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

The manganese chemistry involved in these multistep redox reactions is an important source of information as the manganese intermediates are relatively easy to identify when they have sufficiently long life times and oxidation states of the intermediates permit useful conclusions as to the possible reaction mechanism including the nature of intermediates.

Permanganate ion oxidises a greater variety of substrates and it finds extensive applications in organic syntheses, especially after the advent of phase transfer catalysis 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 and non-aqueous media.
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 used for the study. In strongly alkaline medium, the stable reduction product is the manganate ion, MnO$_4^{-}$. No mechanistic information is available to distinguish between a direct one-electron reduction to Mn(VI) (Scheme 1) and a mechanism in which a hypomanganate is formed in a two-electron step followed by a rapid reaction (Scheme 2).

\[
\text{Mn(VII) + S} \xrightarrow{k_1} \text{Mn(VI) + S}^* \\
\text{Mn(VII) + S}^* \xrightarrow{k_2} \text{Mn(VI) + Products}
\]

Where S = Substrate, \(k_2 \gg k_1\)

Scheme 1

\[
\text{Mn(VII) + S} \xrightarrow{k_3} \text{Mn(V) + Products} \\
\text{Mn(VII) + Mn(V)} \xrightarrow{k_4} 2\text{Mn(VI)}
\]

Where S = Substrate, \(k_4 \gg k_3\)

Scheme 2
L-proline is one of the amino acids, which occurs in relatively high concentrations in plant tissues. Its role in metabolism is crucial and also finds extensive applications in pharmaceuticals and medicines. Enzymatic dehydrogenation of α-amino acids by flavoenzymes has attracted considerable attention in recent years. In fact, a precise understanding of the mechanism of such biological redox reactions is important as it helps in the synthesis of specific reaction products. Many attempts were made to mimic flavin-catalysed oxidations of α-amino acids to the corresponding α-keto acids by non-enzymatic means. These studies were found to yield the corresponding noraldehyde by oxidative decarboxylation of α-amino acids. The kinetic investigation of the oxidation of 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. Jayaprakash Rao et al. suggested that the oxidation of α-amino acids by two electron oxidant such as diperiodatoargentate (III) in alkaline medium involves two electron transfer from the amino acid to the oxidant to give imino acid intermediate which subsequently undergoes hydrolysis to yield keto acids. One electron oxidants such as ceric sulphate, cause decarboxylation during the oxidation of α-amino acids. Hexacyanoferrate(III), a potential one-electron oxidant is reported to oxidize α-amino acids to corresponding α-keto acids. Similarly, L-proline gave different products with different oxidants.
The study of amino acids become important because of their biological significance and selectivity towards the oxidants.

Ruthenium(III) acts as an efficient catalyst in many redox reactions involving different complexities due to the formation of different intermediate complexes, free radicals and multiple oxidation states of ruthenium. The uncatalysed reaction between L-proline and permanganate in an alkaline medium has been studied previously. A micro amount of ruthenium(III) is sufficient to catalyse the reaction in any alkaline medium and a variety of mechanisms are possible. We describe the results of the title reaction in this chapter in order to understand the active species of oxidant, reductant and catalyst in such media and to arrive at a plausible mechanism.

EXPERIMENTAL

Materials

Since the initial reaction was too fast to be monitored by the usual methods kinetic measurements were performed on a Varian CARY 50 UV spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12).

Stock solution of L-proline (sisco-chem.ltd) was prepared by dissolving the appropriate amount of sample in doubly distilled water. The solution of KMnO₄ (BDH) was prepared by dissolving the appropriate amounts of sample in double distilled water and standardized against oxalic acid. A K₂MnO₄ solution was prepared as described by Carrington and Symons as follows: A solution of
KMnO₄ was heated to boiling in 8.0 mol dm⁻³ KOH solution until a green colour appeared. The solid formed on cooling was recrystallised from the same solvent. Using the required amount of recrystallised sample, a stock solution of K₂MnO₄ was prepared in aqueous KOH. The solution was standardized by measuring the absorbance on a Peltier Accessory (temperature control) attached to Varian CARY 50 UV-spectrophotometer with a 1 cm quartz cell at 608 nm (ε = 1530 ± 20 dm⁻³ mol⁻¹ cm⁻¹). The ruthenium(III) solution was prepared by dissolving a known weight of RuCl₃ (s.d.fine-chem) in 0.20 mol dm⁻³ HCl. Mercury was added to the ruthenium(III) solution to reduce any ruthenium(IV) formed during the preparation of ruthenium(III) stock solution and kept for a day. The ruthenium(III) concentration was assayed by EDTA titration²².

