Chapter VII

Kinetics of Oxidative Degradation of L(+)-lysine by alkaline permanganate

Extensive studies have been made on permanganate oxidations of organic and inorganic substrates in both acidic and alkaline media\textsuperscript{1-4}. Furthermore, in aqueous alkaline media the permanganate ion oxidises a number of organic compounds which are either very slow or not attacked in acidic or neutral medium. If $[\text{OH}^-] > 0.1 \text{ mol dm}^{-3}$, permanganate will reduce to manganate in the first step and owing to much lower reactivity, further reaction with manganate will be much slower\textsuperscript{5,6,7}. Thus, the process Mn(VII) to Mn(IV) can be divided into a number of partial steps and examined separately. The Mn(II) appears practically only after permanganate has completely disappeared from the system. In strongly alkaline medium the stable reduction product\textsuperscript{8,9} of permanganate ion is manganate ion, $\text{MnO}_4^{2-}$. Mechanistic information to distinguish between a direct one-electron reduction to Mn(VI) (scheme 1 chapter VI (p.170) and a reaction in which hypomanganate is formed in a two-electron step followed by rapid oxidation of hypomanganate ion\textsuperscript{10} (scheme 2 chapter VI) is not available (discussed in detail in chapter VI (p.170)).

Amino acids play an important role in metabolism and in protein synthesis. Enzymatic dehydrogenation of $\delta$-amino acids by flavoenzymes has attracted considerable attention in recent years. Infact a precise understanding of the mechanism of such biological redox reactions\textsuperscript{11,12,13} is important as it helps in the
synthesis of specific reaction products. Many attempts were made to mimic flavin-catalysed oxidations of \( \alpha \)-amino acids\(^{14} \) by non-enzymatic means. These studies were found to yield the corresponding noraldehydes by oxidative decarboxylation of \( \alpha \)-amino acids\(^{15,16} \). The kinetic investigation of the \( \alpha \)-amino acids by a variety of oxidants has been carried out under different experimental conditions\(^{17-22} \). In many cases it was reported that amino acids undergo oxidative decarboxylation. The study of the oxidation of amino acids become important because of their biological significance and selectivity towards oxidants. L(+)lysine, one of the essential amino acids is most important to life. L(+)lysine also finds applications in medicines and pharmaceutics. There is no report in the literature on the oxidation of L(+)lysine in such media. Although the oxidation of L-valine an essential amino acid with methyl substituted side chain by alkaline permanganate has been studied\(^{19} \) in the previous chapter, the L(+)lysine, another essential amino acid with two amino groups is of interest to verify the nature of active species of permanganate ion, actual site of oxidation, and change in mechanism etc. This reaction has therefore been carried out in order to elucidate the redox chemistry of permanganate in alkaline media and to arrive at a plausible mechanism.

**EXPERIMENTAL**

The stock solution of L(+)lysine (s.d.fine-chem) and potassium permanganate (BDH) were prepared by dissolving the appropriate amount of samples in doubly distilled water. The stock solution of potassium permanganate and potassium
manganate were prepared and standardized as described in chapter VI (p.172). 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 NaClO₄ were used to provide the required alkalinity and to maintain the constant ionic strength respectively.

**KINETIC PROCEDURE**

All kinetic measurements were performed under pseudo-first order conditions with L(+)-lysine in at least ten fold excess over permanganate ion at a constant ionic strength of 0.60 mol dm⁻³. The reaction was initiated by mixing previously thermostatted solutions of MnO₄⁻ and L(+)-lysine which also contained the necessary quantities of NaOH and NaClO₄ to maintain the required alkalinity and ionic strength respectively. The temperature was uniformly maintained at 25 ± 0.1° C. The course of reaction was followed by monitoring the decrease in absorbance of MnO₄⁻ in a 1cm quartz cell of a Hitachi 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 the other reagents at this wavelength. The obedience to Beer’s law for permanganate at 526 nm had been verified as in previous chapter VI (p.174). And molar extinction coefficient ‘ɛ’ was found to be ‘ɛ’ = 2083 ± 50 dm³ mol⁻¹ cm⁻¹ (Literature ɛ = 2200 dm³ mol⁻¹ cm⁻¹). The first order rate constants, kobs were evaluated by the plots of log [Mn(VII)] versus time, an example run is given in Table
Oxidation of L(+)-lysine by aqueous alkaline permanganate at 25° C

