Chapter VI

Kinetics and Mechanistic Study of the Oxidative Deamination and Decarboxylation of L-Valine by alkaline Permanganate

Potassium permanganate is widely used as an oxidising agent in synthetic as well as in analytical chemistry and also as a disinfectant. The reactions with permanganate are governed by pH of the medium. Among six oxidation states of manganese from 2+ to 7+, permanganate, Mn(VII) is the most potent oxidation state in acid as well as in alkaline medium.

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 times and oxidation states of the intermediates permit useful conclusions as to the possible reaction mechanism including the nature of intermediates.

The oxidation by permanganate ion finds extensive applications in organic syntheses\textsuperscript{1,7} especially since the advent of phase transfer catalysis\textsuperscript{3,4,6}. Kinetic studies are important sources of mechanistic information on the reactions, as demonstrated by the results referring to unsaturated acids both in aqueous\textsuperscript{1,3-7} and non-aqueous media\textsuperscript{8}.

During the oxidation by permanganate, it is evident that permanganate is reduced to various oxidation states in acidic, alkaline and neutral media.
Furthermore, the mechanism by which the multivalent oxidant oxidises a substrate depends not only on the substrate but also on the medium used for the study. In strongly alkaline medium, the stable reduction product of permanganate ion is manganate ion, $\text{MnO}_4^{2-}$. No mechanistic information is available to distinguish between a direct one-electron reduction to $\text{Mn(VI)}$ (Scheme 1) and a mechanism, in which a hypomanganate is formed in a two-electron reduction followed by a rapid oxidation of the hypomanganate ion (Scheme 2).

\[
\begin{align*}
\text{Mn(VII)} + S & \xrightarrow{k_1} \text{Mn(VI)} + S' \\
\text{Mn(VII)} + S' & \xrightarrow{k_2} \text{Mn(VI)} + \text{Products}
\end{align*}
\]

Where, $S =$ substrate; $k_2 \gg k_1$

**Scheme 1**

\[
\begin{align*}
\text{Mn(VII)} + S & \xrightarrow{k_3} \text{Mn(V)} + \text{Products} \\
\text{Mn(VII)} + \text{Mn(V)} & \xrightarrow{k_4} 2 \text{Mn(VI)}
\end{align*}
\]

Where, $S =$ substrate; $k_4 \gg k_3$

**Scheme 2**

The general importance of amino acids is discussed in chapter II (p.35). L-
valine is one of the essential basic amino acids, which is essential in the nutrition of animals and man. Its role is crucial in the development of organs, especially in
children. It also finds applications in medicine and pharmaceuticals. Amino acids have been oxidised by a variety of oxidising agents. Although several types of organic and inorganic substrates are oxidised by permanganate in aqueous alkaline medium, there are only a few reports on the oxidation of amino acids by aqueous alkaline permanganate. The kinetic investigation of the oxidation of amino acids has been carried out under different experimental conditions. In many cases it was reported that amino acids undergo oxidative decarboxylation. Jayaprakash Rao et al. suggested that the oxidation of amino acids by two electron oxidant such as diperiodatoargentate(III) in alkaline medium involves two electron transfer which involves imino acid intermediate in the rate determining step. This intermediate subsequently undergoes hydrolysis to yield keto acids. One electron oxidants such as ceric sulphate, peroxomonosulphate and hexacyanoferrate(III) also oxidize amino acids to keto acids. But other studies with amino acids reports the oxidation product as corresponding aldehyde. Thus, the study of amino acids become important because of their biological significance and selectivity towards the oxidants. The literature survey reveals that there are no reports on mechanistic studies of L-valine oxidation by Mn(VII). Thus, in order to explore the mechanism of oxidation by permanganate ion in strongly aqueous alkaline medium and to check the selectivity of L-valine towards permanganate, we have selected L-valine as a substrate. The present study deals with the title reaction to investigate the redox chemistry of permanganate and L-valine in such media.
EXPERIMENTAL

Stock solution of L-valine (Sisco-Chem.Ltd) was prepared by dissolving the appropriate amount of sample in doubly distilled water. The solution of potassium permanganate (BDH) was prepared and standardized against oxalic acid\(^{21}\). Potassium manganate solution was prepared as described by Carrington and Symons\(^{22}\) as follows: an aqueous solution of potassium permanganate was heated to boiling > 120° C in 8.0 mol dm\(^{-3}\) KOH solution until it turned green. The solid potassium manganate, which formed on cooling, was recrystallised from the KOH solution. Using the required amount of recrystallised sample, a stock solution of potassium manganate was then prepared in aqueous KOH. The solution was standardized by measuring the absorbance on a Hitachi 150-20 spectrophotometer with a 1 cm quartz cell at 608 nm (\(\varepsilon = 1530 \pm 20\) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)).