All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts of the samples in double distilled water. NaOH (BDH) and NaClO₄ (BDH) 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-proline]:[MnO₄⁻] 10:1 at a constant ionic strength of 0.20 mol dm⁻³. The reaction was initiated by mixing previously thermostatted solutions of MnO₄⁻, and L-proline which also contained the necessary quantities of Ru(III), 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 the absorbance of MnO₄⁻ in a 1cm quartz cell of 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, giving ε = 2083 ± 50 dm³ mol⁻¹ cm⁻¹ (Literature ε = 2200 dm³ mol⁻¹ cm⁻¹). The first-order rate constants, (k_C) were evaluated by the plots of log (A_t - A_∞) versus time by fitting the data to the expression A_t = A_∞ + (A_0 - A_∞) e⁻^(k_observable t), where A_t, A_0 and A_∞ are absorbances of permanganate at time t, 0 and ∞ respectively. The first order plots in almost all cases were linear to 80% completion of the reaction and k_observable were reproducible within ± 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 MnO₄²⁻. It is probable that the blue colour originated from the violet of permanganate and the green from the manganate, excluding the accumulation of manganese(V). It is also evident from the Fig. VI(i) (p.168) 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
Figure VI (i)
Spectroscopic changes occurring in the ruthenium(III) catalysed oxidation of L-proline by permanganate with \([\text{MnO}_4^-] = 2 \times 10^{-4}; [\text{L-Proline}] = 1 \times 10^{-3}; [\text{Ru (III)}] = 1 \times 10^{-6}; [\text{OH}^-] = 0.1; I = 0.20. \text{mol dm}^{-3} \text{ at } 25^\circ \text{C},\]
scanning time interval = 1 min.
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 as a precaution, fresh solutions were used when conducting the experiments.

In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the rate.

Regression analysis of experimental data to obtain the regression coefficient, $r$ and standard deviation $S$ of points from the regression line was performed using a Pentium-III personnel computer.

RESULTS

Stoichiometry and product analysis

The reaction mixture containing an excess permanganate concentration over L-proline was mixed in presence of $2.0 \times 10^{-6}$ mol dm$^{-3}$ [Ru(III)], 0.1 mol dm$^{-3}$ NaOH, adjusted to a constant ionic strength of 0.20 mol dm$^{-3}$ and allowed to react for ca 2 hours at 25 °C. The remaining permanganate was then analysed spectrophotometrically. The results indicated that two moles of permanganate were consumed by one mole of L-proline according to equation (1). The results are given in Table VI(i) (p171)
The main reaction products were identified as the aminobutaraldehyde by spot test\textsuperscript{26} for amine and aldehyde groups. The product, aminobutaraldehyde was also confirmed by IR spectroscopy\textsuperscript{27} which showed bands at 3444 cm\textsuperscript{-1} for NH stretching, 1773 cm\textsuperscript{-1} for aldehydic >CO stretching and 2956 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**

As the permanganate oxidation of L-proline in alkaline medium proceeds with a measurable rate in the absence of ruthenium(III), the catalysed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus, the total rate constant ($k_T$) is equal to the sum of the rate constants of the catalysed ($k_C$) and uncatalysed ($k_U$) reactions, so $k_C = k_T - k_U$. Hence the reaction orders have been determined from the slopes of log $k_C$ versus log (concentration) plots by varying the concentrations of reductant, Ru(III) and alkali in turn while keeping the others constant.

