CHAPTER VII

KINETICS OF THE OXIDATIVE DEGRADATION OF RAC-SERINE BY AQUEOUS ALKALINE PERMANGANATE

Extensive studies have been made on permanganate oxidations of organic and inorganic substrates in both acidic and alkaline media. Furthermore, in aqueous alkaline media the permanganate ion oxidises a number of organic compounds which are either very slowly 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. Thus, the process \(\text{Mn(VII)} \rightarrow \text{Mn(IV)}\) can be divided into a number of partial steps and examined separately. The \(\text{Mn(II)}\) appears practically only after permanganate has completely disappeared from the system. In strongly alkaline medium the stable reduction product of permanganate ion is manganate ion, \(\text{MnO}_4^{2-}\). Mechanistic information to distinguish between a direct one-electron reduction to \(\text{Mn(VI)}\) (scheme I chapter III (p. 61) and a reaction in which hypomanganate is formed in a two-electron step followed by rapid oxidation of hypomanganate ion (scheme II chapter III) is not available (discussed in detail in chapter III(p.61)).

Amino acids play an important role in metabolism and in protein synthesis. Rac-serine is an important non-essential amino acid which has the
side chain of OH group. OH group plays an integral role in many functions of the several protein like enzymes, hormones, glycoproteins, lipoproteins etc. Rac-serine is a crucial part of the active site of amino acid as residues of the chymotrypsin enzyme which maintains the proper ionic state of the active site for interaction with substrate at particular pH. The kinetic investigation of the α- amino acids by a variety of oxidants has been carried out under different experimental conditions. In many cases it was reported that amino acids undergo oxidative decarboxylation. The study of the oxidations of amino acids become important because of their biological significance and selectivity towards the oxidant.

There is no report in the literature on the oxidation of rac-serine in such media. This reaction has therefore been carried out in order to elucidate the redox chemistry of permanganate in alkaline media and to arrive a plausible mechanism.

EXPERIMENTAL

The stock solution of rac-serine (Sisco) 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 III (p. 62). 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.

KINETICS

All kinetic measurements were performed under pseudo-first order conditions with rac-serine 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 rac-serine 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 III (p. 64). And molar extinction coefficient ε was found to be ε = 2083 ± 15 dm⁻³ mol⁻¹ cm⁻¹ (Literature ε = 2200 dm⁻³ mol⁻¹ cm⁻¹)⁸ was obtained. The first order rate constants, kᵦₑₛ, were evaluated by the plots of log [MnO₄⁻] versus time. The first order plots in almost all cases were linear upto 80% completion of the reaction and the kᵦₑₛ values were reproducible to within ± 5%.

As in chapter III 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 MnO$_4^-$\textsuperscript{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 )\textsuperscript{(p. 202)} 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 in the results was observed.

RESULTS

Stoichiometry

Different sets of reaction mixtures containing the excess permanganate concentration over rac-serine 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 assayed as described in chapter III (p. 70). The result indicated that two moles of MnO$_4^-$ were consumed by one mole of rac-serine as given by equation (1).

\[
\text{HO-CH}_2\text{-CH-COOH} + 2\text{MnO}_4^- + 2\text{OH}^- \rightarrow \text{HO-CH}_2\text{-CHO} + \text{NH}_3 + 2\text{MnO}_4^{2-} + \text{CO}_2 + 2\text{MnO}_4^{2-} + \text{H}_2\text{O} \quad (1)
\]
Uv.-Vis. spectral changes during the oxidation of rac-serine by aqueous alkaline permanganate at 25°C, scanning time interval = 1 min.

