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   22\textsuperscript{nd} Conference of Indian Council of Chemists held at Indian Institute of Technology, Roorke, Uttaranchal State (17-10-2003 to 19-10-2003)
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2. Free radical intervention in the oxidation of sulphanilic acid by alkaline diperiodatocuprate(III) complex. A kinetic and mechanistic approach
   24\textsuperscript{th} Conference of Indian Council of Chemists held at Birla Institute of Technology, Mesra Ranchi, Jarkhand State (16-12-2005 to 18-12-2005)
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A study of the ruthenium(III) catalysed oxidation of L-phenylalanine by heptavalent manganese—A kinetic and mechanistic approach

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The kinetics of the ruthenium(III) catalysed oxidation of L-phenylalanine by alkaline permanganate has been studied spectrophotometrically using a rapid kinetic accessory. The reaction is first order each in [oxidant] and [catalyst] with an apparent less than unit order each in [substrate] and [alkali] respectively. The results suggest the formation of a complex between the phenylalanine and the hydroxyiated species of ruthenium(III). The complex reacts further with the alkaline permanganate species in a rate-determining step, resulting in the formation of a free radical, which again reacts with the alkaline permanganate species in a subsequent fast step to yield the products. The reaction constants involved in the mechanism and the activation parameters have been calculated. There is a good agreement between observed and calculated rate constants under different experimental conditions.

Potassium permanganate is widely used as an oxidising agent in synthetic as well as in analytical chemistry, and also as a disinfectant. Oxidation by permanganate ion is applied extensively in organic syntheses. During the oxidation, it is evident that permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Furthermore, the mechanism by which the multivalent oxidant oxidises a substrate depends not only on the substrate but also on the medium used for the study. No mechanistic information is available to distinguish between a direct one-electron reduction to Mn(VI) and a mechanism, in which a hypomanganate is formed in a two-electron reduction followed by rapid oxidation of the hypomanganate ion.

Phenylalanine, an amino acid, is part of almost all proteins, especially, those of animal origin. Phenylalanine supplementation helps in the suppression of pain and aid weight loss through the suppression of appetite. It is converted into tyrosine which is a precursor to dopamine and dopamine levels have a definite function in sexual desire. The oxidation of amino acids is of interest as the products differ depending on the oxidants.

Ruthenium(III) is known to be an efficient catalyst in several redox reactions, particularly in alkaline medium. The catalysis mechanism 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 studied; 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 variety of techniques. The uncatalysed reaction between phenylalanine and permanganate in alkaline medium has been studied previously. Herein we describe the results of the title reaction in order to determine the active species of oxidant, reductant and catalyst in such media and to arrive at a plausible mechanism.

Materials and Methods

Since the reaction was too fast to monitor by the usual method, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12). Stock solutions of L-phenyl alanine (S.D. Fine Chemicals), potassium permanganate (BDH), ruthenium(III) chloride (S.D. Fine Chemicals) and other reagents of analytical grade were prepared and standardized.

Kinetic studies

All kinetic measurements were performed under pseudo-first order conditions with [phenylalanine]:[MnO$_4^{2-}$] ≥ 10:1 at constant ionic strength (0.50 mol dm$^{-3}$). The reaction was initiated by mixing thermally equilibrated (at 25 ± 0.1°C) solutions of MnO$_4^-$, ruthenium(III) and amino acid, which also contained the necessary quantities of sodium hydroxide and sodium perchlorate. The reaction was followed by monitoring the decrease in absorbance of MnO$_4^-$ in the 1cm quartz cell of a Hitachi model 150-20 Spectrophotometer at 526 nm.
as a function of time. The first order constants, \( k_{\text{obs}} \), were evaluated from the plots of log (\( A_t - A_\infty \)) versus time by fitting the data to the expression \( A_t = A_\infty + (A_0 - A_\infty)e^{-kt} \), where \( A_t \), \( A_0 \), and \( A_\infty \) are absorbances of permanganate at time \( t \), 0 and \( \infty \) respectively. The first order plots in almost all cases were linear to 80% completion of the reaction and \( k_{\text{obs}} \) values were reproducible within ± 5%.