**Effect of [permanganate]**

The potassium permanganate concentration was varied in the range of 5.0 x 10\textsuperscript{-5} to 5.0 x 10\textsuperscript{-4} mol dm\textsuperscript{-3}, and the linearity of plots of log [MnO\textsubscript{4}\textsuperscript{-}] versus time...
Table VI (i)

Stoichiometry of ruthenium(III) catalysed oxidation of L-proline by aqueous alkaline permanganate at 25 °C.

\[ [\text{OH}^-] = 0.1; \]
\[ [\text{Ru (III)}] = 1 \times 10^{-6}; \]
\[ I = 0.20 /\text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>Taken</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ [\text{MnO}_4^-] \times 10^4 ] (mol dm(^{-3}))</td>
<td>[ [\text{L-proline}] \times 10^4 ] (mol dm(^{-3}))</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>6.0</td>
<td>2.0</td>
</tr>
<tr>
<td>8.0</td>
<td>3.0</td>
</tr>
<tr>
<td>4.0</td>
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<tr>
<td>6.0</td>
<td>3.0</td>
</tr>
<tr>
<td>8.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
indicated a reaction order of unity in $[\text{MnO}_4^-]$ (Fig. VI (ii) (p.173)) ($r \geq 0.9994$, $S \leq 0.0261$). This was also confirmed by variation of $[\text{MnO}_4^-]$, which did not result in any change in the pseudo first-order rate constants, $k_C$ (Table VI (ii) (p.174)).

**Effect of [L-proline]**

The substrate concentration was varied in the range $5.0 \times 10^{-4}$ to $5.0 \times 10^{-3}$ mol dm$^{-3}$ at 25°C while keeping all other reactant concentrations and conditions constant (Table VI (ii)(p.174)). The reaction order in L-proline was found to be less than unity as shown in Fig. VI (iii)(p.175).

**Effect of [alkali]**

The effect of alkali on the reaction has been studied at constant concentrations of L-proline, potassium permanganate, ruthenium(III) and a constant ionic strength of 0.20 mol dm$^{-3}$. The rate constants increased with increasing $[\text{OH}^-]$(Table VI (iii) (p.176)). The reaction order in $[\text{OH}^-]$ was found to be less than unity as shown in Fig. VI (iii)(p.175).

**Effect of [Ru(III)]**

The Ru(III) concentration was varied from $5.0 \times 10^{-7}$ to $5.0 \times 10^{-6}$ at constant concentration of permanganate, L-proline, and ionic strength(Table VI(iii)(p.176)). The order in [Ru(III)] was found to be unity (Fig. VI (iv))(p.178)).

**Effect of ionic strength**

The effect of ionic strength was studied by varying the NaClO$_4$ concentration in the reaction medium. The ionic strength was varied from 0.2 to
Figure VI(ii)

First order plots of ruthenium(III) catalysed oxidation of L-proline in aqueous alkaline permanganate at 25 °C.

$[\text{MnO}_4^-] \times 10^4$ (mol dm$^{-3}$):

(1) 0.5, (2) 0.1, (3) 2.0, (4) 3.0, (5) 5.0

(Conditions as in Table VI(i)(p.174))
Table VI(ii)

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

$[\text{OH}^-] = 0.10$; $[\text{Ru (III)}] = 1.0 \times 10^{-6}$; $I = 0.20/\text{mol dm}^{-3}$.

<table>
<thead>
<tr>
<th>$[\text{MnO}_4^-] \times 10^4$ (mol dm$^{-3}$)</th>
<th>$[\text{L-proline}] \times 10^3$ (mol dm$^{-3}$)</th>
<th>$k_T \times 10^4$ (s$^{-1}$)</th>
<th>$k_U \times 10^2$ (s$^{-1}$)</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
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<td>0.80</td>
<td>3.05</td>
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</tr>
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<td>0.80</td>
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<td>0.80</td>
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<td>3.02</td>
</tr>
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<td>3.95</td>
<td>0.80</td>
<td>3.15</td>
<td>3.02</td>
</tr>
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<td>2.0</td>
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<td>0.25</td>
<td>0.95</td>
<td>0.92</td>
</tr>
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<td>0.52</td>
<td>1.58</td>
<td>1.70</td>
</tr>
<tr>
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<td>2.0</td>
<td>3.91</td>
<td>0.80</td>
<td>3.11</td>
<td>3.02</td>
</tr>
<tr>
<td>2.0</td>
<td>3.0</td>
<td>6.00</td>
<td>1.00</td>
<td>5.00</td>
<td>4.83</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>7.50</td>
<td>1.50</td>
<td>6.00</td>
<td>5.50</td>
</tr>
</tbody>
</table>

174
Order in [L-proline] and [OH\(^{-}\)] on the ruthenium (III) catalysed oxidation of L-proline by permanganate in aqueous alkaline medium at 25 °C.