Condition:

\[ [\text{MnO}_4^-] = 2.0 \times 10^{-4}; \quad [\text{rac-serine}] = 2.0 \times 10^{-3}; \]
\[ [\text{OH}^-] = 0.30; \quad I = 0.60/\text{mol dm}^{-3}. \]
The results are represented in Table VII (i) (p. 204). The reaction products were eluted with solvent ether and organic products were submitted to spot test\textsuperscript{14} and chromatographic analysis\textsuperscript{15} which revealed the presence of aldehyde. The aldehyde was also confirmed by its IR spectrum which showed\textsuperscript{16} the bands at 3463-3431 cm\textsuperscript{-1} and 1727-1730 cm\textsuperscript{-1} for OH stretching and C=O stretching respectively, whereas the band at 2925-2930 cm\textsuperscript{-1} is due to aldehydic stretching. Ammonia was identified by Nessler's reagent\textsuperscript{17} test, CO\textsubscript{2} was qualitatively detected\textsuperscript{18} by bubbling N\textsubscript{2} gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water and manganate was identified by its spectrum. 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 $k_{\text{obs}}$ versus log concentration plots by varying the concentration of oxidant, reductant and alkali in turn, while keeping 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\textsuperscript{-3} as shown in Table VII (ii)(p. 205). The linearity of plots of log [MnO\textsubscript{4}\textsuperscript{2-}] versus time ($r > 0.9989 \ s \leq 0.032$) indicated
Table VII (i)

Stoichiometry of oxidation of rac-serine by aqueous alkaline permanganate at 25°C.

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

<table>
<thead>
<tr>
<th>Taken</th>
<th>[MnO_4^-] x 10^4 (mol dm(^{-3}))</th>
<th>Taken</th>
<th>rac-serine x 10^4 (mol dm(^{-3}))</th>
<th>Found</th>
<th>[MnO_4^-] x 10^4 (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>2.0</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>1.0</td>
<td>1.95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>2.0</td>
<td>2.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>3.0</td>
<td>1.99</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Error ± 5%.
Table VII (ii)

Effect of variation of $\left[\text{MnO}_4^-\right]$ on the oxidation of rac-serine by permanganate in aqueous alkaline medium at 25° C.

$$[\text{rac-serine}] = 2.0 \times 10^{-3}; \quad [\text{OH}^-] = 0.30; \quad I = 0.60/\text{mol dm}^{-3}.$$ 

<table>
<thead>
<tr>
<th>$[\text{MnO}_4^-] \times 10^4$ (mol dm$^{-3}$)</th>
<th>$k_{\text{obs}} \times 10^3$ (s$^{-1}$)</th>
<th>Exptl.*</th>
<th>Calcd.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.50</td>
<td>3.48</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>3.48</td>
<td>3.50</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>3.50</td>
<td>3.63</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>3.40</td>
<td>3.38</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>3.42</td>
<td>3.40</td>
<td></td>
</tr>
</tbody>
</table>

*Experimental and Calculated.
a reaction order of unity in 

\[ \text{Mn}_4 \] Fig VII (ii)(p. 207). This was also confirmed by varying \[ \text{Mn}_4 \] which did not show any change in pseudo-first order constants, \( k_{\text{obs}} \) values.

**Effect of \([\text{rac-serine}]\)**

The substrate, \( \text{rac-serine} \) concentration was varied in the range of \( 5.0 \times 10^{-4} \) to \( 5.0 \times 10^{-3} \) mol dm\(^{-3}\) at 25 \( ^\circ \) C as in Table VII (iii)( p. 208), keeping all other conditions constant. From the plot of \( \log k_{\text{obs}} \) versus \( \log [\text{rac-serine}] \) the order in \([\text{rac-serine}]\) was found to be less than unity (Fig. VII (iii)( p. 209).

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

The effect of alkali on the reaction has been studied at concentrations of \( \text{rac-serine} \) and potassium permanganate and a constant ionic strength of \( 0.60 \) mol dm\(^{-3}\) at 25\( ^\circ \) C. The rate constant increased with increasing \([\text{OH}^-]\) as given in Table VII (iii) (p. 208). 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. 209)).

**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 educts did not show any significant effect on the rate of the reaction which evident from the Table VII (iv)(p. 210).
First order plots in $[\text{MnO}_4^-]$ on the oxidation of rac-serine by permanganate in aqueous alkaline medium at 25° C.