**Example Run**

\[
\begin{align*}
[MnO_4^-] &= 2.0 \times 10^{-4}; \\
[L(+)-lys] &= 2.0 \times 10^{-3}; \\
[OH^-] &= 0.30; \\
I &= 0.60/\text{mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density (526 nm)</th>
<th>([MnO_4^-] \times 10^4) (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.401</td>
<td>1.928</td>
</tr>
<tr>
<td>0.4</td>
<td>0.348</td>
<td>1.671</td>
</tr>
<tr>
<td>0.6</td>
<td>0.330</td>
<td>1.582</td>
</tr>
<tr>
<td>1.0</td>
<td>0.301</td>
<td>1.441</td>
</tr>
<tr>
<td>2.0</td>
<td>0.250</td>
<td>1.200</td>
</tr>
<tr>
<td>3.0</td>
<td>0.214</td>
<td>1.027</td>
</tr>
<tr>
<td>4.0</td>
<td>0.185</td>
<td>0.881</td>
</tr>
<tr>
<td>5.0</td>
<td>0.162</td>
<td>0.777</td>
</tr>
<tr>
<td>6.0</td>
<td>0.143</td>
<td>0.686</td>
</tr>
<tr>
<td>7.0</td>
<td>0.128</td>
<td>0.614</td>
</tr>
<tr>
<td>8.0</td>
<td>0.114</td>
<td>0.547</td>
</tr>
<tr>
<td>9.0</td>
<td>0.102</td>
<td>0.489</td>
</tr>
<tr>
<td>10.0</td>
<td>0.096</td>
<td>0.460</td>
</tr>
</tbody>
</table>
V (i) (p.213). The first order plots in almost all cases were linear up to 80% completion of the reaction and the $k_{obs}$ values were reproducible within ± 5%.

As in chapter VI, during the course of the reaction the colour of the solution changed from violet to blue and further to green. The spectrum of the green solution was identical to that of $\text{MnO}_4^{2-}$. It is evident that the blue colour is originated from violet of permanganate and green from manganate, excluding the accumulation of hypomanganate. It is also evident from the Fig. VII (i) (p.215) 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 the reaction was also studied as in previous chapters. No significant difference was observed.

RESULTS

Stoichiometry and product analysis

Different sets of reaction mixtures containing the excess permanganate concentration over $\text{L}(+)$lysine in presence of 0.30 mol dm$^{-3}$ NaOH adjusted to a constant ionic strength of 0.60 mol dm$^{-3}$ were kept to react. After completion of the reaction, the unreacted permanganate was titrated against standard sodium thiosulphate$^{23}$. The results indicated that two moles of $\text{MnO}_4^-$ were consumed by one mole of $\text{L}(+)$lysine as given by equation (1) (Table VII (ii) (p.216).

$$\text{R-CH-COOH} + 2\text{MnO}_4^- + 2\text{OH}^- \quad \rightarrow \quad \text{R-CHO} + \text{NH}_3 + 2\text{MnO}_4^{2-} + \text{CO}_2 + \text{H}_2\text{O}$$

(1)

$\text{R} = \text{H}_2\text{N}-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$
Figure VII (i)

Uv.-Vis. spectral changes during the oxidation of L(+)lysine by aqueous alkaline permanganate at 25° C, scanning time interval = 1 min.