(Conditions as in Table VI (ii)(p.174) and Table VI (iii)(p.176))
Table VI(iii)

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

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

\[ I = 0.20/\ \text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>([\text{OH}^-]) ((\text{mol dm}^{-3}))</th>
<th>([\text{Ru(III)}]\times 10^6) ((\text{mol dm}^{-3}))</th>
<th>(k_T \times 10^2) ((\text{s}^{-1}))</th>
<th>(k_U \times 10^2) ((\text{s}^{-1}))</th>
<th>(k_C \times 10^2) ((\text{s}^{-1}))</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
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<td>0.85</td>
<td>0.15</td>
<td>0.70</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
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<td>1.66</td>
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</tr>
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<td>3.11</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
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<tr>
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<td>7.00</td>
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<td>5.20</td>
<td>5.10</td>
<td></td>
</tr>
<tr>
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<td>0.80</td>
<td>1.40</td>
<td>1.50</td>
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<td>3.11</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
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<td>6.70</td>
<td>0.80</td>
<td>5.90</td>
<td>6.03</td>
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</tr>
<tr>
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<td>9.80</td>
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<td>9.05</td>
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</tr>
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<td>14.8</td>
<td>0.80</td>
<td>14.0</td>
<td>15.1</td>
<td></td>
</tr>
</tbody>
</table>
2.0 mol dm$^{-3}$ at constant concentrations of permanganate, L-proline and alkali. As shown in Table VI (iv)(p.179). It was found that the rate constant increased with increasing concentration of NaClO$_4$; the plot of log $k_c$ versus $I^{1/2}$ was linear with a positive slope as shown in Fig. (VI) (v)(p.180) ($r \geq 0.9984$, $S \leq 0.0145$).

**Effect of relative permittivity**

The effect of relative permittivity ($\varepsilon_T$) 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. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquids$^{28}$. No reaction of the solvent with the oxidant occurred under the experimental conditions employed. The rate constant, $k_c$ increased with decreasing dielectric constant of the medium (Table VI(iv)(p.179)). The plot of log $k_c$ versus $1/\varepsilon_T$ was linear with a positive slope (Fig.(VI)(v)(p.180)) ($r \geq 0.9936$, $S \leq 0.0125$).

**Effect of initially added products**

Initially added reaction products such as manganate, ammonium hydroxide and aldehyde were studied by keeping all other reactants concentration constant. It was found that the added products have negligible effect on the rate of the reaction.
Order in [Ru (III)] on the ruthenium (III) catalysed oxidation of L-proline by permanganate in aqueous alkaline medium at 25 °C.

(Conditions as in Table VI (ii)(p.174))
Table VI (iv)

Effect of ionic strength and dielectric constant ($\varepsilon_T$) on the ruthenium(III) catalysed oxidation of L-proline by permanganate in aqueous alkaline medium at 25 $^\circ$C.

$[\text{MnO}_4^-] = 1.0 \times 10^{-4};$
$[\text{L-proline}] = 2.0 \times 10^{-3};$
$[\text{OH}^-] = 0.1;$
$I = 0.20 /\text{mol dm}^{-3}.$

<table>
<thead>
<tr>
<th>$I$ (mol dm$^{-3}$)</th>
<th>$k_c \times 10^2$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>3.1</td>
</tr>
<tr>
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<td>3.4</td>
</tr>
<tr>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td>1.5</td>
<td>4.5</td>
</tr>
<tr>
<td>2.0</td>
<td>5.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% of *-butanol-water</th>
<th>$\varepsilon_T$</th>
<th>$k_c \times 10^2$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
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</tr>
<tr>
<td>5</td>
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<td>68.36</td>
<td>7.2</td>
</tr>
<tr>
<td>20</td>
<td>64.98</td>
<td>7.6</td>
</tr>
</tbody>
</table>

*-*butanol-water (v/v)
Figure VI(v)

Effect of ionic strength and dielectric constant ($\varepsilon_r$) on the ruthenium(III) catalysed oxidation of L-proline by permanganate in aqueous alkaline medium at 25 °C.

