Kinetics and Mechanistic Study of the Ruthenium(III) Catalysed Oxidative Decarboxylation of L-Proline by Alkaline Heptavalent Manganese (Stopped flow technique)

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Abstract The kinetics of ruthenium(III) catalysed oxidation of L-Proline by permanganate in alkaline medium at a constant ionic strength has been studied spectrophotometrically using a rapid kinetic accessory. The reaction between permanganate and L-Proline in alkaline medium exhibits 2:1 stoichiometry (KMnO_4 : L-Proline). The reaction shows first order dependence on [permanganate] and [ruthenium(III)] and apparent less than unit order dependence each in L-Proline 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. A mechanism involving the formation of a complex between catalyst and substrate has been proposed. The activation parameters were computed with respect to the slow step of the mechanism and discussed.

Key words: Kinetics; Potassium permanganate Ruthenium; Oxidation; L-proline

Introduction

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 chemistry of manganese due to multistep redox reactions is an important source of information. 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. The oxidation by permanganate ion finds extensive applications in organic syntheses¹⁻³ especially since the advent of phase transfer catalysis³ which permits the use of solvents

such as methylene chloride and benzene. Kinetic studies are important sources of mechanistic information on the reactions, as demonstrated by the results referring to unsaturated acids both in aqueous¹ and non-aqueous media⁴. Furthermore, the mechanism by which the multivalent oxidant oxidises a substrate depends not only on the substrate but also on the medium⁵ used for the study. In strongly alkaline medium, the stable reduction product⁶ of permanganate ion is manganate ion, MnO_4^{2-} . 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 reduction followed by a rapid oxidation of the hypomanganate ion (Scheme 2).

Scheme - 1

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. Infact a precise understanding of the mechanism of such biological redox reactions⁷ is important as it helps in the synthesis of specific reaction products. Many attempts were made to mimic flavin-catalysed oxidations of α -amino acids⁸ 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 acids⁹. 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 rao¹⁰ 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 sulphate¹¹, cause decarboxylation during the oxidation of α -amino acids. Hexacyanoferrate(III)¹², a potential one-electron oxidant is reported to oxidize α -amino acids to corresponding α -keto acids. The study of amino acids become important because of their biological significance and selectivity towards the oxidants. Similarly L-Proline gave different products with different oxidants¹³.

Ruthenium(III) is known to be an efficient catalyst in several redox reactions particularly in alkaline medium¹⁴. The mechanism of catalysis can be quite complicated due to the formation of different intermediate complexes, free radicals and different oxidation states of ruthenium. The kinetics of fast reactions between ruthenate(VII), RuO_4^- , and manganate(VI), *i.e.* MnO_4^{2-} have been studied¹⁵ and the reaction is presumed to proceed via an outer-sphere mechanism. The rapid exchange between MnO_4^{2-} and MnO_4^- has been studied in detail by a variety of techniques¹⁶. The uncatalysed reaction between L-Proline and permanganate in alkaline medium has been studied previously¹⁷. A micro amount of ruthenium (III) is sufficient to catalyse the reaction in alkaline medium and a variety of mechanisms are possible. 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 ruthenium (III) as a catalyst. The present study deals with the title

reaction to investigate the redox chemistry of permanganate, ruthenium (III) and L-Proline in such media and to arrive at a plausible mechanism.

Experimental

Since the initial reaction was too fast to be monitored by the usual methods, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12).

Materials: Chemicals

Stock solution of L-Proline (Sisco-Chem.Ltd) was prepared by dissolving the appropriate amount of sample in doubly distilled water. The solution of potassium permanganate (BDH) was prepared and standardized against oxalic acid¹⁸. Potassium manganate solution was prepared as described by Carrington and Symons¹⁹. The solution was standardized by measuring the absorbance on a Hitachi 150-20 spectrophotometer with a 1 cm quartz cell at 608 nm ($\epsilon = 1530 \pm 20 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The ruthenium(III) solution was prepared by dissolving a known weight of RuCl_3 (s.d.fine-chem) in 0.20 mol dm^{-3} HCl. Mercury was added to the ruthenium(III) $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ solution to reduce any Ru(IV) formed during the preparation of ruthenium (III) stock solution and was kept for a day. The ruthenium (III) concentration was assayed²⁰ by EDTA titration.

All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled water. NaOH and NaClO_4 were used to provide the required alkalinity and to maintain the ionic strength respectively.