(Conditions as in Table VII(ii) (p. 205))
Table VII (iii)

Effect of variation of [rac-serine] and [OH'] on the oxidation of rac-serine by permanganate in aqueous alkaline medium at 25° C.

\[ [\text{MnO}_4^-] = 2.0 \times 10^{-4}; \quad I = 0.60/\text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>[rac-serine] x 10^3 (mol dm^{-3})</th>
<th>[OH'] (mol dm^{-3})</th>
<th>( k_{obs} \times 10^3 \text{ (s}^{-1}) )</th>
<th>Exptl.*</th>
<th>Calcd.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.30</td>
<td>1.15</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.30</td>
<td>2.10</td>
<td>2.20</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.30</td>
<td>3.50</td>
<td>3.63</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>0.30</td>
<td>4.70</td>
<td>4.61</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>0.30</td>
<td>5.90</td>
<td>5.87</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.05</td>
<td>1.32</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.10</td>
<td>2.13</td>
<td>2.14</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.30</td>
<td>3.50</td>
<td>3.63</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.40</td>
<td>3.90</td>
<td>3.97</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.50</td>
<td>4.18</td>
<td>4.21</td>
<td></td>
</tr>
</tbody>
</table>

*Experimental and Calculated.
Order plots of [rac-serine] and [OH⁻] on the oxidation of rac-serine by permanganate in aqueous alkaline medium at 25° C.

(Conditions as in Table VII (iii) (p. 208))
Table VII (iv)

Effect of initial addition of products on the oxidation of rac-serine by alkaline permanganate at 25°C.

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

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

<table>
<thead>
<tr>
<th>[MnO$_4$] x 10$^4$ (mol dm$^3$)</th>
<th>[NH$_4$OH] x 10$^3$ (mol dm$^3$)</th>
<th>[Aldehyde] x 10$^3$ (mol dm$^3$)</th>
<th>$k_{obs}$ x 10$^3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>3.50</td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>3.48</td>
</tr>
<tr>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>3.51</td>
</tr>
<tr>
<td>4.0</td>
<td>-</td>
<td>-</td>
<td>3.50</td>
</tr>
<tr>
<td>7.0</td>
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<td>-</td>
<td>3.52</td>
</tr>
<tr>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>3.45</td>
</tr>
<tr>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>3.49</td>
</tr>
<tr>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>3.52</td>
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<td>2.0</td>
<td>-</td>
<td>3.52</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>3.48</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>3.49</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>3.50</td>
</tr>
<tr>
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<td>-</td>
<td>2.0</td>
<td>3.52</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>3.0</td>
<td>3.51</td>
</tr>
</tbody>
</table>
**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, rac-serine and alkali as given in Table VII(v) (p. 212). It was found that the rate constant increased with the increasing concentration of NaClO$_4$ and the plot of $\log k_{ob}$ versus $\sqrt{I}$ was linear with ($r > 0.9389$, $s \leq 0.014$) the positive slope which is given in Fig. VII (iv) (p. 213).

**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, $k_{ob}$ increased with decreasing dielectric constant of the medium (Table VII (v)(p. 212). The plot of $\log k_{ob}$ versus $1/D$ was linear ($r > 0.9994$, $s \leq 0.081$) which is shown in Fig. VII (iv)(p.213).

**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.
Table VII (v)

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

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

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

$[\text{rac-serine}] = 2.0 \times 10^{-3}$;  

$[\text{rac-serine}] = 2.0 \times 10^{-3}$;  

$[\text{OH}^-] = 0.30$;  

$[\text{OH}^-] = 0.30$;  

$I = 0.60/\text{mol dm}^3$.