Conditions:

\[ [\text{MnO}_4^-] = 2.0 \times 10^{-4}; \quad [\text{L}(+)\text{lys}] = 2.0 \times 10^{-3}; \]

\[ [\text{OH}^-] = 0.30; \quad I = 0.60/\text{mol dm}^{-3}. \]
Table VII (ii)

Stoichiometry of oxidation of L(+)lysine by aqueous alkaline permanganate at 25° C.

\[
[\text{OH}^-] = 0.30; \quad I = 0.60/\text{mol dm}^{-3}.
\]

<table>
<thead>
<tr>
<th>Taken \text{[MnO}_4^-\text{]} \times 10^4 \text{(mol dm}^{-3}\text{)}</th>
<th>Taken \text{[L(+)lysine]} \times 10^4 \text{(mol dm}^{-3}\text{)}</th>
<th>Found \text{[MnO}_4^-\text{]} \times 10^4 \text{(mol dm}^{-3}\text{)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>0.009</td>
</tr>
<tr>
<td>4.0</td>
<td>2.0</td>
<td>0.01</td>
</tr>
<tr>
<td>6.0</td>
<td>2.0</td>
<td>2.02</td>
</tr>
<tr>
<td>8.0</td>
<td>3.0</td>
<td>1.99</td>
</tr>
</tbody>
</table>

Error ± 5%.
The main oxidation products were identified as the corresponding aldehyde by spot test\textsuperscript{24} ammonia by Nessler's reagent\textsuperscript{25}, and manganate spectrophotometrically by comparing its spectrum with that of the authentic sample, carbon dioxide was qualitatively detected\textsuperscript{26} by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water. The corresponding aldehyde was confirmed by preparing its 2,4-DNP derivative. It was further observed that the aldehyde does not undergo further oxidation under the present kinetic conditions.

**REACTION ORDERS**

The order of the reactants were determined from the slopes of log $k_{obs}$ versus log concentration plots by varying the concentration of oxidant, reductant and alkali in turn, while keeping concentration of others constant.

**Effect of [Permanganate]**

The potassium permanganate 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 VII (iii) (p.218). The linearity of plots of log $[\text{MnO}_4^-]$ versus time indicated a reaction order of unity in $[\text{MnO}_4^-]$ (Fig VII (ii) (p.219)). This was also confirmed by varying $[\text{MnO}_4^-]$ which did not show any change in pseudo-first order constants, $k_{obs}$ values.
Table VII (iii)

Effect of variation of \([\text{MnO}_4^-]\) on the oxidation of \(L(+)\text{lysine}\) by permanganate in aqueous alkaline medium at 25° C.

\[[L(+)\text{lysine}] = 2.0 \times 10^{-3}; \quad [\text{OH}^-] = 0.30; \quad I = 0.60/\text{mol dm}^{-3}.\]

<table>
<thead>
<tr>
<th>([\text{MnO}_4^-]) x 10^4 (mol dm^{-3})</th>
<th>(k_{\text{obs}} \times 10^3) (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>2.34</td>
</tr>
<tr>
<td>1.0</td>
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<tr>
<td></td>
<td>2.34</td>
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<tr>
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<td>2.30</td>
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<td>2.34</td>
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<td>2.34</td>
</tr>
<tr>
<td>5.0</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>2.34</td>
</tr>
</tbody>
</table>

*Experimental and Calculated.*
Figure VII (ii)

First order plots in $[\text{MnO}_4^-]$ on the oxidation of L(+)lysine by permanganate in aqueous alkaline medium at 25° C.

(Conditions as in Table VII (iii) (p.218))
Effect of \( [\text{L(+)lysine}] \)

The substrate, L(+)lysine concentration was varied in the range of \( 5.0 \times 10^{-4} \) to \( 5.0 \times 10^{-3} \) mol dm\(^{-3}\) at 25 °C as in Table VII (iv) (p.221), keeping all other conditions constant. From the plot of \( \log k_{\text{obs}} \) versus \( \log [\text{L(+)lysine}] \) the order in [L(+)lysine] was found to be less than unity as in Fig. VII (iii) (p.222).