All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled water. NaOH and NaClO\(_4\) were used to provide the required alkalinity and to maintain the ionic strength respectively.
KINETIC PROCEDURE

All kinetic measurements were performed under pseudo-first order conditions with \([\text{L-valine}]:[\text{MnO}_4^-] > 10:1\) at a constant ionic strength of 0.50 mol dm\(^{-3}\). The reaction was initiated by mixing previously thermostatted solutions of \(\text{MnO}_4^-\) and L-valine which also contained the necessary quantities of NaOH and NaClO\(_4\) to maintain the required alkalinity and ionic strength respectively. The temperature was uniformly maintained at \(27 \pm 0.1^\circ\) C. The course of reaction was followed by monitoring the decrease in the absorbance of \(\text{MnO}_4^-\) in a 1 cm quartz cell of a Hitachi model 150-20 Spectrophotometer at its absorption maximum of 526 nm as a function of time. Earlier it was verified that there is negligible interference from other reagents at this wavelength. The application of Beer’s law to permanganate at 526 nm had been verified (Fig. VI (i) (p.174)), giving \(\varepsilon = 2083 \pm 50\) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\) (Literature \(\varepsilon = 2200 \) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\))\(^{10}\). The first order rate constants, \((k_{\text{obs}})\) were evaluated by plots of \(\log \text{[MnO}_4^-]\) versus time. The first order plots in almost all cases were linear 80% completion of the reaction and \((k_{\text{obs}})\) were reproducible within \(\pm 5\%\). An example run is given in Table VI (i) (p.175).
Verification of Beer’s law for [MnO₄⁻] at 526 nm in 0.20 mol dm⁻³ alkali.
**Table VI (i)**

Example run for oxidation of L-valine by aqueous alkaline permanganate

\[
[MnO_4^-] = 2.0 \times 10^{-4}; \quad \text{[L-valine]} = 2.0 \times 10^{-3}; \\
[OH^-] = 0.30; \quad \text{I} = 0.50/\text{mol dm}^{-3}.
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density (526 nm)</th>
<th>([\text{MnO}_4^-] \times 10^4) (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.416</td>
<td>1.997</td>
</tr>
<tr>
<td>0.4</td>
<td>0.398</td>
<td>1.891</td>
</tr>
<tr>
<td>1.0</td>
<td>0.378</td>
<td>1.814</td>
</tr>
<tr>
<td>2.0</td>
<td>0.357</td>
<td>1.713</td>
</tr>
<tr>
<td>4.0</td>
<td>0.318</td>
<td>1.526</td>
</tr>
<tr>
<td>6.0</td>
<td>0.278</td>
<td>1.334</td>
</tr>
<tr>
<td>8.0</td>
<td>0.237</td>
<td>1.137</td>
</tr>
<tr>
<td>10.0</td>
<td>0.203</td>
<td>0.974</td>
</tr>
<tr>
<td>12.0</td>
<td>0.174</td>
<td>0.835</td>
</tr>
<tr>
<td>14.0</td>
<td>0.150</td>
<td>0.720</td>
</tr>
<tr>
<td>16.0</td>
<td>0.132</td>
<td>0.633</td>
</tr>
</tbody>
</table>

Error ± 5%.
During the course of measurements, the solution changed from violet to blue and then to green. The spectrum of the green solution was identical to that of MnO$_4^-$.

It is probable that the blue colour originated from the violet of permanganate and the green from the manganate, excluding the accumulation of hypomanganate. It is also evident from the Fig. VI (ii) (p.177) that the concentration of permanganate decreases at 526 nm whereas the concentration of manganate increases at 608 nm.

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 the presence of air was observed. In view of the ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. However, fresh solutions were used when conducting the experiments.