<table>
<thead>
<tr>
<th>I (mol dm$^{-3}$)</th>
<th>$k_{\text{obs}} \times 10^3$ (s$^{-1}$)</th>
<th>% of t-butanol</th>
<th>D</th>
<th>$k_{\text{obs}} \times 10^3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>2.34</td>
<td>1</td>
<td>77.82</td>
<td>3.19</td>
</tr>
<tr>
<td>0.40</td>
<td>2.55</td>
<td>3</td>
<td>76.47</td>
<td>4.16</td>
</tr>
<tr>
<td>0.60</td>
<td>3.50</td>
<td>5</td>
<td>75.12</td>
<td>4.50</td>
</tr>
<tr>
<td>1.00</td>
<td>4.57</td>
<td>8</td>
<td>73.09</td>
<td>4.85</td>
</tr>
<tr>
<td>1.50</td>
<td>5.47</td>
<td>10</td>
<td>71.74</td>
<td>5.23</td>
</tr>
</tbody>
</table>

Error ± 5%.
Figure VII (iv)

Effect of variation of ionic strength (I) and dielectric constant (D) on the oxidation of rac-serine by permanganate in aqueous alkaline medium.

(Conditions as in Table VII (v) (p. 212))
**Effect of Temperature**

The rate constant, \( k \) of the slow step of scheme I were obtained from the intercepts of the plot of \( 1/k_{\text{obs}} \) versus \( 1/[\text{rac-serine}] \) (\( r > 0.9996, s \leq 0.056 \)) at different temperatures. The data is subjected to least square analysis as in earlier chapters which is given in Table VII (vi)(p. 215). From the plot of log \( k \) versus \( 1/T \) (Fig. VII (v)(p. 216)), the activation parameters have been calculated as in previous chapters and are tabulated in Table VII (vii)(p. 217).

The activation parameters for the oxidation of some amino acids by \( \text{MnO}_4^- \) are summarised in Table VII (viii) (p. 218). The entropy of activation for the \( \text{MnO}_4^- \)-rac-serine reaction falls within the observed range. Variation in the rate within a reaction series may be caused by changes in the enthalpy and/or entropy of activation. Changes in the rate caused by changes in both \( \Delta H^\# \) and \( \Delta S^\# \), but these quantities vary extensively in a parallel fashion. A plot of \( \Delta H^\# \) versus \( \Delta S^\# \) is linear according to equation (2)

\[
\Delta H^\# = \beta \Delta S^\# + \text{constant}
\]

\( \beta \) is called isokinetic temperature; it has been asserted that apparently linear correlations of \( \Delta H^\# \) with \( \Delta S^\# \) are sometimes misleading and that the evaluation of \( \beta \) by means of equation (2) lacks statistical validity\(^9\). Exner\(^2^0\) advocates an alternative method for the treatment of experimental data. If the rates of several reactions in a series have been measured at two temperatures and \( \log k_2 \) (at \( T_2 \)) is linearly related to \( \log k_1 \) (at \( T_1 \)), i.e.
Table VII (vi)

Effect of temperature on the slow step of the mechanism of oxidation of rac- 
serine 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 10^2 (s^-1)</th>
<th>1/T x 10^3 (K^-1)</th>
<th>log k</th>
<th>( Y_{cal}^{**} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.00</td>
<td>3.35</td>
<td>-0.20</td>
<td>-0.2122</td>
</tr>
<tr>
<td>303</td>
<td>1.40</td>
<td>3.30</td>
<td>-1.85</td>
<td>-1.1206</td>
</tr>
<tr>
<td>308</td>
<td>2.00</td>
<td>3.24</td>
<td>-1.69</td>
<td>-1.5162</td>
</tr>
<tr>
<td>313</td>
<td>2.80</td>
<td>3.19</td>
<td>-1.55</td>
<td>-1.8992</td>
</tr>
</tbody>
</table>

*Temperature.

**Calculated.
Effect of temperature on the slow step of the mechanism on oxidation of rac-serine by alkaline permanganate.