Effect of [alkali]

The effect of alkali on the reaction has been studied at concentrations of L(+)lysine and potassium permanganate and a constant ionic strength of 0.60 mol dm\(^{-3}\) at 25° C. The rate constant increased with increasing \([\text{OH}^-]\) as given in Table VII (iv) (p.221). It was found from the slope of \( \log k_{\text{obs}} \) versus \([\text{OH}^-]\) plot, the order with respect to \([\text{OH}^-]\) is less than unity (Fig VII (iii) (p.222)).

Effect of initially added products

Products of the redox reaction such as manganate, ammonia and aldehyde at the beginning of the sequence together with the products did not show any significant effect on the rate of the reaction which is evident from the Table VII (v) (p.223).

Effect of ionic strength

The effect of ionic strength was studied by varying the sodium perchlorate concentration from 0.30 to 1.5 mol dm\(^{-3}\) at constant concentrations of permanganate, L(+)lysine and alkali as given in Table VII (vi) (p.225). It was found that the rate
Table VII (iv)

Effect of variation of \([L(+)^\text{lysine}]\) and \([\text{OH}^-]\) on the oxidation of \(L(+)^\text{lysine}\) by permanganate in aqueous alkaline medium at 25° C.

\[
[MnCO_4^-] = 2.0 \times 10^{-4}; \quad I = 0.60/\text{mol dm}^3.
\]

<table>
<thead>
<tr>
<th>([L(+)^\text{lysine}] \times 10^3) (mol dm(^{-3}))</th>
<th>([\text{OH}^-]) (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>0.30</td>
<td>0.95</td>
<td></td>
<td>0.96</td>
</tr>
<tr>
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<td>0.30</td>
<td>1.58</td>
<td></td>
<td>1.58</td>
</tr>
<tr>
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<td>0.30</td>
<td>2.30</td>
<td></td>
<td>2.34</td>
</tr>
<tr>
<td>3.0</td>
<td>0.30</td>
<td>2.85</td>
<td></td>
<td>2.78</td>
</tr>
<tr>
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<td>0.30</td>
<td>3.33</td>
<td></td>
<td>3.28</td>
</tr>
<tr>
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<td>0.05</td>
<td>0.90</td>
<td></td>
<td>0.95</td>
</tr>
<tr>
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<td>0.10</td>
<td>1.53</td>
<td></td>
<td>1.48</td>
</tr>
<tr>
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<td>2.00</td>
<td></td>
<td>2.04</td>
</tr>
<tr>
<td>2.0</td>
<td>0.30</td>
<td>2.30</td>
<td></td>
<td>2.34</td>
</tr>
<tr>
<td>2.0</td>
<td>0.50</td>
<td>2.63</td>
<td></td>
<td>2.65</td>
</tr>
</tbody>
</table>

*Experimental and Calculated.
Figure VII (iii)

Order plots of [L(+)lysine] and [OH\(^{-}\)] on the oxidation of L(+)lysine by permanganate in aqueous alkaline medium at 25° C.

(Conditions as in Table VII (iv) (p.221))
Table VII (v)

Effect of initial addition of products on the oxidation of L(+)-lysine by alkaline permanganate at 25°C.

\[ [\text{MnO}_4^-] = 2.0 \times 10^{-4}; \quad [\text{L(+)-lysine}] = 2.0 \times 10^{-3}; \]
\[ [\text{OH}^-] = 0.30; \quad I = 0.60/\text{mol dm}^3. \]

<table>
<thead>
<tr>
<th>[\text{MnO}_4^2^- \times 10^4] (mol dm(^3))</th>
<th>[\text{NH}_4\text{OH} \times 10^3] (mol dm(^3))</th>
<th>[\text{Aldehyde} \times 10^3] (mol dm(^3))</th>
<th>[k_{\text{obs}} \times 10^3] (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>2.32</td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>2.34</td>
</tr>
<tr>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>2.33</td>
</tr>
<tr>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>2.35</td>
</tr>
<tr>
<td>4.0</td>
<td>-</td>
<td>-</td>
<td>2.32</td>
</tr>
<tr>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>2.34</td>
</tr>
<tr>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>2.36</td>
</tr>
<tr>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>2.35</td>
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<td>2.0</td>
<td>-</td>
<td>2.32</td>
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<td>0.5</td>
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<td>-</td>
<td>1.0</td>
<td>2.35</td>
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<td>2.33</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>2.32</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>3.0</td>
<td>2.34</td>
</tr>
</tbody>
</table>
constant increased with the increasing concentration of NaClO₄ and the plot of log $k_{\text{obs}}$ versus $I^{1/2}$ was linear with positive slope which is given in Fig. VII (iv) (p.226).