In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the rate.
Uv-Vis. spectral changes during the oxidation of L-valine by aqueous alkaline permanganate at 27 °C, scanning time interval = 2 min.

Conditions:

\[ [\text{MnO}_4^-] = 2.0 \times 10^{-4}; \]
\[ [\text{L-valine}] = 2.0 \times 10^{-3}; \]
\[ [\text{OH}^-] = 0.30; \]
\[ I = 0.50/\text{mol dm}^{-3}. \]
RESULTS

Stoichiometry and product analysis

The reaction mixtures containing an excess permanganate concentration over L-valine, and 0.30 mol dm\(^{-3}\) NaOH and adjusted ionic strength of 0.50 mol dm\(^{-3}\) was allowed to react for 2 hours at 27 ± 0.1\(^\circ\) C. After completion of the reaction, solid KI was added followed by acidification by 10\% H\(_2\)SO\(_4\). The remaining MnO\(_4^-\) was then titrated against standard sodium thiosulphate\(^{33}\). The results indicated that two moles of MnO\(_4^-\) consumed by one mole of L-valine as given by equation (1) (Table VI (ii) (p.179)). The main reaction products were identified as aldehyde\(^{24}\) by spot test, ammonia\(^{25}\) by Nessler’s reagent and manganate by its visible spectrum. CO\(_2\) was qualitatively detected by bubbling N\(_2\) gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water\(^{26}\). The quantitative estimation of aldehyde by 2,4-DNP derivative\(^{27}\), yielded nearly 78\%. The nature of the aldehyde, was confirmed by its IR spectrum\(^{28}\) which showed a carbonyl stretching at 1729 cm\(^{-1}\) and a band at 2928 cm\(^{-1}\) due to aldehydic stretching, thus confirming the presence of isobutylaldehyde. It was further observed that the aldehyde does not undergo further oxidation under the present kinetic conditions. Test for corresponding acid was negative.
Table VI (ii)

Stoichiometry of oxidation of L-valine by alkaline permanganate at 27° C.

\[ [\text{OH}^-] = 0.30; \quad I = 0.50/\text{mol dm}^3. \]

<table>
<thead>
<tr>
<th>Taken [MnO_4^-] \times 10^4 (mol dm(^{-3}))</th>
<th>[L-Val] \times 10^4 (mol dm(^{-3}))</th>
<th>Found [MnO_4^-] \times 10^4 (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>0.00</td>
</tr>
<tr>
<td>3.0</td>
<td>1.0</td>
<td>1.08</td>
</tr>
<tr>
<td>6.0</td>
<td>2.0</td>
<td>2.05</td>
</tr>
<tr>
<td>8.0</td>
<td>3.0</td>
<td>1.95</td>
</tr>
<tr>
<td>8.0</td>
<td>4.0</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Error ±5%.
\[
(\text{CH}_3\text{H}_2-\text{CH}-\text{CH}-\text{COOH} + 2\text{MnO}_4^- + 2\text{OH}^- \rightarrow (\text{CH}_3\text{H}_2-\text{CH}-\text{CHO} + 2\text{MnO}_4^{2-} + \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (1)
\]

**REACTION ORDERS**

The reaction orders were determined from the slopes of log (\(k_{\text{obs}}\)) versus log (concentration) plots by varying the concentration of oxidant, reductant and alkali in each, while keeping others constant.

**Effect of [Permanganate]**

The oxidant, potassium permanagate concentration was varied in the range of \(5.0 \times 10^{-5}\) to \(5.0 \times 10^{-4}\) mol dm\(^{-3}\) as shown in Table VI (iii) (p.181). All the experiments exhibited an identical characteristics. The plots of log[\(\text{MnO}_4^-\)] versus time, for different initial concentrations of \(\text{MnO}_4^-\) are found to be linear as shown in Figure VI (iii) (p.182) and the fairly constant \(k_{\text{obs}}\) values indicate that the order with respect to [\(\text{MnO}_4^-\)] was one. This was also confirmed by varying [\(\text{MnO}_4^-\)] which did not show any change in pseudo-first order constants (\(k_{\text{obs}}\)) values as shown in Table VI (iii) (p.181).