(Conditions as in Table VII (vi) (p. 215))
Table VII (vii)

Thermodynamic activation parameters for the oxidation of rac-serine 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>51 ± 2</td>
</tr>
<tr>
<td>$\Delta H^#$ (kJ mol$^{-1}$)</td>
<td>49 ± 3</td>
</tr>
<tr>
<td>$\Delta G^#$ (kJ mol$^{-1}$)</td>
<td>58 ± 3</td>
</tr>
<tr>
<td>$\Delta S^#$ (J K$^{-1}$mol$^{-1}$)</td>
<td>-28 ± 2</td>
</tr>
</tbody>
</table>
Table VII (viii)

Activation parameters for some amino acids.

<table>
<thead>
<tr>
<th>Amino</th>
<th>$k_{obs} \times 10^3$</th>
<th>$k_{obs} \times 10^3$</th>
<th>$\Delta S^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta G^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>acids</td>
<td>298 K</td>
<td>309 K</td>
<td>(s$^{-1}$)</td>
<td>(s$^{-1}$)</td>
<td>(J K$^{-1}$mol$^{-1}$)</td>
</tr>
<tr>
<td>L-Arginine</td>
<td>0.76</td>
<td>1.16</td>
<td>-190</td>
<td>18</td>
<td>76</td>
</tr>
<tr>
<td>L-Aspartic Acid</td>
<td>4.00</td>
<td>7.10</td>
<td>-99</td>
<td>40</td>
<td>55</td>
</tr>
<tr>
<td>L-glutamic Acid</td>
<td>2.22</td>
<td>6.13</td>
<td>-86</td>
<td>45</td>
<td>19</td>
</tr>
<tr>
<td>Rac-serine</td>
<td>10.0</td>
<td>14.0</td>
<td>-28</td>
<td>49</td>
<td>57</td>
</tr>
</tbody>
</table>

L-arginine$^{21}$
L-aspartic acid$^{22}$
L-glutamic acid$^{23}$
Rac-serine$^{\text{present work}}$
he proposes that $\beta$ be evaluated from equation (4)

$$B = \frac{T_1 T_2 (b - 1)}{b (T_2 - T_1)}$$

we have calculated the isokinetic temperatures as 424 K by plotting log $k_{obs}$ at 298 K versus log $k_{obs}$ at 309 K as shown in the Fig. VII (vi) (p. 220) ($r > 0.9989$, $s < 0.021$). The value of $\beta$ (424 K) is much higher than the experimental temperature (298 K). The linearity and slope of the plot obtained may confirm that the kinetics of these reactions follow similar reaction mechanisms as previously suggested.

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. Diode Array Rapid Scan Spectrophotometric studies have shown that at pH > 12, Mn(VII) is reduced to Mn(VI), and further reduction has been observed. However, upon prolonged standing Mn(VI) is slowly reduced to Mn(IV) under experimental conditions. The reaction
Figure VII (vi)

Isokinetic relationship of Exner’s plot for oxidation of some amino acids by

$\text{MnO}_4^-$ 1: L-arginine, 2: L-aspartic acid, 3: L-glutamic acid, 4: Rac-serine.

\[6 + \log k_{\text{obs}} (298)\]

\[6 + k_{\text{obs}} (309)\]
between rac-serine and permanganate in alkaline medium has a stoichiometry of 1:2 with less than unit order dependence on both alkali and rac-serine concentrations and a first order dependence on [permanganate]. No effect of the products was observed. The results suggest that first the alkali combines with permanganate to give an alkali-permanganate species $[\text{MnO}_4^-\cdot\text{OH}^-]^2$ in a prior equilibrium step\textsuperscript{24} which is also supported by the observed fractional order in $[\text{OH}^-]$ and Michaelis Menten plot (Fig. VII(vii)(p. 227) which is linear with the positive intercept. The permanganate species then reacts with the substrate in its deprotonated form\textsuperscript{25} to give a complex (C) which decomposes in a slow step to a free radical derive from decarboxylated rac-serine. This radical inturn reacts with another molecule of permanganate in fast step to yield the products as given in scheme I.