**Effect of solvent polarity**

The effect of dielectric constant (D) on the rate constant has been studied by varying the t-butanol -water content in the reaction mixture with all other conditions being maintained constant. It was observed that there is no reaction of the solvent with the oxidant occurred under the experimental conditions employed. The rate constant, $k_{\text{obs}}$ increased with decreasing dielectric constant of the medium (Table VII (vi) (p.225)). The plot of log $k_{\text{obs}}$ versus $1/D$ was linear which is shown in Fig. VII (iv) (p.226).

**Test for free radicals**

To test for the intervention of free radical, the reaction mixture was mixed with acrylonitrile monomer and kept for 4 hours in an inert atmosphere. On diluting with methanol a white precipitate was formed, indicating the participation of free radicals in the reaction.

**Effect of Temperature**

The rate of reaction was measured at different temperatures under varying [$L(+)\text{lysine}$]. The rate of reaction increased with increase of temperature. The rate constants, $k$ of the slow step of scheme 1 were obtained from the intercepts of the plot
Table VII (vi)

Effect of variation of ionic strength (I) and dielectric constant (D) on the oxidation of L(+)lysine by permanganate in aqueous alkaline medium at 25° C.

\[
[MnO_4^-] = 2.0 \times 10^{-4}; \quad [MnO_4^-] = 2.0 \times 10^{-4};
\]

\[
[L(+)lysine] = 2.0 \times 10^{-3}; \quad [L(+)lysine] = 2.0 \times 10^{-3};
\]

\[
[OH^-] = 0.30; \quad [OH^-] = 0.30;
\]

I = 0.60/mol dm\(^{-3}\).

<table>
<thead>
<tr>
<th>I (mol dm(^{-3}))</th>
<th>(k_{obs} \times 10^3) (s(^{-1}))</th>
<th>% of *t-butanol</th>
<th>D</th>
<th>(k_{obs} \times 10^3) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>2.30</td>
<td>1</td>
<td>77.82</td>
<td>2.40</td>
</tr>
<tr>
<td>0.60</td>
<td>2.80</td>
<td>3</td>
<td>76.47</td>
<td>2.66</td>
</tr>
<tr>
<td>0.80</td>
<td>3.61</td>
<td>5</td>
<td>75.12</td>
<td>2.90</td>
</tr>
<tr>
<td>1.20</td>
<td>5.32</td>
<td>8</td>
<td>73.09</td>
<td>3.20</td>
</tr>
<tr>
<td>2.00</td>
<td>5.97</td>
<td>10</td>
<td>71.74</td>
<td>3.51</td>
</tr>
</tbody>
</table>

* t-butanol-water (v/v)

Error ± 5%.
Figure VII (iv)

Effect of variation of ionic strength (I) and dielectric constant (D) on the oxidation of L(+)lysine by permanganate in aqueous alkaline medium.

(Conditions as in Table VII (vi) (p.225))
of $1/k_{obs}$ versus $1/[L(+)]$lysine] at four different temperatures. The data is subjected to least square analysis as in earlier chapters which is given in Table VII (vii) (p.228). From the plot of log $k$ versus $1/T$ (Fig. VII (v) (p.229)), the activation parameters have been calculated as in previous chapters and are tabulated in Table VII (viii) (p.230).