**Effect of [L-valine]**

The substrate L-valine was varied in the range of \(5.0 \times 10^{-4}\) to \(5.0 \times 10^{-3}\) mol dm\(^{-3}\)at 27\(^\circ\) C, keeping all other reactant concentrations and conditions
Table VI (iii)

Effect of variation of $[\text{MnO}_4^-]$, on oxidation of L-valine by aqueous alkaline permanganate at 27° C.

$[\text{L-Val}] = 2.0 \times 10^{-3}; \quad [\text{OH}^-] = 0.30; \quad I = 0.50/\text{mol dm}^{-3}$.

<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>Calc*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.15</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.18</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1.15</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>1.16</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>1.15</td>
<td>1.10</td>
<td></td>
</tr>
</tbody>
</table>

*Experimental and Calculated. Error ± 5%.
Figure VI (iii)

First order plot of $[\text{MnO}_4^-]$ on oxidation of L-valine by aqueous alkaline permanganate at $27^\circ \text{C}$.

(Conditions as in Table VI (iii) (p.181))
constant (Table VI (iv) (p.184)). The rate constant \( k_{\text{obs}} \) values increased in concentration of L-valine indicating an apparent less than unit order dependence on substrate concentration which is shown in Fig. VI (iv) (p.185).

**Effect of \([\text{alkali}]\)**

The effect of alkali on the reaction was studied at constant concentrations of L-valine and potassium permanganate and at a constant ionic strength of 0.5 mol dm\(^{-3}\) at 27\(^\circ\) C. The rate constant increased with the increase in \([\text{alkali}]\), indicating an apparent less than unit order dependence on \([\text{alkali}]\) as given in Table VI (iv) (p.184) and Fig. VI (iv) (p.185).

**Effect of initially added products**

The externally added products such as manganate, ammonium hydroxide and aldehyde did not show any significant effect on the rate of the reaction (Table VI(v) (p.186)).

**Effect of ionic strength**

The effect of ionic strength was studied by varying the sodium perchlorate concentration from 0.3 to 2.0 mol dm\(^{-3}\) at constant concentrations of permanganate, L-valine, alkali as given in Table VI (vi) (p.188). It was found that the rate constant decreased with increase in concentration of NaClO\(_4\) and the plot
Table VI (iv)

Effect of variation of [L-valine] and [OH⁻] on the oxidation of L-valine by aqueous alkaline permanganate at 27°C.

\[
[MnO_4^-] = 2.0 \times 10^{-4}; \quad I = 0.50/mol\ dm^{-3}.
\]

<table>
<thead>
<tr>
<th>[L-Val] (\times 10^3) (mol dm(^{-3}))</th>
<th>[OH⁻] (mol dm(^{-3}))</th>
<th>(k_{obs} \times 10^3) (s(^{-1}))</th>
<th>Expt.</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.3</td>
<td>0.49</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.3</td>
<td>0.76</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.3</td>
<td>1.15</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.3</td>
<td>1.70</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>0.3</td>
<td>2.60</td>
<td>2.32</td>
<td></td>
</tr>
</tbody>
</table>

| 2.0                                      | 0.05                     | 0.32                          | 0.32 |      |
| 2.0                                      | 0.10                     | 0.56                          | 0.55 |      |
| 2.0                                      | 0.20                     | 0.82                          | 0.85 |      |
| 2.0                                      | 0.30                     | 1.15                          | 1.10 |      |
| 2.0                                      | 0.50                     | 1.54                          | 1.45 |      |
Figure VI (iv)

Order of reaction with respect to [L-valine] and [OH'] on oxidation of L-valine by aqueous alkaline permanganate at 27° C.

(Conditions as in Table VI (iv) (p.184))
Table VI (v)

Effect of variation of [MnO$_4^-$], [aldehyde] and [NH$_4$OH] on oxidation of L-valine by aqueous alkaline permanganate at 27°C.

[MnO$_4^-$] = 2.0 x $10^{-4}$; [L-Val] = 2.0 x $10^{-3}$; [OH$^-$] = 0.30; I = 0.50/mol dm$^{-3}$.