Results

The reaction mixtures containing an excess of permanganate over phenyl alanine, and 0.05 mol dm\(^{-3}\) sodium hydroxide at a constant ionic strength of 0.50 mol dm\(^{-3}\) was allowed to react for ca. 2 hr. at 25 ± 0.1°C under inert atmosphere. After completion of the reaction, the remaining Mn\(^{4+}\) was analysed spectrophotometrically. Some results showed that two moles of Mn\(^{4+}\) were consumed by one mole of phenylalanine. Other results indicated that four moles of Mn\(^{4+}\) were consumed by one mole of phenylalanine. The reaction products for the first series were identified as phenyl acetaldehyde, by boiling point, spot test and ammonia by Nessler’s reagent and manganate by its visible spectrum. The product aldehyde was quantitatively estimated to about 78%, which is evidenced by its 2,4-DNP derivative. The nature of the aldehyde was confirmed by its IR spectrum carbonyl stretching at 1729 cm\(^{-1}\) and a band at 2928 cm\(^{-1}\) due to the aldehydic stretching. The reaction product for the second series were identified as phenyl acetic acid by its melting point and spot test, ammonia by Nessler’s reagent and manganate by its visible spectrum. The nature of the carboxylic acid was confirmed by its IR spectrum which showed a carbonyl (C=O) stretch at 1657 cm\(^{-1}\) and OH\(^{-}\) stretch at 2854 cm\(^{-1}\). The same type of aldehyde as above was obtained when the product analysis was carried under pseudo-first order conditions. It was also observed that the aldehyde does not undergo further oxidation under the present kinetic conditions. A test for corresponding acid was negative, so, it is concluded that the stoichiometry of the reaction under kinetic study is,

\[
\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CO}_2\text{H} + 2\text{MnO}_4^- + 2\text{OH}^- \rightarrow \text{NH}_2
\]

\[
\text{C}_6\text{H}_5\text{CH}_2\text{CHO} + 2\text{MnO}_4^{2-} + \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}
\]

... (1)

The permanganate in alkaline medium exhibits various oxidation states, such as Mn(VII), Mn(V) and Mn(VI). The solution changed from violet to blue and then to green, excluding the accumulation of hypomanganate. [Mn(VII)] decreases at 526 nm whereas [Mn(VI)] increases at 608 nm during the reaction.

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

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, while keeping others constant. The oxidant concentration was varied as shown in Table 1. The plots of log (\( A_t - A_\infty \)) versus time, for different initial concentrations of Mn\(^{4+}\) are linear (\( r = 0.9964, \sigma = 0.021 \)), and the fairly constant \( k_{\text{obs}} \) values indicate that the order in \([\text{MnO}_4^-]\) is unity (Table 1). L-phenylalanine concentration was varied in the 1.0x10\(^{-3}\) to 1.0x10\(^{-2}\) mol dm\(^{-3}\) range at 25°C, keeping all other concentrations fixed. The rate constant, \( k_{\text{obs}} \), increased with increase in concentration of phenylalanine, indicating a less than unit order dependence in [substrate].

The rate constants increased with increase in [alkali], and the order in [ruthenium(III)] was found to be unity. Under the conditions used, the uncatalysed reaction rate is negligible compared to the catalysed reaction rate.

Added products such as manganate, ammonia and aldehyde did not show any significant effect on the rate of the reaction.

The effect of ionic strength was studied by varying [sodium perchlorate] from 0.05 to 0.50-mol dm\(^{-3}\) at fixed [permanganate], [amino acid], [alkali] and [catalyst]. The rate constants increased with increase in [sodium perchlorate] and the plot of log \( k_{\text{obs}} \) versus \( I^{1/2} \) was linear with a positive slope, (\( r = 0.9989, \sigma = 0.031 \)).

The effect of dielectric constant \( (D) \) on the reaction rate has been studied by varying the \( r \)-butanol-water content in the reaction mixture. The rate constant, increased with decrease in dielectric constant of the medium. The plot of log \( k_{\text{obs}} \) versus \( 1/D \) was linear with a positive slope (\( r = 0.9989, \sigma = 0.034 \)).

The reaction mixture was mixed with acrylonitrile monomer and kept for 2 hr in an inert atmosphere. On diluting with methanol, a white precipitate was
formed indicating the intervention of free radicals in the reaction.