**DISCUSSION**

The permanganate ion is a powerful oxidant in aqueous alkaline medium. As manganese exhibits a multitude oxidation states, the stoichiometry and the pH of the reaction medium play an important role in the determination of products. Under the present experimental conditions (pH $> 12$) the reduction product of Mn(VII) being Mn(VI) is stable and further reduction is not to be expected$^9$. Diode Array Rapid Scan Spectrophotometric studies have shown that at pH $> 12$, Mn(VII) is reduced to Mn(VI), and no further reduction was observed as reported$^9$ by earlier work. However, upon prolonged standing Mn(VI) is slowly reduced to Mn(IV) under our experimental conditions. The reaction between L(+)-lysine and permanganate in alkaline medium has a stoichiometry of 1:2 with less than unit order dependence on both alkali and L(+)-lysine concentrations and a first order dependence on [permanganate]. No effect of the products was observed. In aqueous solution, amino acids exist as zwitterionic form where as in aqueous alkaline solution they exist as anionic form. The results suggest that first the alkali combines with permanganate to give an alkali-permanganate complex$^{27}$, which then reacts with the substrate,
**Table VII (vii)**

Effect of temperature on the slow step of the mechanism of oxidation of L(+)lysine by alkaline permanganate.

\[ [\text{MnO}_4^-] = 2.0 \times 10^{-4}; \quad [\text{OH}^-] = 0.30; \]

\[ I = 0.60/\text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>T* (K)</th>
<th>k x 10^3 (s(^{-1}))</th>
<th>1/T x 10^3 (K(^{-1}))</th>
<th>X</th>
<th>log k</th>
<th>Y calc**</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>4.5</td>
<td>3.35</td>
<td>-2.34</td>
<td>-2.3311</td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>6.8</td>
<td>3.30</td>
<td>-2.17</td>
<td>-2.1873</td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>9.3</td>
<td>3.24</td>
<td>-2.03</td>
<td>-2.0333</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>12.8</td>
<td>3.19</td>
<td>-1.89</td>
<td>-1.8837</td>
<td></td>
</tr>
</tbody>
</table>

*Temperature.

**Calculated.
Figure VII (v)

Effect of temperature on the slow step of the mechanism on oxidation of L(+)-lysine by alkaline permanganate.

(Conditions as in Table VII (vii) (p.228))
**Table VII (viii)**

Thermodynamic activation parameters for the oxidation of L(+)lysine by alkaline permanganate.

<table>
<thead>
<tr>
<th>Activation Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>53 ± 2</td>
</tr>
<tr>
<td>$\log A$</td>
<td>11.8 ± 0.5</td>
</tr>
<tr>
<td>$\Delta H^#$ (kJ mol$^{-1}$)</td>
<td>51 ± 2</td>
</tr>
<tr>
<td>$\Delta S^#$ (J K$^{-1}$mol$^{-1}$)</td>
<td>-28 ± 2</td>
</tr>
<tr>
<td>$\Delta G^#$ (kJ mol$^{-1}$)</td>
<td>60 ± 3</td>
</tr>
</tbody>
</table>
L(+)lysine, in its deprotonated form to give another complex. The latter complex decomposes in a slow step to give a free radical derived from decorboxylated L(+)lysine, which further reacts with another molecule of permanganate in a fast step to yield the products, as given in scheme 1.

\[
\text{MnO}_4^- + \text{OH}^- \rightleftharpoons K_1 \left\{ \begin{array}{c}
\text{O} \\
\text{Mn} \\
\text{OH} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array} \right\} ^{2-} \text{Complex (C}_1\text{)}
\]

\[
\left\{ \begin{array}{c}
\text{O} \\
\text{Mn} \\
\text{OH} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array} \right\} ^{2-} + \text{R-CH-} + \text{COO}^- + K_2 \text{NH}_2 \rightleftharpoons \text{Complex (C}_2\text{)}
\]

\[
\text{Complex (C}_2\text{)} \xrightarrow{k_{\text{slow}}} \text{R-}^*\text{CH} + \text{HCO}_3^- + \text{MnO}_4^{2-}
\]

\[
\text{R-}^*\text{CH} + \text{MnO}_4^- + \text{OH}^- \xrightarrow{\text{fast}} \text{R-CHO} + \text{MnO}_4^{2-} + \text{NH}_3
\]

\[
\text{R} = \text{H}_2\text{N-CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2
\]