<table>
<thead>
<tr>
<th>[MnO$_4^-$] x 10$^{-4}$ (mol dm$^{-3}$)</th>
<th>[Aldehyde] x 10$^3$ (mol dm$^{-3}$)</th>
<th>[NH$_4$OH] x 10$^3$ (mol dm$^{-3}$)</th>
<th>$k_{obs}$ x 10$^3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>1.16</td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>1.19</td>
</tr>
<tr>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>1.18</td>
</tr>
<tr>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>1.16</td>
</tr>
<tr>
<td>5.0</td>
<td>-</td>
<td>-</td>
<td>1.18</td>
</tr>
<tr>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>1.21</td>
</tr>
<tr>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>1.24</td>
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<td>1.21</td>
</tr>
<tr>
<td>-</td>
<td>2.0</td>
<td>-</td>
<td>1.20</td>
</tr>
<tr>
<td>-</td>
<td>3.0</td>
<td>-</td>
<td>1.23</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>1.22</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>1.24</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>1.23</td>
</tr>
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<td>-</td>
<td>1.5</td>
<td>1.23</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>1.21</td>
</tr>
</tbody>
</table>

186
of \( \log k_{\text{obs}} \) versus \( I^{1/2} \) was linear with positive slope which is given in Fig. VI (v) (p.189).

**Effect of dielectric constant**

The effect of dielectric constant (D) effect was studied by varying the t-butanol water content in the reaction mixture with all other conditions being maintain constant. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquids as given in chapter III (p.83). The solvent did not react with the oxidant under the experimental conditions. The rate constants, \( k_{\text{obs}} \) increased with decrease in the dielectric constant of the medium (Table VI (vi) (p.188). The plot of \( \log k_{\text{obs}} \) versus \( 1/D \) was linear with positive slope as shown in Fig. VI (v) (p.189).

**Test for free radicals**

The reaction mixture was mixed with acrylonitrile monomer and kept for 2 hours in an inert atmosphere. On diluting with methanol a white precipitate was formed, indicating the intervention of free radicals in the reaction.
Table VI (vi)

Effect of variation of ionic strength (I) and solvent polarity (D) on the oxidation of L-valine by aqueous alkaline permanganate at 27° C.

\[ [\text{MnO}_4^-] = 2.0 \times 10^{-4}; \quad [\text{MnO}_4^-] = 2.0 \times 10^{-4}; \]
\[ [\text{L-Val}] = 2.0 \times 10^{-3}; \quad [\text{L-Val}] = 2.0 \times 10^{-3}; \]
\[ [\text{OH}^-] = 0.30; \quad [\text{OH}^-] = 0.30; \]
\[ I = 0.50/\text{mol dm}^3. \]

<table>
<thead>
<tr>
<th>I (mol dm(^{-3}))</th>
<th>(k_{\text{obs}} \times 10^3) (s(^{-1}))</th>
<th>% of D</th>
<th>D</th>
<th>(k_{\text{obs}} \times 10^3) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>1.15</td>
<td>5</td>
<td>75.12</td>
<td>1.53</td>
</tr>
<tr>
<td>0.5</td>
<td>1.29</td>
<td>10</td>
<td>72.52</td>
<td>1.89</td>
</tr>
<tr>
<td>1.0</td>
<td>1.69</td>
<td>15</td>
<td>68.49</td>
<td>2.32</td>
</tr>
<tr>
<td>1.5</td>
<td>1.96</td>
<td>20</td>
<td>65.35</td>
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</tr>
<tr>
<td>2.0</td>
<td>2.31</td>
<td>25</td>
<td>61.72</td>
<td>3.89</td>
</tr>
</tbody>
</table>

\*t-butanol-water (V/V)

Error ± 5%.
Figure VI (v)

Effect of ionic strength (I) and solvent polarity (D) on the oxidation of L-valine by aqueous alkaline permanganate at 27°C.

(Conditions as in Table VI (vi) (p.188))
**Effect of temperature**

The rate of the reaction was measured at four different temperatures with varying [L-Val] and [OH⁻] keeping other conditions constant. The rate of reaction was found to increase with increase in temperature. The rate constants, $k_1$ and $k_2$ of the slow step of scheme 3 were obtained from the intercept of the plots of $k_{obs}$ versus [L-Val] and $1/k_{obs}-k_2[OH^-]$ versus $1/[OH^-]$ for different temperatures (Table VI (vii) (p.191)). The energy of activation corresponding to these constants was evaluated from the plot of log $k_1$ and log $k_2$ versus $1/T$ each (Fig. VI (vi) (p.192)) from which two sets of activation parameters (for path I and path II of scheme 3) were calculated as in previous chapter and are given in Table VI (viii) (p.193).
Table VI (vii)