The rate constants, $k$ of the slow step of Scheme 1 were obtained from the intercept of the plots of $\frac{[\text{Ru(III)}]}{[\text{Phe.ala.}]}$ versus $1/[\text{Phe.ala.}]$ for different temperatures. The energy of activation corresponding to these constants was evaluated from the plot of $\log k$ versus $1/T$, from which the activation parameters were calculated as $E_a = 20.7 \pm 2.0$ kJ mol$^{-1}$, $\log A = 9.33 \pm 1.3$, $\Delta H^\circ = 18.2 \pm 2.0$ kJ mol$^{-1}$, $\Delta S^\circ = 75.2 \pm 10$ J K$^{-1}$ mol$^{-1}$ and $\Delta G^\circ = 41.2 \pm 3.0$ kJ mol$^{-1}$. The thermodynamic quantities of the first step of Scheme 1 were evaluated by varying $[\text{OH}^-]$ at 298, 303, 308 and 313K and the values of $K_1$ are 6.74, 8.41, 10.6 and 14.1 dm$^3$ mol$^{-1}$ respectively. The thermodynamic quantities of the second step of Scheme 1 were evaluated by varying $[\text{phenylalanine}]$ at several temperatures, and determining the values of $K_2$ (dm$^3$ mol$^{-1}$) at 298, 303, 308 and 313K as, 184, 197, 209 and 221 respectively. The van’t Hoff’s plots were drawn for the variation of $K_1$ and $K_2$ with temperature ($\log K_i$ versus $1/T$, $r = 0.9972$, $\sigma = 0.0231$ and $(\log K_2$ versus $1/T$, $r = 0.9983$, $\sigma = 0.0245$). The values of thermodynamic quantities for the first step are, $\Delta H = 37.6 \pm 3.0$ kJ mol$^{-1}$, $\Delta S = 142.2 \pm 10$ J K$^{-1}$ mol$^{-1}$ and $\Delta G = 5.75 \pm 1.0$ kJ mol$^{-1}$. The values of thermodynamic quantities for the second step are, $\Delta H = 9.45 \pm 1.0$ kJ mol$^{-1}$, $\Delta S = 75 \pm 5$ J K$^{-1}$ mol$^{-1}$ and $\Delta G = 13.5 \pm 2.0$ kJ mol$^{-1}$. A comparison of these values with those values obtained for the slow step shows that the reactions before the rate determining step is fairly fast.

Discussion

Permanganate ion, 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 manganese(VII) is stable and further reduction of manganese(VI) might be stopped. Diode Array Rapid Scan Spectrophotometric (DARSS) studies have shown that at pH $>$ 12, the product of manganese(VII) is manganese(VI) and no further reduction was observed as reported$^{2,3}$ by Simandi et al. However, on prolonged standing, green manganese (VI) is reduced to manganese(IV) under our experimental conditions. It is known that in aqueous solution, amino acid exists in zwitterionic$^8$ form, whereas in aqueous alkaline medium it exists an anionic form according to the following equilibria.

\[
\text{RCH(NH}_2\text{)COOH} \leftrightarrow \text{RCH(NH}_3\text{)COO}^- \quad (\text{Zwitterion})
\]

\[
\text{RCH(NH}_2\text{)COOH} + \text{OH}^- \leftrightarrow \text{RCH(NH}_3\text{)COO}^- + \text{H}_2\text{O}
\]
The reaction between permanganate and phenylalanine under study in alkaline medium has a 2:1 stoichiometry with a first order dependence on both \([\text{MnO}_4^-]\) and ruthenium(III) and less than unit order dependence on both the [alkali] and [phenylalanine]. Under the conditions \([\text{OH}^-] \gg [\text{Ru}^{	ext{III}}]\), ruthenium(III) is mostly present as the hydroxylated species, \([\text{Ru(H}_2\text{O})_5\text{OH}]^{2+}\). Increase in rate with increase in \([\text{OH}^-]\) indicates the presence of the hydroxylated species of ruthenium(III) as a reactive species, which is shown by the following equilibrium in accordance with the earlier work.

\[
\text{Ru(H}_2\text{O})_6^{3+} + \text{OH}^- \rightleftharpoons [\text{Ru(H}_2\text{O})_5\text{OH}]^{2+} + \text{H}_2\text{O}
\]