\[
\begin{align*}
\text{MnO}_4^- + \text{OH}^- & \overset{K_1}{\rightleftharpoons} \left\{ \begin{array}{c}
\text{O} \\
\text{OH} \\
\text{Mn} \\
\text{O} \\
\text{O}
\end{array} \right\}^2^- \\
\text{OH}^- & \overset{K_2}{\rightarrow} \text{NH}_2 \\
\text{O} & \overset{k}{\rightarrow} \text{HOH}_2\text{C} - \text{CH} + \text{HCO}_3^- + \text{MnO}_4^- \\
\text{O} & \overset{\text{Slow}}{\rightarrow} \text{NH}_2
\end{align*}
\]
The probable structure of the complex \( (C) \) might be as given below.

\[
\begin{align*}
\text{OHH}_2\text{C-CH}_2 + \\
\text{NH}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{OH} \\
\mid & \quad \mid \\
\text{Mn} & \quad \text{O} \\
\mid & \quad \mid \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\text{fast} \rightarrow \text{HO-CH}_2\text{-CHO} + \text{MnO}_4^{2-} + \text{NH}_2
\]

**Scheme I**

The spectral evidence for the complex formation between oxidant and substrate was obtained from UV-vis spectra of the substrate and mixtures of substrate and oxidant. A bathochromic shift of about 7 nm from 226 to 233 nm is observed, and hyperchromicity is also observed at \( \lambda_{\text{max}} \) of about 233 nm. 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 \( 1/k_{\text{obs}} \) versus \( 1/[\text{rac-serine}] \).

Since scheme I 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 thermodynamic parameters for the equilibrium step i of scheme I and activation parameters for the rate limiting step ii in scheme I could be evaluated as follows: hydroxyl ion concentration as given in Table VII(iii) (p.208) was varied at several temperature and values of $K_i$ were determined at each temperature. The values of $K_i$ obtained are 2.80, 3.72, 5.52 and 7.36 dm$^3$mol$^{-1}$ at 25, 30, 35 and 40°C respectively. A Van't Hoff’s plot was made for the variation of $K_i$ with the temperature (i.e, log $K_i$ versus $1/T$), and values of the enthalpy of the reaction, $\Delta H$, entropy of reaction, $\Delta S$ and free energy of reaction, $\Delta G$ were calculated as $51.0 \pm 2.5$ kJ mol$^{-1}$, $-53 \pm 2.6$ J K$^{-1}$ mol$^{-1}$ and $67 \pm 3.3$ kJ mol$^{-1}$ respectively were derived. An Arrhenius plot of log $k$ versus $1/T(r > 0.9997, s < 0.091)$ yielded the activation parameters for the rate limiting step in scheme I which are shown in Table VII(vii) (p. 218). A comparison of the values supports the fact that reaction before the rate determining step is fairly rapid, involving little activation energy.

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

$$\text{Rate} = k [C_2]$$  \hspace{1cm} (3)

$$[C_2] = K_2 \text{[rac-serine]} [C_1]$$  \hspace{1cm} (4)

substituting the value of $[C_2]$ in equation (3), we get

$$\text{Rate} = k K_2 \text{[rac-serine]} [C_1]$$  \hspace{1cm} (5)
But \[ C_1 = K_1[MnO_4^-][OH']_r \] (6)

Substituting the value \( [C_1] \) in equation (5) we get,

\[ \text{Rate} = k K_1 K_2 [\text{rac-serine}]_r [MnO_4^-][OH']_r \] (7)

Now,

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

\[ = [MnO_4^-]_f + K_1 [OH'][MnO_4^-] + K_2 [\text{rac-serine}][C_1] \]

\[ = [MnO_4^-]_f + K_1 [OH'][MnO_4^-]_f + K_1 K_2 [\text{rac-serine}][OH'][MnO_4^-]_f \]

\[ = [MnO_4^-]_f \{ 1 + K_1 [OH'] + K_1 K_2 [\text{rac-serine}][OH'] \} \]

\[ [MnO_4^-]_f = \frac{[MnO_4^-]_r}{1 + K[OH'] + K_1 K_2 [\text{rac-serine}][OH']} \] (8)