Scheme 1

The structure of the complex (C2) might be as given below.
The spectral evidence for the complex formation between oxidant and substrate was obtained from uv-vis spectra of the MnO_4^- and MnO_4^- - L(+:lysine mixture, in which a bathochromic shift of MnO_4^- from 318 to 345 nm is observed, and hyperchromicity at 345 nm was observed. The formation of alkali-permanganate complex is supported by the observed fractional order in [OH^-] and Michaelis Menten plot (Fig. VII (vi) (p.236) which is linear with the positive intercept. Analogous effects upon complex formation between a substrate and an oxidant have been observed in other investigations. The formation of the complex is proved kinetically by the non-zero intercept of the plot of 1/k_{obs} versus 1/[L(+):lysine]. Since scheme 1 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in sequence of one electron steps, the reaction between the substrate and oxidant would afford radical intermediate. A free radical scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in earlier work on the alkaline permanganate oxidation of various organic substrates.

The rate law of the reaction can be derived from scheme 1 as below.

\[
\text{Rate} = k \ [C_2] \quad (2)
\]

\[
[C_2] = K_2[L\text{-lys}][C_1] \quad (3)
\]

Substituting the value of \([C_2]\) in equation (2), we get

\[
\text{Rate} = k \ K_2[L\text{-lys}][C_1] \quad (4)
\]
But \[ [C_1] = K_j[MnO_4^\cdot][OH^\cdot]_f \] \hspace{1cm} (5)

Substituting the value \([C_1]\) in equation (4) we get,

\[
\text{Rate} = k K_1 K_2 [Lys]_f [MnO_4^\cdot][OH^\cdot]_f \hspace{1cm} (6)
\]

Now,

\[
[MnO_4^\cdot]_T = [MnO_4^\cdot]_f + [C_1] + [C_2]
\]

\[
= [MnO_4^\cdot]_f + K_i[OH^-][MnO_4^\cdot] + K_2[Lys][C_1]
\]

\[
= [MnO_4^\cdot]_f + K_i[OH^-][MnO_4^\cdot] + K_iK_2[Lys][OH^-][MnO_4^\cdot]_f
\]

\[
= [MnO_4^\cdot]_f \{ 1 + K_i[OH^-] + K_iK_2[Lys][OH^-] \}
\]

\[
[MnO_4^\cdot]_f = \frac{[MnO_4^\cdot]_T}{1 + K_i[OH^-] + K_iK_2[Lys][OH^-]} \hspace{1cm} (7)
\]

Where \(T\) and \(f\) stands for total and free,

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

\[
= [OH^-]_f + K_i[OH^-][MnO_4^\cdot] + K_2[Lys][C_1]
\]

\[
= [OH^-]_f + K_i[OH^-][MnO_4^\cdot] + K_iK_2[Lys][OH^-][MnO_4^\cdot]_f
\]

\[
= [OH^-]_f\{ 1 + K_i[MnO_4^\cdot] + K_iK_2[Lys][MnO_4^\cdot] \}
\]

Therefore,
\[
[\text{OH}]_r = \frac{[\text{OH}]}{1 + K_1[\text{MnO}_4^-] + K_1K_2[\text{Lys}]\text{[MnO}_4^-]} \quad (8)
\]

Similarly,

\[
[\text{Lys}]_T = [\text{Lys}]_r + C_2
\]

\[= [\text{Lys}]_r + K_2[\text{Lys}]\text{[C}_1]\]

\[= [\text{Lys}]_r + K_1K_2[\text{OH}][\text{MnO}_4^-][\text{Lys}]_r
\]

\[= [\text{Lys}]_r[1 + K_1K_2[\text{OH}][\text{MnO}_4^-]]
\]

\[
[\text{Lys}]_r = \frac{[\text{Lys}]_r}{1 + K_1K_2[\text{OH}][\text{MnO}_4^-]} \quad (9)
\]