Effect of temperature on the slow step of the mechanism of oxidation of L-valine by alkaline permanganate.

\[[\text{MnO}_4^-] = 2.0 \times 10^{-4}; \quad [\text{L-Val}] = 2.0 \times 10^{-3}; \]
\[[\text{OH}] = 0.30; \quad I = 0.50/\text{mol dm}^{-3}.\]

<table>
<thead>
<tr>
<th>T* (K)</th>
<th>k_1 \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1})</th>
<th>k_2 \times 10^3 \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1})</th>
<th>1/T \times 10^3 \text{ (K}^{-1})</th>
<th>\log k_1</th>
<th>\log k_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.66</td>
<td>1.0</td>
<td>3.33</td>
<td>-0.180</td>
<td>-3.000</td>
</tr>
<tr>
<td>305</td>
<td>1.0</td>
<td>1.66</td>
<td>3.27</td>
<td>0.000</td>
<td>-2.779</td>
</tr>
<tr>
<td>310</td>
<td>1.34</td>
<td>2.33</td>
<td>3.22</td>
<td>0.127</td>
<td>-2.632</td>
</tr>
<tr>
<td>315</td>
<td>1.99</td>
<td>3.20</td>
<td>3.17</td>
<td>0.298</td>
<td>-2.988</td>
</tr>
</tbody>
</table>

*Temperature
Effect of temperature on the slow step of the mechanism of oxidation of L-valine by aqueous alkaline permanganate.

(Conditions as in Table VI (vii) (p.191)

**Figure VI (vi)**

![Graph of Path I and Path II](image)
Table VI (viii)

Thermodynamic activation parameters for the oxidation of L-valine by aqueous alkaline permanganate with respect to slow step of scheme 3.

\[ \text{[MnO}_4^-\text{]} = 2.0 \times 10^{-4}; \quad \text{[L-Valine]} = 2.0 \times 10^{-3}; \]

\[ \text{[OH}] = 0.30; \quad \text{I} = 0.50/\text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>Activation Parameters</th>
<th>Path I</th>
<th>Path II</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a ) (kJ mol(^{-1}))</td>
<td>42 ± 4</td>
<td>51 ± 5</td>
</tr>
<tr>
<td>( \log A )</td>
<td>9.6 ± 3.0</td>
<td>7.6 ± 2.0</td>
</tr>
<tr>
<td>( \Delta H^\circ ) (kJ mol(^{-1}))</td>
<td>40 ± 3</td>
<td>48.6 ± 4.0</td>
</tr>
<tr>
<td>( \Delta S^\circ ) (J K(^{-1}) mol(^{-1}))</td>
<td>-116 ± 6</td>
<td>-140 ± 7</td>
</tr>
<tr>
<td>( \Delta G^\circ ) (kJ mol(^{-1}))</td>
<td>75 ± 4</td>
<td>90 ± 5</td>
</tr>
</tbody>
</table>
DISCUSSION

Permanganate ion, MnO₄⁻, is a powerful oxidant in an aqueous alkaline medium. As it exhibits many oxidation states, the stoichiometric results and pH of the reaction media play an important role. Under the prevailing experimental conditions at pH >12, the reduction product of Mn(VII) is stable and further reduction of Mn(VI) might be stopped¹⁰,¹¹. The Diode Array Rapid Scan Spectrophotometric (DRASS) studies have shown that at pH > 12, the product of Mn(VII) is Mn(VI) and no further reduction was observed as reported¹⁰,¹¹ by Simandi et al. However, on prolonged standing, the green Mn(VI) is reduced to Mn(IV) under our experimental conditions.

The permanganate in alkaline medium exhibits various oxidation states, such as Mn(VII), Mn(V) and Mn(VI). The colour of the solution changed from violet to blue and further to green excluding the accumulation of hypomanganate. The violet colour originates from pink of permanganate and blue from hypomanganate is observed during the course of the reaction. The colour change of KMnO₄ solution from violet Mn(VII) ion to dark green Mn(VI) ion through blue Mn(V) ion has been observed.