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

\[ [OH']_T = [OH']_f + C_1 + C_2 \]

\[ = [OH']_f + K[OH'][MnO_4^-] + K_2 [\text{rac-serine}][C_1] \]

\[ = [OH']_f + K_1 [OH'][MnO_4^-] + K_1 K_2 [\text{rac-serine}][OH'][MnO_4^-] \]

\[ = [OH']_f \{ 1 + K_1 [MnO_4^-] + K_1 K_2 [\text{rac-serine}][MnO_4^-] \} \]

Therefore,
\[ [\text{OH}]_T = \frac{[\text{OH}]_f}{1 + K_1[K_2' + K_2[\text{rac-serine}][\text{MnO}_4']]} \]  

(9)

Similarly,

\[ [\text{rac-serine}]_T = [\text{rac-serine}]_f + C_2 \]

\[ = [\text{rac-serine}]_f + K_2 [\text{rac-serine}][C_1] \]

\[ = [\text{rac-serine}]_f + K_1K_2[\text{OH}'][\text{MnO}_4'][\text{rac-serine}]_f \]

\[ = [\text{rac-serine}]_f \{1 + K_1K_2[\text{OH}'][\text{MnO}_4']\} \]

(10)

\[ [\text{rac-serine}]_f = \frac{[\text{rac-serine}]_T}{1 + K_1K_2[\text{OH}'][\text{MnO}_4']}, \]

(10)

Substituting the values of equation (8), (9) and (10) in equation (7) and omitting subscripts T and f, we get

\[ \frac{d[\text{MnO}_4']}{dt} = \frac{-kK_1K_2[\text{rac-serine}][\text{MnO}_4'][\text{OH}']}{\{1 + K_1K_2[\text{OH}'][\text{MnO}_4']\}\{1 + K_1[\text{MnO}_4'] + K_1K_2[\text{rac-serine}][\text{MnO}_4']\}} \]

(11)

The terms such as \((1 + K_1K_2[\text{MnO}_4'][\text{OH}'])\) and \((1 + K_1[\text{MnO}_4'] + K_1K_2[\text{rac-serine}][\text{MnO}_4']\) in the denominator of equation (11) approximates to unity in view of low concentration of \text{MnO}_4' used. Therefore equation (11) becomes equation (12)
Thus, equation (13) can be rearranged to the following form which is used for the verification of rate law:

\[ \frac{1}{k_{\text{obs}}} = \frac{1}{k K_1 K_2 [\text{rac-serine}] [\text{OH}^-]} + \frac{1}{k K_2 [\text{rac-serine}]} + \frac{1}{k} \]  

(14)

According to equation (14) the plots of \(1/k_{\text{obs}}\) versus \(1/[\text{rac-serine}]\) \((r > 0.9996, s \leq 0.078)\) and \(1/k_{\text{obs}}\) versus \(1/[\text{OH}^-]\) \((r > 0.9999, s \leq 0.021)\) should be linear which is verified in Fig. VII (vii) (p. 227). The slopes and intercepts of such plots lead to the values of \(k, K_1\) and \(K_2\) at 25° C of \(0.01 \pm 0.0006\) s\(^{-1}\), \(2.80 \pm 0.14\) dm\(^3\) mol\(^{-1}\) and \(625 \pm 31\) dm\(^3\) 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 (ii) (p. 205) and Table VII (iii)(p. 208). Experimental and calculated values agree reasonably well supporting the assumptions of scheme I. The value of \(K_1\) is in agreement with that derived in earlier work\(^{24}\).
Verification of rate law (13) in the form of (14) for the oxidation of rac-serine by aqueous alkaline permanganate at 25° C.

(Conditions as in Table VII (ii)(p. 205) and Table VII (iii)(p. 208))
The effect of increasing ionic strength on the rate qualitatively explains the reaction between the two negatively charged ions as shown in scheme I.

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 values of $\Delta S^\#$ within the range of 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 a rigid transition state.

FINDINGS

The reaction between permanganate and rac-serine 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 rac-serine 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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