PART - II
MECHANISMS OF CATALYSED REACTIONS
Palladium(II) catalyzed oxidation of L-proline by heptavalent manganese in aqueous alkaline medium: A free radical intervention and decarboxylation

Potassium permanganate is widely used as an oxidising agent in synthetic as well as in analytical chemistry and as a disinfectant. Permanganate ion oxidises a greater variety of substrates and finds extensive applications in organic synthesis\textsuperscript{1,2} especially after the advent of phase transfer catalysis\textsuperscript{3,4}, which permits the use of solvents such as methylene chloride and benzene. Kinetic studies constitute important source of mechanistic information on the reaction, as demonstrated by results referring to unsaturated acids in both aqueous\textsuperscript{1,3} and non-aqueous media\textsuperscript{5}.

During oxidation by permanganate, it is evident that the Mn(VII) in permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Furthermore, the mechanism by which this multivalent oxidant oxidises a substrate depends not only on the substrate but also on the medium\textsuperscript{6} used for the study. In strongly alkaline medium, the stable reduction product\textsuperscript{7} is the manganate ion, MnO\textsubscript{4}\textsuperscript{2−}. No mechanistic information is available to distinguish between a direct one-electron reduction to Mn (VI)(Scheme 1) and
a mechanism in which hypomanganate is formed in a two-electron step followed by a rapid reaction\(^7\) (Scheme 2).

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

Where \(S = \text{Substrate}, k_3 \gg k_1\)

Scheme 1

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

Where \(S = \text{Substrate}, k_4 \gg k_1\)

Scheme 2

Amino acids have been oxidised by a variety of oxidising agents\(^8\). The oxidation of amino acids is of interest as the oxidation products differ for different oxidants\(^9,10\). L-proline (L-pro) is a non-essential amino acid and is an important constituent of collagen. As per recent report\(^11\), L-proline is considered to be the world’s smallest natural enzyme and it is used in catalysing the aldol condensation of the acetone to various aldehydes with high stereo-specificity. Although some work on the oxidation of organic\(^12\) and inorganic\(^13\) substrates by permanganate in aqueous alkaline medium has been carried out, there has been no report on the oxidation of L-proline in such media.

Palladium (II) is known to catalyze various reactions\(^14\). Most studies using palladium (II) as a catalyst have employed it in the form of palladium (II)
chloride and the nature of its active form in such reactions remains obscure. The uncatalysed reaction between L-proline and permanganate in alkaline medium was studied previously. The rapid exchange between MnO_4^- and MnO_4^2- has been studied in detail by a variety of techniques. A micro amount (1x10^-5 mol dm^-3) of palladium (II) is sufficient to catalyze the reaction in an alkaline medium and variety of mechanisms are possible. The redox potentials of the couple Mn(VII)/Mn(VI) and Pd(IV)/Pd(II) in alkaline medium make the palladium (II) catalysis for oxidation of L-proline by permanganate more feasible. Thus, in order to explore the mechanism of oxidation by permanganate ion in aqueous alkaline medium and to check the selectivity of L-proline towards permanganate in catalysed system, we have selected palladium (II) as a catalyst. The present chapter deals with the title reaction to investigate the redox chemistry of permanganate, palladium (II) and L-proline in such media and to arrive at a plausible mechanism.

