mn(IV) slowly under our experimental conditions.

The reaction between mandelic acid and permanganate in alkaline medium has a stoichiometry of 1:2 with fractional order dependence each on alkali and mandelic acid concentrations and first order on permanganate concentration. No products effect has been observed. The results suggest that first the alkali combines with permanganate to give a alkali permanganate complex$^{18}$ which then reacts with substrate, mandelic acid to give another complex. This complex formed decomposes in a slow step to give free radical derived from decarboxylated mandelic acid which further reacts.
with another molecule of permanganate in a fast step to yield the products (Scheme 1).

\[
\begin{align*}
\text{MnO}_4^- + \text{OH}^- & \rightleftharpoons K_1 \quad \text{[} \begin{array}{c}
0 \\
\text{O} \\
\text{Mn} \\
\text{O} \\
0
\end{array} \text{]}^{2-} \quad \text{(C}_1\text{)} \\
\text{C}_6\text{H}_5\text{-CH} + \text{CO}_2 + \text{MnO}_4^- + \text{OH}^- & \rightarrow \text{C}_6\text{H}_5\text{CHO} + \text{MnO}_4^- + \text{H}_2\text{O} \\
\text{Complex } (C_2) & \xrightarrow{k} \text{C}_6\text{H}_5\text{-CH} + \text{CO}_2 + \text{MnO}_4^- + \text{OH}^- \\
\text{C}_6\text{H}_5\text{-CH} + \text{MnO}_4^- + \text{OH}^- & \rightarrow \text{C}_6\text{H}_5\text{CHO} + \text{MnO}_4^- + \text{H}_2\text{O}
\end{align*}
\]
The structure of the Complex (C\textsubscript{2}) might be as given below.

\[
\begin{array}{c}
\text{OH} & \text{0} & \text{0} \\
\text{C}_6\text{H}_5 & \text{CH} & \text{C} & \text{O} & \text{Mn} & \text{O} \\
\text{2-} & \text{0} & \text{0} \\
\end{array}
\]

Attempts to obtain the spectral UV.-VIS. evidence for the complex formation failed. Such complex formation between substrates and oxidants has been observed in other studies\textsuperscript{19}. However, the evidence for the complex formed is proved kinetically i.e. by the non-zero intercept of the plot of \(1/k_{\text{obs}}\) Vs. \(1/[\text{MA}]\) (Fig. III(v) (p.111)). Since Scheme 1 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in sequences of one electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. Free radical scavenging experiment reveals such a possibility (see infra). This type of radical intermediate has also been observed in earlier work\textsuperscript{20} with alkaline permanganate oxidation of various organic substrates.

The rate law of the reaction can be derived from scheme 1 as below.
Rate = $k [C_2]$

= $k K_2 [MA] [C_1]$

= $k K_1 K_2 [MA] [OH^-] [MnO_4^-]_f$  \hspace{1cm} (3)

Now,

$[MnO_4^-]_T = [MnO_4^-]_f + C_1 + C_2$

= $[MnO_4^-]_f + K_1 [OH^-] [MnO_4^-]_f + K_2 [MA] [C_1]$

= $[MnO_4^-]_f + K_1 [OH^-] [MnO_4^-]_f + K_1 K_2 [MA] [OH^-][MnO_4^-]_f$

= $[MnO_4^-]_f \left\{ 1 + K_1 [OH^-] + K_1 K_2 [MA] [OH^-]\right\}$

∴ $[MnO_4^-]_f = [MnO_4^-]_T / \left\{ 1 + K_1 [OH^-] + K_1 K_2 [MA] [OH^-]\right\}$  \hspace{1cm} (4)

$[OH^-]_T = [OH^-]_f + C_1 + C_2$

$[OH^-]_T = [OH^-]_f + K_1 [OH^-] [MnO_4^-]_f + K_2 [MA] [C_1]$

$[OH^-]_T = [OH^-]_f + K_1 [OH^-] [MnO_4^-]_f + K_1 K_2 [MA] [OH^-][MnO_4^-]_f$

$[OH^-]_T = [OH^-]_f \left\{ 1 + K_1 [MnO_4^-] + K_1 K_2 [MA] [MnO_4^-]\right\}$

$[OH^-]_f = [OH^-]_T / \left\{ 1 + K_1 [MnO_4^-] + K_1 K_2 [MA] [MnO_4^-]\right\}$  \hspace{1cm} (6)
and

\[ [\text{MA}]_T = [\text{MA}]_f + C_2 \]  \hspace{1cm} (7)

\[ = [\text{MA}]_f + K_2 [\text{MA}]_f [C_1] \]

\[ = [\text{MA}]_f + K_1 K_2 [\text{MA}]_f [\text{OH}^-][\text{MnO}_4^-] \]

\[ = [\text{MA}]_f \left\{ 1 + K_1 K_2 [\text{OH}^-][\text{MnO}_4^-] \right\} \]

\[ [\text{MA}]_f = [\text{MA}]_T / \left\{ 1 + K_1 K_2 [\text{OH}^-][\text{MnO}_4^-] \right\} \]  \hspace{1cm} (8)

Substituting the values of equation (4), (6) and (8) into equation (3) we get.