Kinetic procedure:

All kinetic measurements were performed under pseudo-first order conditions with [L-Proline] excess over $[\text{MnO}_4^-]$ at a constant ionic strength of 0.20 mol dm^{-3} . The reaction was initiated by mixing previously thermostatted solutions of MnO_4^- and L-Proline which also contained the necessary quantities of Ru(III), NaOH and NaClO_4 to maintain the required alkalinity and ionic strength respectively. The temperature was uniformly maintained at $25 \pm 0.1^\circ\text{C}$. The course of reaction was followed by monitoring the decrease in the absorbance of MnO_4^- in a 1cm quartz cell of a Hitachi model 150-20 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, giving $\epsilon = 2083 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (Literature $\epsilon = 2200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)¹⁰. The first order rate constants, k_{obs} were evaluated by plots of $\log (A_t - A_\infty)$ versus time (Fig.1), where A_t and A_∞ refers to absorbencies at time t and ∞ respectively. The first order plots in almost all cases were linear to 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^{2-} . 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.2 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.

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 Pentium - IV personal computer.

Results

Stoichiometry and product analysis

The reaction mixtures containing an excess permanganate concentration over L-Proline, constant [Ru (III)], 0.10 mol dm^{-3} NaOH and adjusted ionic strength of 0.20 mol dm^{-3} was allowed to react for 2 hours in an inert atmosphere at $25 \pm 0.1^\circ\text{C}$. After completion of the reaction, solid KI was added

followed by acidification by 10% H_2SO_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 .

The main reaction products were identified as the aminobuturaldehyde by spot test²¹ for amine and aldehyde groups. The product, aminobuturaldehyde was also confirmed by IR spectroscopy²² which showed bands at 3444 cm^{-1} for NH stretching, 1773 cm^{-1} for aldehydic $>\text{CO}$ stretching and 2956 cm^{-1} , for aldehydic $-\text{CH}$ stretching respectively. The only organic product obtained in the oxidation is aminobuturaldehyde, 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. The oxidant, potassium permanganate at a constant concentration of L-Proline, Ru(III) and alkali, while maintaining constant ionic strength of 0.20 mol dm^{-3} , concentration was varied in the range of 5.0×10^{-5} to $5.0 \times 10^{-4}\text{ mol dm}^{-3}$. The linearity of plots of $\log (A_t - A_\infty)$ versus time indicates the order in $[\text{MnO}_4^-]$ as unity (Table1). This was also confirmed by varying $[\text{MnO}_4^-]$ which did not show any change in pseudo-first order constants k_{obs} values as shown in Table 1. The substrate L-Proline was varied in the range of 5.0×10^{-4} to $5.0 \times 10^{-3}\text{ mol dm}^{-3}$ at 25°C ; the order with respect to $[\text{L-Proline}]$ was found to be less than unity. The catalyst Ru(III) was varied in the range of 5.0×10^{-7} to $1.0 \times 10^{-6}\text{ mol dm}^{-3}$ at 25°C ; the order with respect to $[\text{Ru(III)}]$ was found to be unity. The effect of alkali on the reaction was studied at constant concentrations of L-Proline, Ru(III) and potassium permanganate and at a constant ionic strength of 0.20 mol dm^{-3} at 25°C . The rate constant increased with the increase in [alkali], indicating an apparent less than unit order dependence on [alkali] as given in Table1.

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 relative permittivity and ionic strength

The effect of dielectric constant (ϵ_T) effect was studied by varying the t-butanol water content in the reaction mixture with all other conditions being maintain constant. Attempts to measure the dielectric constants were not successful. However, they were computed from the values of pure liquids²³. 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. The plot of $\log k_{\text{obs}}$ versus $1/\epsilon_T$ was linear with positive slope ($r > 0.9983$, $s \leq 0.0341$). The effect of ionic strength was studied by varying the sodium perchlorate concentration from 0.2 to 2.0 mol dm^{-3} at constant concentrations of permanganate, L-Proline, ruthenium (III) and alkali. The rate constant increased with increasing concentration of NaClO_4 ; the plot of $\log k_C$ vs $I^{1/2}$ was linear ($r > 0.9978$, $S \leq 0.018$) with a positive.

Test for free radicals:

The reaction mixture was mixed with acrylonitrile monomer and kept for 2 hours in an inert atmosphere. On diluting with methanol a white precipitate was formed, indicating the intervention of free radicals in the reaction. The blank experiments of either MnO_4^- 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 work²⁴.