**EXPERIMENTAL**

**Materials**

All Chemicals used were of reagent grade and double distilled water was used throughout the work. Kinetic measurements were performed on a Varian CARY 50 Bio UV-Visible Spectrophotometer. Stock solution of L-proline (Sisco-Chem.Ltd) was prepared by dissolving the appropriate amount of sample in double distilled water. The solution of potassium permanganate (BDH) was prepared and standardized against oxalic acid. Potassium manganate solution
was prepared as described by Carrington and Symons\textsuperscript{20}. The solution was standardized by measuring the absorbance on a Varian CARY 50 Bio UV-Visible spectrophotometer with a 1 cm quartz cell at 608 nm ($ε = 1530 \pm 20$ dm$^3$ mol$^{-1}$ cm$^{-1}$). The palladium (II) solution was prepared by dissolving a known weight of PdCl$_2$ (sd. fine chem.) in 0.20 mol dm$^{-3}$ HCl and standardized against EDTA\textsuperscript{21}. For some kinetic runs, chloride had to be absent and, hence, the chloride in the palladium (II) stock solution was removed by precipitation with AgNO$_3$ followed by repeated centrifugation. The resulting clear solution contained less than $1.0 \times 10^{-6}$ mol dm$^{-3}$ chloride and silver ions. Such extremely low concentrations of Ag$^+$ and Cl$^-$ were found to have no significant effect on the reaction. The required chloride concentration was maintained with NaCl. 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 [L-pro] excess over [MnO$_4^-$] at a constant ionic strength of 0.50 mol dm$^{-3}$ in presence of palladium(II). The reaction was initiated by mixing previously thermostatted solutions of MnO$_4^-$, and L-proline which also contained the necessary quantities of palladium (II), NaOH and NaClO$_4$ to maintain the required alkalinity and ionic strength respectively. The temperature was uniformly maintained at $25 \pm 0.1^\circ$C. The course of reaction was followed by monitoring the decrease in the absorbance of MnO$_4^-$ in a 1cm quartz cell of a
UV-Visible Spectrophotometer at its absorption maximum of 526 nm as a function of time. The application of Beer's law to permanganate at 526 nm had been verified, as shown in Fig.IV (i) (p.107) giving $\varepsilon = 2083 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (Literature $\varepsilon = 2200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). An example run is given in Table IV (i) (p.108). The first order rate constants, $k_{obs}$ were evaluated by plots of $\log (A_t - A_\infty)$ versus time, where $A_t$ and $A_\infty$ refer to absorbencies at time $t$ and $\infty$ respectively. The first order plots in almost all cases were linear upto 80% completion of the reaction and $k_{obs}$ were reproducible within $\pm 5\%$. 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$_4^-$ and 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.IV (ii) (p.111) that the absorbance of permanganate decreases at 526 nm whereas the absorbance 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.
Verification of Beer's law for $[\text{MnO}_4^-]$ at 526 nm in 0.10 mol dm$^{-3}$ alkali.

$I = 0.50$ mol dm$^{-3}$

Fig. IV (i)
Table IV (i)

Example run for the palladium (II) catalysed oxidation of L-proline by permanganate in aqueous alkaline medium at 25 °C.

\[
\begin{align*}
[L-\text{pro}] &= 2.0 \times 10^{-3} \\
[MnO_4^-] &= 1.0 \times 10^{-4}; \\
[\text{OH}] &= 0.10; \\
Pd(\text{II}) &= 1.0 \times 10^{-5}; \quad I = 0.50 \text{ mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density ($A_t$)</th>
<th>$\Delta A$</th>
<th>$\log (A_t - A_w)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.492</td>
<td>0.442</td>
<td>0.354</td>
</tr>
<tr>
<td>0.5</td>
<td>0.429</td>
<td>0.379</td>
<td>0.421</td>
</tr>
<tr>
<td>1.0</td>
<td>0.381</td>
<td>0.331</td>
<td>0.480</td>
</tr>
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<td>1.5</td>
<td>0.359</td>
<td>0.309</td>
<td>0.510</td>
</tr>
<tr>
<td>2.0</td>
<td>0.323</td>
<td>0.273</td>
<td>0.563</td>
</tr>
<tr>
<td>2.5</td>
<td>0.294</td>
<td>0.244</td>
<td>0.612</td>
</tr>
<tr>
<td>3.0</td>
<td>0.265</td>
<td>0.215</td>
<td>0.667</td>
</tr>
<tr>
<td>3.5</td>
<td>0.247</td>
<td>0.197</td>
<td>0.705</td>
</tr>
<tr>
<td>4.0</td>
<td>0.224</td>
<td>0.174</td>
<td>0.759</td>
</tr>
<tr>
<td>4.5</td>
<td>0.208</td>
<td>0.158</td>
<td>0.801</td>
</tr>
<tr>
<td>5.0</td>
<td>0.182</td>
<td>0.132</td>
<td>0.879</td>
</tr>
<tr>
<td>5.5</td>
<td>0.169</td>
<td>0.119</td>
<td>0.924</td>
</tr>
<tr>
<td>6.0</td>
<td>0.142</td>
<td>0.092</td>
<td>1.036</td>
</tr>
</tbody>
</table>

$A_w = 0.05$
In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect 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 did not have any significant effect on the rate. A regression analysis of experimental data in order to obtain the regression coefficient, $r$ and standard deviation, $S$ of plots from the regression line was performed with a Microsoft Excel-2003 Programme.