(Conditions as in Table VI (ii)(p.174))
Test for free radical

The intervention of free radicals in the reaction was examined as follows. The reaction mixture to which a known quantity of acrylonitrile scavenger has been added initially was kept for two hours in an inert atmosphere. On diluting the reaction mixture with methanol, a precipitate resulted, suggesting the possibility of free radical intervention. The blank experiments of either MnO₄⁻ or L-proline in with acrylonitrile alone did not induce polymerization under the same conditions as those induced with reaction mixture. Initially added acrylonitrile decreases the rate indicating the free radical intervention, which is also the case in earlier work.

Effect of temperature

The rate of the reaction was measured at four different temperatures, with varying [OH⁻] and [L-Proline], keeping other conditions constant. The rate was found to increase with increase in temperature. The rate constants, k, of the slow step of Scheme 3 were obtained from the slopes and intercepts of the plots of [Ru(III)]/k_C versus 1/[OH⁻] (r > 0.9959, S ≤ 0.0450) and [Ru (III)]/k_C versus 1/[L-Proline] (r ≥ 0.9989, S ≤ 0.0410). The values of k are given in the Table VI(v)(p.182). The activation parameters were evaluated from the Arrhenius plot of log k versus 1/T (Fig. VI (vi) (p.183)) (r ≥ 0.9983, S ≤ 0.0461) and are given in Table VI(v)(p.182). These values are comparable with the uncatalysed reaction.
Table VI (v)

(a) Effect of temperature on the ruthenium(III) catalysed oxidation of L-proline by permanganate in an aqueous alkaline medium.

\[
[MnO_4^-] = 2.0 \times 10^{-4}; \quad [\text{L-proline}] = 1.0 \times 10^{-3}; \\
[OH^-] = 0.10; \quad [\text{Ru(III)}] = 2.0 \times 10^{-6}; \\
I = 0.20/\text{mol dm}^{-3}.
\]

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>(k \times 10^{-5}) (Y)</th>
<th>(\log k) (X)</th>
<th>(1/T \times 10^3)</th>
<th>(Y_{\text{calc}}^*)</th>
</tr>
</thead>
<tbody>
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<td>5.8102</td>
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<td>5.8145</td>
</tr>
<tr>
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<td>7.10</td>
<td>5.8540</td>
<td>3.30</td>
<td>5.8549</td>
</tr>
<tr>
<td>308</td>
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<td>5.9030</td>
<td>3.25</td>
<td>5.9036</td>
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<tr>
<td>313</td>
<td>9.52</td>
<td>5.9170</td>
<td>3.19</td>
<td>5.9182</td>
</tr>
</tbody>
</table>

*Calculated

(b) 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>19.8 ± 1.0</td>
</tr>
<tr>
<td>(\log A)</td>
<td>11.5 ± 0.8</td>
</tr>
<tr>
<td>(\Delta H^#) (kJ mol(^{-1}))</td>
<td>17.5 ± 1.5</td>
</tr>
<tr>
<td>(\Delta S^#) (J K(^{-1}) mol(^{-1}))</td>
<td>-75.4 ± 4.0</td>
</tr>
<tr>
<td>(\Delta G^#) (kJ mol(^{-1}))</td>
<td>23 ± 2</td>
</tr>
</tbody>
</table>

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Figure VI (vi)

Effect of temperature on the ruthenium (III) catalysed oxidation of L-proline by permanganate in an aqueous alkaline medium.

(Conditions as in Table VI (v) (p.182))
DISCUSSION

Permanganate ion, MnO₄⁻, is a powerful oxidant in an aqueous alkaline medium. As it exhibits many oxidation states, the stoichiometric results and pH of the reaction media play an important role. Under the prevailing experimental conditions at pH >12, the reduction product of Mn(VII), is Mn(VI), it is stable and further reduction of Mn(VI) might be stopped¹⁰,¹¹. 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 reported¹⁰ by Simandi et al. However, on prolonged standing, the green Mn(VI) is reduced to Mn(IV) under our experimental conditions.