Effect of temperature:

The rate of the reaction was measured at four different temperatures with varying $[\text{OH}^-]$, 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 intercept of the plots of $[\text{Ru(III)}]/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ for different temperatures. The values of $k \times 10^{-4} (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ at temperatures, 298K, 303K, 308K, and 313K are 6.5, 7.2, 8.0 and 9.6 respectively. The energy of activation corresponding to these constants were evaluated from the plot of $\log k$ versus $1/T$ ($r \geq 0.945$ & $s \leq 0.0062$) and other activation parameters are calculated. The values of E_a , $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ are 19.8 ± 1.0 , 17.5 ± 1.5 (kJ mol^{-1}), -18.3 ± 1.5 ($\text{J K}^{-1} \text{mol}^{-1}$) and 23 ± 2 respectively.

Discussion

Permanganate ion, 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 $\text{pH} > 12$, the reduction product of Mn(VII) is stable and further reduction of Mn(VI) might be stopped⁶. The Diode Array Rapid Scan Spectrophotometric (DARSS) studies have shown that at $\text{pH} > 12$, the product of Mn(VII) is Mn(VI) and no further reduction was observed as reported⁶ 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.

It is interesting to identify the probable species of ruthenium (III) chloride in alkaline medium. Electronic spectral studies¹⁴ have confirmed that ruthenium(III) chloride exists in hydrated form as $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$. In the present study it is quite probable that the species $[\text{Ru}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ 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 $[\text{OH}^-] \gg [\text{Ru}^{\text{III}}]$, Ru^{III} is mostly present as the hydroxylated species $[\text{Ru}(\text{H}_2\text{O})_5\text{OH}]^{2+}$.

The reaction between permanganate and L-Proline in alkaline medium 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 such as aldehyde and ammonia was observed.

The results suggest that first alkali combines with permanganate to form an alkali-permanganate species $[\text{MnO}_4 \cdot \text{OH}]^{2-}$ in a pre-equilibrium step which explains the less than unit order in alkali. Such type of alkali permanganate species is observed in earlier work²⁵. L-Proline in the deprotonated form 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.

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, λ_{max} , of ca 6nm from 224 to 230 nm is observed, together with hyperchromicity at λ_{max} 230 nm. However, the evidence for complex formation is obtained by kinetic studies (*i.e.*, from the *Michaelis-Menten* plot). The plot of $[\text{Ru(III)}]/k_{\text{obs}}$ versus $1/[\text{L-Proline}]$ is linear with an intercept supporting the Ru(III)- L-Proline complex. Such type of substrate-catalyst complex formation has been reported previously²⁶. 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 work²⁷. 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 earlier²⁷.

Scheme 3

The probable structure of complex (C) is given as

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 1 was varied at four different temperatures and the K_1 value was determined at each temperature. The values of K_1 ($\text{dm}^3 \text{mol}^{-1}$) were obtained as 2.3, 4.01, 6.1, and 8.4 at 25, 30, 35 and 40° C respectively. A Vant Hoff's plot was made for the variation of K_1 with temperature (i.e., $\log K_1$ versus $1/T$) ($r > 0.9847$, $s \leq 0.038$). Similarly the L-Proline concentration as in **Table 1** was varied at four different temperature and the K_2 value was determined at each temperature. 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.

Scheme 3 leads to the following rate law (2)

$$\frac{\text{Rate}}{[\text{MnO}_4^-]} = k_{\text{obs}} = \frac{kK_1K_2[\text{L-Proline}][\text{Ru(III)}][\text{OH}^-]}{1 + K_1[\text{OH}^-] + K_2[\text{L-Proline}] + K_1K_2[\text{OH}^-][\text{L-Proline}]} \quad (2)$$

$$\begin{aligned} \frac{\text{rate}}{[\text{MnO}_4^-]} - k_C = k_T - k_U &= \frac{k K_1 K_2 [\text{L-proline}] [\text{OH}^-] [\text{Ru (III)}]}{1 + K_1 [\text{OH}^-] + K_2 [\text{L-proline}] + K_1 K_2 [\text{L-proline}] [\text{OH}^-]} \\ \frac{[\text{Ru(III)}]}{k_{\text{ob}}} &= \frac{1}{k K_1 K_2 [\text{L-Pro}][\text{OH}^-]} + \frac{1}{k K_2 [\text{L-Pr}]} + \frac{1}{k K_1 [\text{OH}^-]} + \frac{1}{k} \end{aligned} \quad (3)$$