RESULTS

Stoichiometry and product analysis

The reaction mixtures containing an excess permanganate concentration over L-Proline at constant concentrations Pd(II), NaOH and NaClO$_4$ to adjusted ionic strength of 0.50 mol dm$^{-3}$ was allowed to react for 2 hours in an inert atmosphere at $25 \pm 0.1^\circ$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 determined by spectrophotometrically. The results indicated that two moles of MnO$_4^-$ consumed by one mole of L-proline as given by equation (1). The results are given in Table IV (ii) (p.110).

$$\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH-COO}^- + 2\text{MnO}_4^- + 2\text{OH}^- \rightarrow \text{NH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHO} + 2\text{MnO}_4^{2-} + \text{HCO}_3^-$$

The products were eluted with solvent ether and the organic product was submitted to spot tests. The main reaction products were identified as the
Stoichiometry of palladium(II) catalysed oxidation of L-proline by permanganate in aqueous alkaline medium at 25 °C.

\[ [\text{OH}^-] = 0.10; \quad [\text{Pd}^{2+}] = 1.0 \times 10^{-5}; \]
\[ I = 0.50 / \text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>[MnO₄⁻] x 10⁴ (mol dm⁻³)</th>
<th>[L-pro] x 10⁴ (mol dm⁻³)</th>
<th>Found [MnO₄⁻] x 10⁴ (mol dm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>0.02</td>
</tr>
<tr>
<td>3.0</td>
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</tr>
<tr>
<td>8.0</td>
<td>3.0</td>
<td>2.12</td>
</tr>
</tbody>
</table>
Spectroscopic changes in the oxidation of palladium(II) catalysed oxidation of L-proline by permanganate. Scanning time interval 1.0 min, at 25°C.

\[ [\text{L-pro}] = 2.0 \times 10^{-3}; \quad [\text{MnO}_4^-] = 1.0 \times 10^{-4}; \]

\[ [\text{Pd(II)}] = 1.0 \times 10^{-4}; \quad [\text{OH}^-] = 0.10; \]

\[ I = 0.50 \text{ mol dm}^{-3}. \]
aminobutaraldehyde by spot test\textsuperscript{22} for amine and aldehyde groups. The product, aminobutaraldehyde was also confirmed by IR spectroscopy\textsuperscript{23} which showed bands at 3442 cm\textsuperscript{-1} for NH stretching, 1775 cm\textsuperscript{-1} for aldehydic >C=O stretching and 2952 cm\textsuperscript{-1}, for aldehydic –CH stretching respectively. The only organic product obtained in the oxidation is aminobutaraldehyde, which is further confirmed by single spot in TLC. Test for the corresponding acid was negative. It was further observed that the aldehyde does not undergo further oxidation under prevailing kinetic conditions.

Reaction orders

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

Effect of [permanganate]

The [permanganate] concentration was varied in the range of 0.5 x 10\textsuperscript{-4} to 5.0 x 10\textsuperscript{-4} mol dm\textsuperscript{-3} and the linearity and parallel plots of log ($A_t - A_w$) versus time indicated a reaction order as unity in [MnO\textsubscript{4}\textsuperscript{-}] (Fig.IV (iii) (p.115). This was also confirmed by variation of [MnO\textsubscript{4}\textsuperscript{-}], which did not result any change in the pseudo-first order rate constants, $k_{\text{obs}}$ as shown in Table IV (iii) (p.114).

Effect of [L-pro]

The substrate, L-proline concentration was varied in the range 5.0 x 10\textsuperscript{-4} to 5.0 x 10\textsuperscript{-3} mol dm\textsuperscript{-3} at 25° C while keeping all other reactant concentrations
constant (Table IV (iii) (p.114). The rate of reaction was almost found to be independent of [L-pro].

**Effect of [palladium(II)]**

The palladium(II) concentration was varied from $0.1 \times 10^{-5}$ to $1.0 \times 10^{-5}$ mol dm$^{-3}$ range, at constant concentrations of permanganate, L-proline, and alkali and at constant ionic strength (Table IV (iv) (p.116). The order with respect to palladium(II) was found to be unity from the linearity of the plots of \( \log k_c \) versus \( \log [\text{Pd(II)}] \) (Fig. IV (v) (p.118)) \( (r \geq 0.8723, S \leq 0.029) \).

**Effect of [alkali]**

The effect of alkali on the reaction has been studied in the range of 0.03 to 0.5 mol dm$^{-3}$ at constant concentrations of L-proline, permanganate and a constant ionic strength of 0.50 mol dm$^{-3}$. The rate constants increased with increasing [alkali] (Table IV (iv) (p.116)) and the order was found to be less than unity (Fig. IV (iv) (p.117)).