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

It is interesting to identify the probable species of ruthenium(III) chloride in alkaline medium. Electronic spectral studies³⁰ have confirmed that ruthenium(III) chloride exists in hydrated form as [Ru(H₂O)₆]³⁺. In the present study of alkaline
medium, it is quite probable that the species $[\text{Ru(H}_2\text{O})_6\text{OH}]^{2+}$ might assume the general form $[\text{Ru(III)(OH)}_x]^3-x$. The value of $x$ would always be less than six because there are no definite reports of any hexahydroxy species of ruthenium. The remainder of the coordination sphere will be filled by water molecule. Hence under the experimental conditions $[\text{OH}^+] >> [\text{Ru(III)}]$, ruthenium(III) is mostly present$^{31}$ as the hydroxylated species $[\text{Ru(H}_2\text{O})_5\text{OH}]^{2+}$.

The reaction between permanganate and L-proline in alkaline medium in presence of ruthenium(III) has a stoichiometry of 1:2 with a first order dependence on the $[\text{MnO}_4^-]$ and $[\text{Ru(III)}]$ and less than unit order dependence on both the [alkali] and [L-proline]. No effect of added products was observed.

The results indicate that first alkali combines with permanganate to form an alkali-permanganate species $[\text{MnO}_4\text{OH}]^{2+}$ in a pre-equilibrium step$^{32}$ which is also supported by the observed fractional order in$[\text{OH}^+]$. L-proline reacts with ruthenium(III) species to form a complex (C). This complex (C) reacts with alkali permanganate species in a slow step to form a free radical derived from L-proline, which further reacts with another permanganate species in a fast step to yield the products. The experimental results can be accommodated in Scheme 3 as given below.

\[
\text{MnO}_4^- + \text{OH}^- \rightleftharpoons K_1
\]

$\text{OH}^- \quad \text{Mn} \quad \text{O}$

\[
\begin{array}{c}
\text{O} \\
\hline
\text{O} \\
\hline
\text{O} \\
\hline
\text{O} \\
\hline
\text{O} \\
\hline
\text{O} \\
\hline
\text{O} \\
\hline
\end{array}
\]

$2^-
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 ruthenium (III) species and mixture of ruthenium (III) and L-proline. A bathochromic shift, $\lambda_{\text{max}}$, of ca 6 nm from 224 to 230 nm is observed, together with hyperchromicity at $\lambda_{\text{max}}$ 230 nm. However, the evidence for complex formation is obtained by kinetic studies (i.e., from the *Michaelis-Menten* plot). Furthermore, the plot of [Ru(III)]/$k_c$ versus 1/[L-proline] (Fig. VI(vii)(p.191)) ($r \geq 0.9989$, $S \leq 0.0410$) is linear with an intercept supporting the Ru(III) L-proline - complex. Such type of substrate–catalyst complex formation has been reported $^{33,34}$ previously. Since Scheme 3 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in sequences of one-electron steps, the reaction would involve a radical intermediate. A free radical scavenging experiment revealed such a possibility (vide infra). This type of radical intermediate has also been observed in earlier work $^{35}$ on alkaline-permanganate oxidations of organic substrates.

The permanganate oxidation of L-proline in aqueous alkaline medium proceeds at a measurable rate in the absence of Ru(III) catalyst. Hence, in the presence of catalyst the reaction is understood to occur in parallel paths with contributions from the uncatalysed and catalysed paths. Thus, the total rate constant ($k_t$) is equal to the sum of the rate constants of the catalysed ($k_c$) and uncatalysed ($k_u$) reactions. Scheme 3 leads to rate law (8) as follows.
From Scheme 3,

\[ \text{rate}_{\text{cat}} = \text{rate}_{\text{total}} - \text{rate}_{\text{uncat}} \]

\[ \text{Rate}_{\text{cat}} = k [C][\text{MnO}_4^- \cdot \text{OH}]^{2-} \]

\[ = k K_1 K_2 [\text{L-proline}]_t [\text{MnO}_4^-]_t [\text{OH}^-]_t [\text{Ru(III)}]_t \]  