The terms $(1 + K_1K_2[\text{OH}^-][\text{Ru(III)}][\text{MnO}_4^-])$, $(1 + K_1[\text{MnO}_4^-])$ and $(1 + K_2[\text{Ru(III)}])$ also should be in the denominator of equation (2). But in view of low concentrations of MnO_4^- and ruthenium(III) used, they approximate to unity. Thus the above equation (2) can be rearranged to the following form which is suitable for the verification of the rate law.

According to equation (3), the plots of $[\text{Ru(III)}]/k_{\text{obs}}$ versus $1/[\text{L-asp}]$ ($r > 0.9988$, $s \leq 0.045$) and $[\text{Ru(III)}]/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ ($r > 0.9913$, $s \leq 0.046$) should be linear, which is verified in Fig. 3. The slopes and intercepts of the plots lead to the values of K_1 , K_2 and k which were found to be $2.276 \pm 0.16 \text{ dm}^3 \cdot \text{mol}^{-1}$, $1.67 \pm 0.10 \times 10^2 \text{ dm}^3 \cdot \text{mol}^{-1}$ and $6.46 \pm 0.24 \times 10^5 \text{ dm}^3 \cdot \text{mol}^{-1} \text{ s}^{-1}$, respectively. Using these values, the rate constants under different experimental conditions were calculated by equation (2) and compared with experimental data. There is a good agreement between them which supports the **Scheme 3**. The value of K_1 is in good agreement with earlier work²⁸.

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 detail in the literature. In the present study the rate determining step involves the reaction between two ions and so equation (4) is applicable:

$$\ln k = \ln k_{\infty} - Z_A Z_B e^2 / k_B T r_{AB} \epsilon_T \quad (4)$$

where 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 ϵ_T is the dielectric constant of the medium. The observed linear plot of $\log k_{\text{obs}}$ versus $1/\epsilon_T$ with positive slope is in accordance with equation (4) as Z_A and Z_B have opposite charges (**Scheme 3**). The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were both favourable for electron transfer process. The more negative value of $\Delta S^\ddagger$, suggests the complex is more ordered than the reactants.

We have calculated the isokinetic temperature as 220.6 K for L-Proline and other amino acids studied earlier, ($r \geq 0.957$ & $s \leq 0.0038$). The value of β (220.6K) is lower than experimental temperature (303K). This indicates that the rate is being governed by the entropy of activation.

Catalytic Effect:

The activation parameters are compared with the uncatalysed reaction¹⁷. The difference in the activation parameters for the catalysed and uncatalysed reactions, explains the catalytic effect on reaction. The catalyst, ruthenium(III) forms a complex with L-Proline which shows more reducing property than L-Proline itself and hence the catalyst, Ru(III) lowers the energy of activation.

Conclusion:

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**). The description of the mechanism is consistent with all the experimental evidence including both kinetic and product studies.

Appendix

According to **Scheme 3**,

$$\text{Rate} = - \frac{d [\text{MnO}_4^-]}{dt} = k [\text{C}][\text{MnO}_4.\text{OH}]^2 \quad (\text{I})$$

$$\text{Rate} = k K_1 K_2 [\text{L-proline}]_f [\text{MnO}_4^-]_f [\text{OH}^-]_f [\text{Ru(III)}]_f \quad (\text{II})$$

Total concentration of reductant, $[\text{L-Proline}]_T$ is given by, (where the subscripts T and f stand for total and free respectively)

$$\begin{aligned} [\text{L-Proline}]_T &= [\text{L-Proline}]_f + [\text{C}] \\ &= [\text{L-Proline}]_f + K_2 [\text{L-Proline}]_f [\text{Ru(III)}] \\ [\text{L-Proline}]_T &= [\text{L-Proline}]_f \{ 1 + K_2 [\text{Ru(III)}] \} \end{aligned}$$

$$\text{Therefore, } [\text{L-Proline}]_f = \frac{[\text{L-Proli}]_T}{1 + K_2 [\text{Ru(III)}]} \quad (\text{III})$$

$$\text{Similarly, } [\text{MnO}_4^-]_f = \frac{[\text{MnO}_4^-]_T}{1 + K_1 [\text{OH}^-]_f} \quad (\text{IV})$$

$$[\text{OH}^-]_f = \frac{[\text{OH}^-]_T}{1 + K_1 [\text{MnO}_4^-]_f} \quad (\text{V})$$