**Effect of added chloride**

Palladium (II) is known to form different complexes$^{24}$ of the general formula \( \text{Pd(II)}(\text{Cl})_n^{(2-n)} \) with \( n \) having values from 1 to 4. Hence the effect of chloride on the reaction rate was studied. Although the stock solution of Pd (II) contained chloride, for this series of runs, a Pd (II) solution which did not contain chloride was used. However, it was found that chloride has no effect on the reaction rate. Hence palladium chloride complexes are precluded in the title reaction.
Table IV (iii)

Effect of variation of $[\text{MnO}_4^-]$ and $[\text{L-pro}]$ on palladium(II) catalysed oxidation of L-proline by permanganate in aqueous alkaline medium at 25 °C.

$[\text{Pd}^{\text{II}}] = 1.0 \times 10^5$; $[\text{OH}^-] = 0.10$;

$I = 0.50 \text{/mol dm}^{-3}$.

<table>
<thead>
<tr>
<th>$[\text{MnO}_4^-] \times 10^4$ (mol dm$^{-3}$)</th>
<th>$[\text{L-pro}] \times 10^3$ (mol dm$^{-3}$)</th>
<th>$k_{\text{obs}} \times 10^3 \text{(s}^{-1})$</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
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<tr>
<td>0.5</td>
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<td>3.35</td>
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</tr>
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<td>3.35</td>
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</tr>
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<td>3.32</td>
<td>3.35</td>
<td></td>
</tr>
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<td>4.0</td>
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</tr>
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</tr>
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<td>3.35</td>
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</tr>
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</tr>
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</tr>
<tr>
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<td>3.0</td>
<td>3.63</td>
<td>3.35</td>
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<td>5.0</td>
<td>3.60</td>
<td>3.35</td>
<td></td>
</tr>
</tbody>
</table>
First order plots of palladium(II) catalysed oxidation of L-proline by alkaline permanganate at 25°C.

\[ [\text{MnO}_4^-] \times 10^4 = (1) 0.5 \quad (2) 1.0 \quad (3) 2.0 \quad (4) 3.0 \quad (5) 5.0 \text{ molar} \cdot \text{dm}^{-3} \]

(Conditions as given in Table IV (iii) (p.114))
Table IV (iv)

Effect of variation of $[\text{Pd(II)}]$ and $[\text{OH}^-]$ on palladium(II) catalysed oxidation of L-proline by permanganate in aqueous alkaline medium at 25 °C.

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

<table>
<thead>
<tr>
<th>$[\text{Pd(II)}] \times 10^3$ (mol dm$^{-3}$)</th>
<th>$[\text{OH}^-]$ (mol dm$^{-3}$)</th>
<th>$k_{\text{obs}} \times 10^3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
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<td>0.34</td>
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<td>0.2</td>
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</tr>
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<td>0.10</td>
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<td>0.10</td>
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<tr>
<td>1.0</td>
<td>0.50</td>
<td>4.82</td>
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</table>
Fig. IV (iv)

Order in $[\text{OH}^-]$ on the palladium(II) catalysed oxidation of 
L-proline by permanganate in aqueous alkaline medium at $25^\circ$ C.

(Conditions as given in Table IV (iv) (p.116))
Fig. IV (v)

Order in [OH\(^-\)] on the palladium(II) catalysed oxidation of L-proline by permanganate in aqueous alkaline medium at 25\(^\circ\) C.

(Conditions as given in Table IV (iv) (p.116))

\[ 6 + \log k_{obs} \]

\[ 2 + \log [\text{Pd(II)}] \]
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.

Effect of ionic strength

The effect of ionic strength was studied by varying the sodium perchlorate concentration from 0.20 to 2.0 mol dm$^{-3}$ at constant concentrations of permanganate, L-proline, palladium(II) and alkali. The rate constant increased with increasing concentration of NaClO$_4$ (Table IV (V) (p.120)) the plot of log $k_{obs}$ versus $I^{1/2}$ was linear with a positive slope (Fig.IV (vi) (p.121)) ($r \geq 0.9928$, $S \leq 0.014$).