(2)

The total concentration of L-proline, \([\text{L-proline}]_t\), is given by (Subscripts t and f stand for total and free)

\[ [\text{L-proline}]_t = [\text{L-proline}]_f + [C] \]

\[ = [\text{L-proline}]_f + K_2 [\text{L-proline}]_f [\text{Ru(III)}] = [\text{L-proline}]_t (1 + K_2 [\text{Ru(III)}]) \]  

Therefore,

\[ [\text{L-proline}]_f = \frac{[\text{L-proline}]_t}{1 + K_2 [\text{Ru(III)}]} \]  

(3)

\[ [\text{MnO}_4^-]_t = \frac{[\text{MnO}_4^-]_t}{1 + K_1 [\text{OH}^-]_t} \]

Similarly

\[ [\text{OH}^-]_t = \frac{[\text{OH}^-]_t}{1 + K_1 [\text{MnO}_4^-]_t} \]  

(4)

\[ [\text{Ru(III)}]_t = \frac{[\text{Ru(III)}]_t}{1 + K_2 [\text{L-proline}]_t} \]  

(5)

Substituting equations (3), (4), (5) and (6) in (1), we get

\[ \frac{d}{dt} [\text{MnO}_4^-] = - \frac{k K_1 K_2 [\text{L-proline}]_t [\text{MnO}_4^-]_t [\text{Ru(III)}]_t [\text{OH}^-]_t}{(1 + K_2 [\text{L-proline}]) (1 + K_2 [\text{Ru(III)}]) (1 + K_1 [\text{MnO}_4^-]) (1 + K_1 [\text{OH}^-])} \]  

(7)
The terms \((1+K_1[MnO_4^-])\) and \((1+K_2[Ru(III)])\) in the denominator of equation (7) approximate to unity in view of low concentration of MnO_4^- and ruthenium(III) used. Omitting the subscripts 'T' and 'f')& in terms of rate constants,

\[
\text{rate} \quad \frac{k_K}{[MnO_4^-]} = k_C = k_4 - k_0 = \frac{k K_1 K_2 [L\text{-proline}] [OH^-][Ru (III)]}{1+K_1[OH^-]+K_2 [L\text{-proline}]+K_1 K_2 [L\text{-proline}] [OH^-]}
\]

Thus the above equation (8) can be rearranged to the following form, which is used for the verification of the rate law.

\[
\frac{[Ru(III)]}{k_C} = \frac{1}{k K_1 K_2 [L\text{-proline}][OH^-]} + \frac{1}{k K_2 [L\text{-proline}]} + \frac{1}{k K_1 [OH^-]} + \frac{1}{k}
\]

According to equation (9), the plots of \([Ru(III)]/k_C\) versus \(1/[ L\text{-proline}]\) \((r \geq 0.9989, S \leq 0.041)\) and \([Ru(III)]/k_C\) versus \(1/[OH^-]\) \((r \geq 0.9959, S \leq 0.045)\) should be linear, which is verified in Fig. VI (vii) (p.191). From the slopes and intercepts of such plots, \(K_1\), the equilibrium constant for the formation of alkaline species of the oxidant, \(K_2\), the formation constant of the complex between the catalyst and substrate, and \(k\), the rate constant of the rate limiting step were found to be 2.27 ±0.16 dm^3.mol^{-1}, \((1.67 ±0.10) \times 10^2 \text{ dm}^3\text{mol}^{-1}\) and \((6.46 ± 0.24) \times 10^5 \text{ dm}^3\text{mol}^{-1} \text{s}^{-1}\), respectively. Using these values, the rate constants under different experimental conditions were calculated by equation (8) and compared with experimental data. There is a good agreement between them (Table VI(ii)(p.174) and Table VI(iii)(p.176)).
The thermodynamic quantities for the first equilibrium step in Scheme 3 and activation parameters for the limiting step in scheme 3 can be evaluated as follows: The hydroxyl ion concentration as in Table VI (iii) (p. 176) was varied at four different temperatures and the $K_i$ value was determined at each temperature. The values of $K_i$ are given in the Table VI (vi a) (p. 192). A vant Hoff's plot was made for the variation of $K_i$ with temperature (i.e., log $K_i$ versus $1/T$) ($r \geq 0.9847$, $S \leq 0.038$). The values of the enthalpy of reaction $\Delta H$, entropy of reaction $\Delta S$, and free energy of reaction $\Delta G$, were calculated and values are given in Table VI (vi b) (p. 192). A comparison of these values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step is fairly rapid and involves only little activation energy$^{36}$.