Substituting the values of equation (7), (8) and (9) in equation (6) and omitting subscripts \(T\) and \(f\), we get

\[
\frac{d[\text{MnO}_4^-]}{dt} = \frac{kK_1K_2[\text{Lys}][\text{MnO}_4^-][\text{OH}]}{(1 + K_1K_2[\text{OH}][\text{MnO}_4^-]) \{1 + K_1[\text{MnO}_4^-] + K_1K_2[\text{Lys}]\text{[MnO}_4^-]\}}
\]

\[
\{1 + K_1[\text{OH}]+K_1K_2[\text{Lys}]\text{[OH}]}\right)\quad (10)
\]

The terms such as \((1 + K_1K_2[\text{MnO}_4^-][\text{OH}])\) and \((1 + K_1[\text{MnO}_4^-] + K_1K_2[\text{Lys}]\text{[MnO}_4^-]\)) in the denominator of equation (10) approximates to unity in view of low concentration of \text{MnO}_4^- used. Therefore equation (10) becomes equation (11)
Thus, equation (12) can be rearranged to the following form, which is used for the verification of rate law:

\[
\frac{1}{k_{\text{obs}}} = \frac{1}{k K_1 K_2 [\text{Lys}] [\text{OH}]} + \frac{1}{k K_2 [\text{Lys}]} + \frac{1}{k} \quad (13)
\]

According to equation (13) the plots of \(1/k_{\text{obs}}\) versus \(1/[\text{Lys}]\) and \(1/k_{\text{obs}}\) versus \(1/[\text{OH}]\) should be linear which is verified in Fig. VII (vii) (p.236). The slopes and intercepts of such plots lead to the values of \(k, K_1\) and \(K_2\) at 25°C as 4.5 ± 0.2 \(\text{x} 10^{-3}\) \(\text{s}^{-1}\), 2.1 ± 0.1 \(\text{dm}^3\) \(\text{mol}^{-1}\) and 1.38 ± 0.07 \(\text{x} 10^{3}\) \(\text{dm}^3\) \(\text{mol}^{-1}\) respectively. Using these values, the rate constants under different experimental conditions were calculated and compared with experimental data which is given in Table VII (iii) (p.218) and Table VII (iv) (p.221). Experimental and calculated values agree reasonably well supporting the assumptions of scheme 1. The value of \(K_1\) is in agreement with that derived in earlier work\(^{27}\).
Verification of rate law (12) in the form of (13) for the oxidation of L(+)-lysine by aqueous alkaline permanganate at 25° C.

(Conditions as in Table VII (iv) (p.221))
The effect of increasing ionic strength on the rate qualitatively explains the reaction between the two negatively charged ions as shown in scheme 1. However, increasing the content of t-butanol in the reaction medium leads to increase in the rate of reaction, contrary to the expected slower reaction between like ions in the media of lower relative permittivity. Perhaps this effect is countered substantially by the formation of active reaction species to a greater extent in a low relative permittivity media leading to the net increase in reaction rate\textsuperscript{34}.

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 of solution changes in the transition state. The negative value of $\Delta S^\#$ within the range of radical reactions have been ascribed\textsuperscript{35} 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 a rigid transition state. The observed modest enthalpy of activation and relatively low value of entropy of activation and higher rate constant indicate that the oxidation presumably occurs by an inner sphere mechanism. This conclusion is supported by earlier work\textsuperscript{36}.

**Findings**

The reaction between permanganate and L(+)lysine in alkaline medium exhibits 1:2 stoichiometry (reductant : oxidant). The reaction shown first order dependence of rate on permanganate concentration and fractional order dependence
each in L(+)lysine 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. Investigations at different temperatures allowed the determination of the activation parameters with respect to slow step of the proposed mechanism.

**Importance of chapter VII**

It is interesting that the oxidant species $[\text{MnO}_4^-]$ required 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(VI), which slowly develops yellow turbidity. Hence, it becomes apparent that in carrying out this reaction the role of pH in the reaction medium is crucial.
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