Effect of Dielectric constant

The effect of dielectric constant ($D$) was studied by varying the t-butylalcohol - water content in the reaction mixture with all other conditions being maintained constant. Attempts to measure the dielectric constants were not successful. However, they were computed from the values of pure liquids$^{25}$. The solvent did not react with the oxidant under the experimental conditions. The rate constants, $k_{obs}$ increased with decrease in the dielectric constant of the medium Table IV (vi) (p.120). The plot of log $k_{obs}$ versus $1/D$ was linear with positive slope (Fig.IV (vi) (p.121)) ($r \geq 0.9983$, $S \leq 0.0341$).
Table IV (v)

Effect of ionic strength and dielectric constant on the palladium(II) catalysed oxidation of L-proline by aqueous alkaline permanganate at 25° C.

\[
\begin{align*}
[MnO_4^-] &= 1.0 \times 10^{-4}; \\
[L\text{-pro}] &= 2.0 \times 10^{-3}; \\
[Pd(II)] &= 1.0 \times 10^{-5}; \\
[OH^-] &= 0.10 /\text{mol dm}^{-3}
\end{align*}
\]

\[I = 0.50 /\text{mol dm}^{-3}\]

<table>
<thead>
<tr>
<th>I (mol dm$^{-3}$)</th>
<th>$k_{obs} \times 10^3$ (s$^{-1}$)</th>
<th>% of t-butyl alcohol-water (v/v)</th>
<th>$k_{obs} \times 10^3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>2.28</td>
<td>5</td>
<td>75.12</td>
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<td></td>
<td></td>
<td>10</td>
<td>71.74</td>
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<td>2.0</td>
<td>6.46</td>
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</table>
Fig. IV (vi)

Effect of ionic strength (I) and dielectric constant D on the Pd(II) catalysed oxidation of L-proline by aqueous alkaline permanganate at 25°.

(Conditions as in Table IV (v) (p.120))
Test for free radicals

The reaction mixture was mixed with acrylonitrile monomer and kept for 3 hours in an inert atmosphere. On diluting with methanol a white precipitate was formed, indicating the intervention of free radicals in the reaction. The blank experiments of either MnO₄⁻ or L-proline alone with acrylonitrile did not induce polymerization under the same conditions as those induced with reaction mixtures. Initially added acrylonitrile decreases the rate indicating the free radical intervention, which is the case in earlier work.²⁶

Effect of temperature

The rate of the reaction was measured at four different temperatures with varying [OH⁻], keeping other conditions constant. The rate was found to increase with increase in temperature. The rate constants, k, of the slow step of the mechanism were obtained from the plots of [Pd(II)] / kₘₚ versus 1/[OH⁻] at four different temperatures. The values of k at different temperatures are given in Table IV (vi) (a) (p.123). From the Arrhenius plot of log k versus 1/T (Fig. IV(vii) (p.124) (r ≥ 0.9978, S ≤ 0.0068) with least square analysis, the activation parameters are calculated and are given in Table IV (vi) (b) (p.123).

The thermodynamic quantities for the equilibrium step of Scheme 1 and the activation parameters for the rate-determining step in Scheme 3 could be evaluated as follows: The hydroxyl ion concentration as in Table1 was varied at four different temperatures and values of the K were determined. A van't Hoff's plot was drawn for the variation of K with temperature [i.e., log K versus 1/T].
Table IV (vi)

(a) Effect of temperature on the oxidation of Pd(II) catalysed oxidation of L-proline by alkaline permanganate.

\[ [\text{L-pro}] = 2.0 \times 10^{-3}; \quad [\text{MnO}_4^-] = 1.0 \times 10^{-4}; \quad [\text{Pd(II)}] = 1.0 \times 10^{-5}; \quad I = 0.50 / \text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>(k \times 10^2) (dm(^3)mol(^{-1}) s(^{-1}))</th>
<th>log (k)</th>
<th>(1/T \times 10^3)</th>
<th>(Y) calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>6.21</td>
<td>2.79</td>
<td>3.35</td>
<td>2.7935</td>
</tr>
<tr>
<td>303</td>
<td>6.52</td>
<td>2.81</td>
<td>3.30</td>
<td>2.8128</td>
</tr>
<tr>
<td>308</td>
<td>6.76</td>
<td>2.82</td>
<td>3.25</td>
<td>2.8314</td>
</tr>
<tr>
<td>313</td>
<td>7.08</td>
<td>2.85</td>
<td>3.19</td>
<td>2.8495</td>
</tr>
</tbody>
</table>

*Calculated

(b) Thermodynamic activation parameters with respect to slow step of Scheme 1.