The effect of ionic strength on the rate can be understood essentially on the basis of ionic species as in Scheme 3. The effect of solvent on the reaction kinetics has been described in detail in the literature$^{37}$. Increasing the content of t-butanol in the reaction medium leads to an increase in the rate of reaction, which seems to be contrary to the expected interaction between neutral and anionic species in media of lower relative permittivity. However, an increase in the rate of reaction with decreasing dielectric constant may be due to stabilization of the divalent complex C at low relative permittivity, which is less solvated than $\text{MnO}_4^-$ at higher dielectric constant because of its larger size. In the present study the rate
Figure VI(vii)
Verification of rate law (8) in the form of (9)
(Conditions as in Table VI(ii)(p.174) and Table VI (iii)(p.176))
Table VI (vi)

(a) Effect of temperature on values of $K_4$ for the oxidation of L-proline by KMnO$_4$ in alkaline medium.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$K_4$ (dm$^3$/mol$^1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>2.3</td>
</tr>
<tr>
<td>303</td>
<td>4.0</td>
</tr>
<tr>
<td>308</td>
<td>6.1</td>
</tr>
<tr>
<td>313</td>
<td>8.4</td>
</tr>
</tbody>
</table>

(b) Thermodynamic quantities using $K_4$ values

<table>
<thead>
<tr>
<th>Thermodynamic quantities</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (kJ mol$^{-1}$)</td>
<td>66 ±3</td>
</tr>
<tr>
<td>$\Delta S$ (J K$^{-1}$ mol$^{-1}$)</td>
<td>56.5 ±2</td>
</tr>
<tr>
<td>$\Delta G$ (kJ mol$^{-1}$)</td>
<td>-49.2 ±1.5</td>
</tr>
</tbody>
</table>
determining step involves the reaction between two ions and so equation applicable is:

$$\ln k = \ln k_0 - Z_A Z_B e^2 / k_B T r_{AB} \epsilon_T$$

$k$ is the rate constant in a medium of infinite dielectric constant $r_{AB}$ is the sum of the ionic radii and $Z_A$ and $Z_B$ are the charges on the two ions and $\epsilon_T$ is the dielectric constant of the medium. The observed linear plot of $\log k_o$ versus $1/\epsilon_T$ with positive slope is in accordance with equation as $Z_A$ and $Z_B$ have opposite charges (Scheme 3). The values of $\Delta H^\#$ and $\Delta S^\#$ were both favourable for electron transfer process. The difference in the activation parameters for the catalysed and uncatalysed reaction explains the catalytic effect on the reaction. The catalyst, Ru(III) forms the complex with L-proline which shows more reducing property than L-proline itself. Hence the catalyst, Ru(III) lowers energy of activation. The negative value of $\Delta S^\#$ indicates that the complex(C) is more ordered than the reactants.

Findings of Chapter VI

In view of medicinal value of L-proline, the present study deals with the title reaction to investigate the oxidative behavior of permanganate using Ru(III) as catalyst Ru(III) increases the rate of reaction and lowers the activation energy. A mechanism involving the formation of a complex between catalyst and substrate has been proposed.
Importance of Chapter VI

It is interesting that the oxidant species $\text{[MnO}_4^-\text{]}$ requires a pH $> 12$, below which the system becomes disturbed and the reaction will proceed further to give a reduced product of the oxidant as Mn(IV), which slowly develops yellow turbidity. Hence, it becomes apparent that in carrying out this reaction the role of pH in a reaction medium is crucial. It is also noteworthy that under the conditions studied the reaction occurs in two successive one-electron reductions (Scheme 3) rather than two-electron in a single step (Scheme 2). Ru(III) is known to be an efficient catalyst especially in alkaline medium, a micro amount of Ru(III) is sufficient to catalyse the title reaction with measurable rate. The overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.
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