\[ \frac{d[\text{MnO}_4^-]}{dt} = \]

\[ k K_1 K_2 [\text{MA}]_T [\text{OH}^-]_T [\text{MnO}_4^-]_T \]

\[ \frac{1}{\left\{ 1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{MA}] [\text{OH}^-] \right\} \times \left\{ 1 + K_1 K_2 [\text{OH}^-][\text{MnO}_4^-] \right\} \times \left\{ 1 + K_1 [\text{MnO}_4^-] + K_1 K_2 [\text{MA}] [\text{MnO}_4^-] \right\} } \]

\[ (9) \]

The terms such as \((1 + K_1 K_2 [\text{MnO}_4^-][\text{OH}^-])\) and \((1 + K_1 [\text{MnO}_4^-] + K_1 K_2 [\text{MA}][\text{MnO}_4^-])\) in the denominator of equation (9) approximate to unity in view of low concentration of \(\text{MnO}_4^-\) used. Therefore, equation (9) becomes equation (10).
\[
\text{Rate} = -\frac{d[\text{MnO}_4^-]}{dt} = \frac{k K_1 K_2 [\text{MA}]_T [\text{MnO}_4^-]_T [\text{OH}^-]_T}{(1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{MA}] [\text{OH}^-])} \quad (10)
\]

or
\[
\frac{\text{Rate}}{[\text{MnO}_4^-]_T} = k_{\text{obs}} = \frac{k K_1 K_2 [\text{MA}]_T [\text{OH}^-]_T}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{MA}] [\text{OH}^-]} \quad (11)
\]

Equation (11) can be rearranged to the form (12) which is used for verification of the rate law, by omitting subscript "T" in the equation (12) we have,

\[
\frac{1}{k_{\text{obs}}} = \frac{1}{k K_1 K_2 [\text{MA}] [\text{OH}^-]} + \frac{1}{k K_2 [\text{MA}]} + \frac{1}{k} \quad (12)
\]

According to (12) the plots of \(1/k_{\text{obs}}\) Vs \(1/[\text{MA}]\) and \(1/k_{\text{obs}}\) Vs \(1/[\text{OH}^-]\) should be linear and are verified in Fig. III(v) (p.111). The slopes and intercepts of such plots lead to the values of \(k\), \(K_1\) and \(K_2\) at 26 °C as \(0.9 \pm 0.04 \times 10^{-2}\) s\(^{-1}\), \(1.6 \pm 0.08\) dm\(^3\) mol\(^{-1}\) and 265 \pm 13\) respectively. Using these values rate constants over different experimental conditions were calculated and compared with experimental data (Table III(iii and iv) (p.93 and 94). There is a reasonable agreement between them, which fortifies the scheme 1.
Verification of rate law for the oxidation of mandelic acid by alkaline permanganate at 26 °C

(Conditions as in Table III(iv) (p.94))
The effect of increasing ionic strength on rate qualitatively explains the reaction between same charged ions as shown in scheme 1. The effect of solvent on the reaction kinetics has been described in detail in chapter II (p.73). In the present study increase in rate with decrease in dielectric constant of the medium has been observed, which cannot be explained by Amis theory\textsuperscript{21}, as the presence of a positive ion is unlikely in the alkaline medium employed. Applying the Born equation, Laidler and Eyring have derived,

\[
\ln k = \ln k_0 + \frac{N Z^2 e^2}{2 D R T} \left[ \frac{1}{r} - \frac{1}{r^*} \right] \tag{13}
\]

where \( k_0 \) is the rate constant in a medium of infinite dielectric constant and \( r^* \) refer to the radius of the reacting species and activated complex respectively. It can be seen from the equation (13) that rate should be greater in a medium of lower dielectric constant when \( r^* > r \). There is a possibility of intra-molecular hydrogen bonding that could stabilize the transition state increasing the size of activated complex by attracting solvent molecules due to solvation effect. The fairly high positive values of \( \Delta H^\# \) and \( \Delta G^\# \) (Table III(viii) (p.104)) also indicate that the transition state is highly solvated which results in increase
in the size of transition state. It is likely that $r^* > r$ for the mandelic acid, thus explaining the experimental observation. Thus one can expect the intramolecular hydrogen bonding in mandelic acid since it contains $-\text{OH}$ and $-\text{COOH}$ groups on the same carbon atom. Such type of hydrogen bonding is quite common for molecules having $-\text{COOH}$ and $-\text{NH}_2$, $-\text{COOH}$ and $-\text{OH}$ groups etc. either on the adjacent carbon atom or on the same carbon atom of the molecule as so found in simple amino acids.

The moderate values of $\Delta H^\#$ and $\Delta S^\#$ were both favourable for electron transfer processes. The value of $\Delta H^\#$ was due to release of energy on solution changes in the transition state. The negative value of $\Delta S^\#$ within the range for radical reactions have been ascribed to the nature of electron pairing and electron unpairing processes, and to the loss of degrees of freedom, formerly available to the reactions on the formation of rigid transition state.

Findings of Chapter III

The reaction between permanganate and mandelic acid in alkaline medium exhibits 2:1 stoichiometry (Oxidant : Reductant). The reaction shows first order dependence of rate
on permanganate concentration and fractional order dependence each in mandelic acid and alkali concentrations. Reaction rate increases with increase in ionic strength and decrease in solvent polarity of the medium. Initial addition of reaction products did not affect the rate significantly. The rate of the reaction increases with increase in temperature. Activation parameters with respect to slow step of the mechanism were evaluated.
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