<table>
<thead>
<tr>
<th>Activation parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_a) (kJ mol(^{-1}))</td>
<td>6.6 ± 0.2</td>
</tr>
<tr>
<td>(\Delta H^#) (kJ mol(^{-1}))</td>
<td>4.1 ± 0.1</td>
</tr>
<tr>
<td>(\Delta S^#) (J K(^{-1})mol(^{-1}))</td>
<td>-177 ± 10</td>
</tr>
<tr>
<td>(\Delta G^#) (kJ mol(^{-1}))</td>
<td>49 ± 2</td>
</tr>
<tr>
<td>log (A)</td>
<td>4.0 ± 0.1</td>
</tr>
</tbody>
</table>

(c) Thermodynamic quantities for equilibrium as in Scheme 1

<table>
<thead>
<tr>
<th></th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta H) (kJ mol(^{-1}))</td>
<td>30.7 ± 0.6</td>
</tr>
<tr>
<td>(\Delta S) (J K(^{-1})mol(^{-1}))</td>
<td>123 ± 7</td>
</tr>
<tr>
<td>(\Delta G) (kJ mol(^{-1}))</td>
<td>-6.0 ± 0.1</td>
</tr>
</tbody>
</table>
Fig. IV (vii)

Effect of temperature on the palladium(II) catalyzed oxidation of L-proline by heptavalent manganese in aqueous alkaline medium with respect to slow step of Scheme 3.

(Conditions as in Table IV(vi) (p.123 (a))

\[
\begin{array}{|c|c|}
\hline
\text{log } k \text{ (Y* Cal)} & \\
\hline
2.86 & \\
2.84 & \\
2.82 & \\
2.80 & \\
2.78 & \\
\hline
\end{array}
\]

\[
\begin{array}{|c|c|}
\hline
1/T \times 10^3 \text{K}^{-1} & \\
3.15 & \\
3.2 & \\
3.25 & \\
3.3 & \\
3.35 & \\
3.4 & \\
\hline
\end{array}
\]
and the values of the enthalpy of reaction $\Delta H$, entropy of reaction $\Delta S$ and free energy of reaction $\Delta G$, were calculated. These values are also given in Table IV (vi) (c) (p.123).

**DISCUSSION**

Permanganate ion, $\text{MnO}_4^-$, 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 stopped. The Diode Array Rapid Scan Spectrophotometric (DARSS) studies have shown that at pH $>$ 12, the product of Mn (VII) is Mn (VI) and no further reduction was observed as reported 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 KMnO$_4$ solution from violet Mn (VII) ion to dark green Mn (VI) ion through blue Mn (V) ion has been observed.

The reaction between permanganate and L-proline in alkaline medium has a stoichiometry of 1:2 with a unit order dependence on the [MnO$_4^-$] and [Pd(II)] and less than unit order dependence on both the [alkali] and [L-pro]. No
products effect was observed. It is known that L-proline exists in the form of a Zwitter ion $^{27}$ in aqueous medium. In highly acidic medium, it exists in the protonated form, whereas in highly basic medium, it is in the fully deprotonated form.

\[
\text{NH-CH}_2\text{-CH}_2\text{-CH-CH-COO}^-
\]

It is noteworthy that the reaction is not influenced by chloride ions, to be expected in Pd (II) catalysed reactions$^{15}$. However in alkaline solutions, Pd (II) is mostly present as hydroxylated species (Pd(OH)Cl) which is in accordance with earlier work$^{28}$ and not as its chloride complex as in other cases$^{15}$. The results suggest that first alkali combines with permanganate to form an alkali-permanganate species [MnO$_4$.OH]$^{2-}$ in a pre-equilibrium step$^{29}$ which explains the less than unit order in alkali. The alkali permanganate reacts with the catalyst [Pd(OH)(Cl)] in a slow step to give the intermediate[Pd(OH)(Cl)]$^+$ which oxides the anionic form of L-proline free radical. This explains the polymerization study of intervention of free radical during the progress of reaction. The free radical derived from L-proline, which further react with another molecule of alkali permanganate in a fast step to yield the products. The experimental results can be accommodated in Scheme 3.
Scheme 3.