And

$$[\text{Ru(III)}]_f = \frac{[\text{Ru(III)}]_T}{1 + K_2 [\text{L-Proline}]_f} \quad (\text{VI})$$

Substituting equation (III), (IV), (V) and (VI) in (I), we get

$$\begin{aligned} \text{Rate} = - \frac{d [\text{MnO}_4^-]}{dt} &= \frac{k K_1 K_2 [\text{L-Proline}]_T [\text{MnO}_4^-]_T [\text{Ru(III)}]_T [\text{OH}^-]_T}{(1 + K_2 [\text{L-Proline}]) (1 + K_2 [\text{Ru(III)}]) (1 + K_1 [\text{MnO}_4^-]) (1 + K_1 [\text{OH}^-])} \quad (\text{VII}) \end{aligned}$$

Figure 1. First order plots of aqueous alkaline permanganate oxidation of L-Proline at 25°C. $[\text{MnO}_4^-] \times 10^4 \text{ (mol dm}^{-3}\text{)}$;

Figure 2. UV-VIS spectral changes during the oxidation of L-Proline by aqueous alkaline permanganate at 25°C, catalysed by ruthenium (III).

Scanning time interval = 1 min.

$[\text{MnO}_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$;

$[\text{OH}^-] = 0.1 \text{ mol dm}^{-3}$;

$I = 0.20 \text{ mol dm}^{-3}$.

$[\text{L-Asp}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$;

$[\text{Ru(III)}] = 2.0 \times 10^{-6} \text{ mol dm}^{-3}$;

Figure 3. Plot of $[\text{Ru(III)}]/k_{\text{obs}}$ vs $1/[\text{L-Proline}]$ and $[\text{Ru(III)}]/k_{\text{obs}}$ vs $1/[\text{OH}^-]$ (conditions as in Table 1). **Table 1.** Effect of variation of $[\text{MnO}_4^-]$, $[\text{L-proline}]$, $[\text{Ru(III)}]$ and $[\text{OH}^-]$ on oxidation of L-proline by alkaline permanganate at 25 °C, $I=0.20 \text{ mol dm}^{-3}$

$10^4 [\text{MnO}_4^-]$ (mol dm^{-3})	$10^3 [\text{L-pro}]$ (mol dm^{-3})	10^6Ru(III) (mol dm^{-3})	$[\text{OH}^-]$ (mol dm^{-3})	$10^3 k_T$ (s^{-1})	$10^2 k_U$ (s^{-1})	$10^3 k_C$ (s^{-1})	
						Expt.	Cal
0.5	2.0	1.0	0.10	3.85	0.80	3.05	3.02
1.0	2.0	1.0	0.10	3.94	0.80	3.14	3.02
2.0	2.0	1.0	0.10	3.91	0.80	3.11	3.02
4.0	2.0	1.0	0.10	3.90	0.80	3.10	3.02
5.0	2.0	1.0	0.10	3.95	0.80	3.15	3.02
1.0	0.5	1.0	0.10	1.20	0.25	0.95	0.92
1.0	1.0	1.0	0.10	2.10	0.52	1.58	1.70
1.0	2.0	1.0	0.10	3.91	0.80	3.11	3.02
1.0	3.0	1.0	0.10	6.00	1.00	5.00	4.83
1.0	5.0	1.0	0.10	7.50	1.50	6.00	5.50
1.0	2.0	0.5	0.10	2.2	0.80	1.40	1.50
1.0	2.0	1.0	0.10	3.91	0.80	3.11	3.02
1.0	2.0	2.0	0.10	6.70	0.80	5.90	6.03
1.0	2.0	3.0	0.10	9.80	0.80	9.00	9.05
1.0	2.0	5.0	0.10	14.8	0.80	14.0	15.1
1.0	2.0	1.0	0.02	0.85	0.15	0.70	0.71
1.0	2.0	1.0	0.05	2.00	0.55	1.45	1.66
1.0	2.0	1.0	0.10	3.91	0.80	3.11	3.02
1.0	2.0	1.0	0.15	5.00	0.97	4.63	4.75
1.0	2.0		0.20	7.00	1.02	5.20	5.10

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