It is known that in aqueous solution, amino acid exists as zwitterionic³⁰ form where as in aqueous alkaline medium they exist as anionic form according to the following equilibria.
The reaction between permanganate and L-valine in alkaline medium has a stoichiometry of 1:2 with a first order dependence on the [MnO₄⁻] and less than unit order dependence on both the [alkali] and [L-valine]. No effect of added products such as aldehyde and ammonia was observed. The direct plot of $k_{obs}$ versus [L-valine] gave better correlation than the reciprocal plot (Fig. VI (vii) (p.197). Hence, the observed kinetic and other results may be explained by two path mechanism, one of which depends on substrate concentration, whereas the other independent of substrate concentration as in scheme 3. The observed kinetics and other results are supported by the following two path mechanism.

**Path I**

\[
\text{CH}_3\text{C} \equiv \text{CH-COOH} + \text{OH}^{-} \xleftrightarrow{K} \text{CH}_3\text{C} \equiv \text{CH-COO}^{-} + \text{H}_2\text{O}
\]

Slow

\[
\text{CH}_3\text{C} \equiv \text{CH-COO}^{-} + \text{MnO}_4^{-} \xrightarrow{k_1} \text{CH}_3\text{C} \equiv \text{CH-COO}^{2-} + \text{MnO}_4^{2-}
\]

(Scheme 3)
Path II

\[
\text{MnO}_4^- + \text{OH}^- \quad \stackrel{k_2}{\longrightarrow} \quad \text{MnO}_4^{2-} + \text{OH}^- \quad \text{Slow}
\]

\[
\text{CH}_3\text{C} = \text{CH}-\text{COOH} + \text{OH}^- \quad \stackrel{\text{fast}}{\longrightarrow} \quad \text{CH}_3\text{C} = \text{CH}-\text{COO}^- + \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{C} = \text{CH}-\text{COO}^- \quad \stackrel{\text{fast}}{\longrightarrow} \quad \text{CH}_3\text{C} = \text{CH}^- + \text{CO}_2
\]

\[
\text{CH}_3\text{C} = \text{CH}^- + \text{MnO}_4^- + \text{OH}^- \quad \stackrel{\text{fast}}{\longrightarrow} \quad \text{CH}_3\text{C} = \text{CHO} + \text{MnO}_4^{2-} + \text{NH}_3
\]

**Scheme 3**
Figure VI (vii)

Linear correlation plot of $k_{\text{obs}}$ versus [L-valine] and $1/k_{\text{obs}}$ versus $1/[\text{L-valine}]$.

(Conditions as in Table VI (iv) (p.184)
The observed fractional order in alkali concentration may be due to the substantial existence of L-valine in its anionic form in alkaline medium. This anionic form will react with active species of permanganate ion, MnO₄⁻, in a slow step, giving a radical of L-valine with decarboxylation, which reacts further with another molecule of permanganate in a fast step to afford the products. Since permanganate is a one electron oxidant in alkaline medium, the reaction between substrate and oxidant would give rise to a radical intermediate. Free radical scavenging experiment revealed such a possibility. This type of radical intervention in the oxidation of amino acids has also been observed earlier.

Scheme 3 leads to the following rate law, and can be derived as follows

\[
\text{Rate} = k_1 [\text{L-Val}][\text{MnO}_4^-]
\]

\[
K = \frac{[\text{L-Val}][\text{H}_2\text{O}]}{[\text{L-Val}][\text{OH}^+]} 
\]

\[
[\text{L-Val}]^\cdot = \frac{K [\text{L-Val}][\text{OH}^-]}{[\text{H}_2\text{O}]} 
\]

Therefore, rate for path I is

\[
\text{Rate} = \frac{k_1 K [\text{L-Val}][\text{OH}^-][\text{MnO}_4^-]}{\text{H}_2\text{O}} 
\]

Similarly rate for path II

\[
\text{Rate} = k_2 [\text{OH}^-][\text{MnO}_4^-] 
\]

Therefore combined rate law can be given as below

\[
(2)
\]
Rate = \( \frac{K k_i [L-Val]_f [OH^-][MnO_4^-]}{H_2O} + k_2 [OH^-][MnO_4^-] \)  

\[ \frac{\text{Rate}}{[MnO_4^-]} = \frac{K k_i [L-Val]_f [OH^-]}{H_2O} + k_2 [OH^-] \]  