The probable structure of complex (C) is given as,
Spectral evidence for complex formation between catalyst and substrate was obtained from the UV-VIS spectra of the palladium(II) species and mixture of palladium(II) and L-proline. A bathochromic shift, $\lambda_{\text{max}}$, of 8 nm from 224 to 232 nm is observed, together with hyperchromicity at $\lambda_{\text{max}}$ 232 nm. However, the evidence for complex formation is obtained by kinetic studies (i.e., from the Michaelis-Menten plot). The plot of $[\text{Pd(II)}]/k_{\text{obs}}$ versus $1/[\text{L-pro}]$ are linear with an intercept supporting the Pd(II)-L-proline complex. Such type of substrate-catalyst complex formation has been reported previously. The observed modest enthalpy of activation, relatively low value of the entropy of activation and higher rate constant for the slow step of the mechanism, indicate that oxidation presumably occurs by an inner-sphere mechanism. This conclusion is supported by earlier work. Since Scheme 3 is in accordance with generally well accepted principle of non-complementary oxidations taking place in a sequence of one-electron steps, the reaction would involve a radical intermediate. 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 rate law (6) as follows,

According to Scheme 3,
Rate $= -\frac{d[MnO_4^-]}{dt} = k [MnO_4^- \cdot OH]^2[Pd(II)]$

$= k K [MnO_4^-][OH^-][Pd(II)]$  \hspace{1cm} (2)

The total concentration of $MnO_4^-$ is given by,

$[MnO_4^-]_T = [MnO_4^-]_f + [MnO_4^-OH]^2$

$= [MnO_4^-]_f + K [MnO_4^-][OH^-]$

$= [MnO_4^-]_f (1 + K [OH^-])$

Where $T$ and $f$ stand for total and free,

$[MnO_4^-]_T = \frac{[MnO_4^-]_f}{1 + K [OH^-]}$  \hspace{1cm} (3)

Similarly,

$[OH^-]_T = \frac{[OH^-]_f}{1 + K [MnO_4^-]}$

In view of low concentrations of $MnO_4^-$ used, denominator becomes unity.

$[MnO_4^-]_f = \frac{[MnO_4^-]}{1 + K [OH^-]}$

$[OH^-]_f = [OH^-]_T$  \hspace{1cm} (4)

and

$[[Pd(II)]_f = [Pd(II)]_T$  \hspace{1cm} (5)

Substituting the values of equation (3), (4) and (5) in equation (2) and omitting subscripts $T$ and $f$, we get,

Rate $= -\frac{d[MnO_4^-]}{dt} = \frac{k K [MnO_4^-][OH^-][Pd(II)]}{1 + K [OH^-]}$  \hspace{1cm} (6)

or

Rate $= k_{obs} = \frac{k K [OH^-][Pd(II)]}{1 + K [OH^-]}$  \hspace{1cm} (6)
Verification of rate law (7): Plot of $[\text{Pd(II)}]/k_{\text{obs}}$ versus $1/\left[\text{OH}^-\right]$

(Conditions as in Table IV(iii) (p.114); (iv) (p.116))
Equation (6) can be rearranged to equation (7) which is suitable for verification.

\[
\frac{[\text{Pd(II)}]}{k_{\text{obs}}} = \frac{1}{k K[\text{OH}^-]} + \frac{1}{k}
\]  

(7)

According to equation (7), the plot of \([\text{Pd(II)}]/k_{\text{obs}}\) versus \(1/[\text{OH}^-]\) \((r \geq 0.9933, S \leq 0.041)\) should be linear, which is verified in Fig. IV (viii) (p. 131). The slope and intercept of such plot leads to the values of \(K\) and \(k\) as \((298 \text{ K})\), \((1.11 \pm 0.05) \times 10^1 \text{dm}^3\text{mol}^{-1}\), and \((6.21 \pm 0.2) \times 10^2 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}\) respectively. Using these values, the rate constants under different experimental conditions were calculated by Eqn (6) and compared with experimental data. Experimental and Calculated values agree reasonably well.

The effect of ionic strength and solvent polarity on the rate of reaction in the present case is entirely different from that of earlier studies on other amino acids. In case of oxidation of L-asparagine-permanganate reaction\(^{32}\), there was no effect of ionic strength and relative permittivity on the rate of reaction. In case of L-phenylalanine\(^{33}\) also the rate was independent of ionic strength. But in our present study the effect of increasing ionic strength on the rate explains qualitatively the reaction between two negatively charged ions, as in Scheme 3. However, the rate constants, \(k_{\text{obs}}\) increased with decrease in the dielectric constant of the medium. The plot of log \(k_{\text{obs}}\) versus \(1/D\) was linear with positive slope, which is contrary to the expected reaction. Perhaps the effect is countered substantially by the formation of active reaction species to a greater extent in low relative permittivity media leading to the net increase in rate\(^{34}\).
The entropy of activation (ΔS°) in earlier work on L-aspargine was found to be positive indicating the complex is less ordered than reactant molecules, whereas in case of phenylalanine, negative value of ΔS° and high value of frequency factor indicates that the electrostatic effects are unimportant. However, in the present study, the negative values of ΔS° indicates that the complex is more ordered than the reactants. The activation parameters for the oxidation of some amino acids by alkaline permanganate in presence of catalyst are summarized in Table IV (vii) (p.133). The entropy of the activation for the title reaction falls within the observed range. Variation in the rate within a reaction series may be caused by change in the enthalpy or entropy of activation. Changes in the rate are caused by changes in both ΔH° and ΔS°, but these quantities vary extensively in a parallel fashion. A plot of ΔH° versus ΔS° is linear according to equation.

ΔH° = βΔS° + constant

β is called the isokinetic temperature; it has been asserted that apparently linear correlation of ΔH° with ΔS° are sometimes misleading and the evaluation of β by means of the above equation lacks statistical validity. Exner 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 k₂ (at T₂) is linearly related to log k₁ (at T₁) i.e. log k₂ = a + b log k₁, he proposes that β can be evaluated from the equation,
**Table IV (vii)**

Activation parameters for some amino acids (for iso kinetic temperature) in presence of different catalysts.

<table>
<thead>
<tr>
<th>Amino acids</th>
<th>$k_1 \times 10^4$ (dm$^3$mol$^{-1}$s$^{-1}$) at 298K</th>
<th>$k_2 \times 10^4$ (dm$^3$mol$^{-1}$s$^{-1}$) at 303K</th>
<th>$\Delta S^\circ$ (JK$^{-1}$mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-aspargine</td>
<td>133</td>
<td>192</td>
<td>12</td>
<td>64.5</td>
<td>60</td>
<td>[37]</td>
</tr>
<tr>
<td>L-Alanine</td>
<td>62.1</td>
<td>73.8</td>
<td>-75.1</td>
<td>17.6</td>
<td>40.6</td>
<td>[38]</td>
</tr>
<tr>
<td>Rac-serine</td>
<td>1.06</td>
<td>1.27</td>
<td>-17.1</td>
<td>28.6</td>
<td>36.4</td>
<td>[38]</td>
</tr>
<tr>
<td>L-Leucine</td>
<td>1.53</td>
<td>1.96</td>
<td>-62</td>
<td>30.7</td>
<td>49.2</td>
<td>[38]</td>
</tr>
<tr>
<td>L-Isoleucine</td>
<td>1.10</td>
<td>1.39</td>
<td>-71.0</td>
<td>28.8</td>
<td>49.3</td>
<td>[38]</td>
</tr>
<tr>
<td>L-Arginine</td>
<td>5.80</td>
<td>8.0</td>
<td>-13.1</td>
<td>29.4</td>
<td>33.4</td>
<td>[38]</td>
</tr>
<tr>
<td>L-Proline</td>
<td>667</td>
<td>693</td>
<td>-180</td>
<td>3.1</td>
<td>57</td>
<td>Present work</td>
</tr>
</tbody>
</table>

133
Fig. IV (ix)

Plot of $\log k_2$ at 303K versus $\log k_1$ at 298K for isokinetic temperature.

1) L-asparagine, 2) L-alanine, 3) Rac-serine, 4) L-leucine, 5) L-Isoleucine,
6) L-arginine, 7) L-proline (present study).

(Conditions as in Table IV(vii) (p.133))
\[ \beta = \frac{T_1 T_2 (b-1)}{T_2 b - T_1} \]

We have calculated the isokinetic temperature as 184 K by plotting $\log k_1$ at 298 K versus $\log k_2$ at 303K (Figure IV (ix) (p.134) ($r \geq 0.977$ & $s \leq 0.0052$). The value of $\beta$ (184K) is lower than experimental temperature (303K). This indicates that the rate is governed by the entropy of activation\(^39\). The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow similar mechanism, as previously suggested.

**Importance of Chapter IV**

It is interesting to note that the oxidant species [MnO₄⁻] required 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 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. The description of the mechanism is consistent with all the experimental evidence including both kinetic and product studies.
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