Now,

\[ [L-Val]_T = [L-Val]_f + [L-Val'] \]  

\[ [L-Val]_T = [L-Val]_f + \frac{K [L-Val]_f + [OH]}{H_2O} \]  

\[ [L-Val]_T = [L-Val]_f \left\{ 1 + \frac{K [OH]}{[H_2O]} \right\} \]  

\[ [L-Val]_f = \frac{[L-Val]_T [H_2O]}{(1 + K [OH])[H_2O]} \]  

Substituting the equation (8) in equation (4)

\[ k_{obs} = \frac{K k_i [L-Val]_T [OH^-][H_2O]}{(1 + K [OH][H_2O])} + k_2 [OH^-] \]  

Therefore,

\[ k_{obs} = \frac{K k_i [L-Val]_T [OH]}{(1 + K [OH])} + k_2 [OH^-] \]
On rearrangement of equation (10), we get

\[
k_{\text{obs}} - k_2 [\text{OH}^-] = \frac{K k_1[\text{L-Val}]_T [\text{OH}^-]}{(1 + K [\text{OH}^-])}
\]  

(11)

Equation (11) may be rearranged to (12) which is suitable for verification

\[
\frac{1}{k_{\text{obs}} - k_2 [\text{OH}^-]} = \frac{1}{K k_1[\text{L-Val}] [\text{OH}^-]} + \frac{1}{k_1[\text{L-Val}]}
\]  

(12)

According to the above equations (11) and (12), the plots of \(k_{\text{obs}}\) versus [L-Val] and \(1/(k_{\text{obs}} - k_2[\text{OH}^-])\) versus \(1/[\text{OH}^-]\) should be linear, which is verified in Fig. VI (vii) (p.197) and Fig. VI (viii) (p.201) respectively. The intercept and slope of such plots lead to the values of \(k_1, k_2\) and \(K\) at 27° C as \(0.66 \pm 0.03 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\), \(1.0 \pm 0.05 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) and \(5.14 \pm 0.25 \text{ dm}^3 \text{ mol}^{-1}\) respectively. Using these values, the rate constants under different experimental conditions were calculated and compared with experimental data. There is a good agreement between the calculated and observed rate constants (Table VI (iii) (p.181) and Table VI (iv) (p.184)), which supports the scheme 3. The value of \(k_2\) obtained in this work is in agreement with the value reported earlier\(^{32}\) and vary depending upon the concentration of alkali used.

The effect of increasing ionic strength on the rate qualitatively explains the reaction between the two negatively charged ions as shown in scheme 3. However,
Figure VI (viii)

Verification of rate law (10) in the form of (12) on oxidation of L-valine by aqueous alkaline permanganate.

(Conditions as in Table VI (iv) (p.184))
increasing the content of t-butanol in the reaction medium leads to an increase of the reaction rate which is contrary to the expected slower reaction between ions of a same polarity in media of lower relative permittivity. Perhaps the effect is opposed substantially by an increased formation of active reaction species in low permittivity media, thus leading to the observed net increase in the rate\textsuperscript{33}. The values of $\Delta H^\#$ and $\Delta S^\#$ were both favourable for electron transfer process. The values of $\Delta S^\#$, within the range for radical reaction, have been ascribed to the nature of electron pairing and unpairing processes and to the loss of degree of freedom formerly available to the reactants upon the formation of a rigid transition state\textsuperscript{34}.

**Findings**

The kinetics of the oxidation of L-valine by alkaline permanganate was studied spectrophotometrically. It is interesting to note that the reaction follows a two stage mechanism. The reaction is first order with respect to [oxidant] and an apparent less than unit in [substrate] and [alkali]. The reaction constants involved in the mechanism were evaluated. There is a good agreement between observed and calculated rate constants under different experimental conditions for both stages of reaction. The activation parameters for the slow step were calculated and are discussed.
*Importance of chapter VI*

It is interesting that the oxidant species $[\text{MnO}_4^-]$ requires a pH $> 12$, below which the system becomes disturbed and the reaction will proceed further to give a reduced product of the oxidant as Mn(IV), which slowly develops yellow turbidity. Hence, it becomes apparent that in carrying out this reaction the role of pH in a reaction medium is crucial. It is also noteworthy that under the conditions studied the reaction occurs in two successive one-electron reductions (Scheme 3) rather than two-electron in a single step (Scheme 2).
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