The results suggest the formation of a complex between the amino acid and the hydroxylated ruthenium(III) species. Such complex formation between substrate and catalyst has also been observed in earlier work. Evidence is provided by the fractional order found in [amino acid]. The spectral evidence for complex formation between catalyst and substrate was obtained from the UV-vis spectra of the catalyst and a mixture of catalyst and amino acid in the alkaline medium. A bathochromic shift of 7 nm from 233 to 240 nm is observed for phenylalanine. The formation of the complex was also proved kinetically by the non-zero intercept of the plot of \([\text{Ru}^{	ext{III}}]/k_{obs} \text{ versus } 1/\text{phenylalanine}\) (Fig.1). The existence of two isosbestic points in the UV-vis spectrum of permanganate in alkaline medium indicates the presence of two equilibrium steps before the slow step of the mechanism. The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as a higher rate constant for the slow step, indicate that the oxidation presumably occurs via inner-sphere mechanism. This conclusion is supported by earlier observation. Since Scheme 1 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in sequence of activation.
one electron steps, the reaction between the substrate and oxidant would afford 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 on the alkaline permanganate oxidation of amino acids. In agreement with the experimental results obtained, a mechanism, as in Scheme 1, may be envisaged.

The probable structure of complex (C) is

\[
\text{H}_2\text{O} \quad \text{OH} \\
\text{H}_2\text{O} \quad \text{Ru} \quad \text{OC}(-\text{CH(NH}_2\text{)CH}_2\text{C}_6\text{H}_3) \\
\text{H}_2\text{O} \quad \text{OH}_2
\]

Scheme 1 leads to rate law, (2),

\[
\text{Rate} = k_{\text{obs}} = \frac{kK_2\text{[Phe.ala.]}\text{[Ru(III)]}\text{[OH}^-\text{]}}{1 + K_1\text{[OH}^-\text{]} + K_2\text{[Phe.ala.]} + K_4\text{[OH}^-\text{][Phe.ala.]}} \quad \ldots \ (2)
\]

Equation (2) can be rearranged to Eq. (3)

\[
\frac{[\text{Ru(III)}]}{k_{\text{obs}}} = \frac{kK_2\text{[Phe.ala.]}\text{[OH}^-\text{]}}{kk'K_2\text{[Phe.ala.]}\text{[OH}^-\text{]}} + \frac{1}{kk'K_2\text{[Phe.ala.]}\text{[OH}^-\text{]}} + \frac{1}{kk'K_2\text{[Phe.ala.]}\text{[OH}^-\text{]}} + \frac{1}{k} \quad \ldots \ (3)
\]

According to Eq. (3) the plots of \([\text{Ru(III)}]/k_{\text{obs}}\) versus \([\text{Phe.ala.}]\) \((r = 0.9988, \sigma = 0.045)\) and \([\text{Ru(III)}]/k_{\text{obs}}\) versus \([\text{OH}^-]\) \((r = 0.9928, \sigma = 0.052)\) should be linear, which is verified in Fig.1. 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 \(6.75 \pm 0.2 \text{ dm}^3\text{mol}^{-1}\), \(1.84 \pm 0.1 \times 10^2 \text{ dm}^3\text{mol}^{-1}\) and \(4.92 \pm 0.05 \times 10^5 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}\) respectively at 298 K.

Using these values, the rate constants under different experimental conditions were calculated by Eq. (2) and compared with experimental data. There is a good agreement between them, which supports Scheme 1. The \(K_4\) value is in the neighborhood of the earlier work.14

The effect of ionic strength on the rate can be understood essentially on the basis of ionic species as in Scheme 1. For the limiting case of a zero angle approach between two dipoles or an ion-dipole system, Amis15 has shown that a plot of log \(k_{\text{obs}}\) versus \(1/D\) is linear with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and with a positive slope for a positive ion and dipole interaction. In the present study, an increase in the rate with a decrease in the dielectric constant of the medium was observed, which cannot be explained by the Amis theory15, as the presence of a positive ion is unlikely in the alkaline medium employed. Applying Born equation, Laidler and Eyring derived the equation

\[
\ln k = \ln k_0 + \frac{N\varepsilon^2}{2 DR T} (1/r - 1/r^*)
\]

where \(k_0\) is the rate constant in a medium of infinite dielectric constant and \(r\) and \(r^*\) refer to radius of the reacting species and the activated complex, respectively. It can be seen from the equation that the rate should be greater in a medium of lower dielectric constant when \(r^* > r\). Intramolecular hydrogen bonding, that could stabilise the transition by increasing the size of activated complex by solvation is possible. It is likely that \(r^* > r\) for phenylalanine, thus explaining the experimental observation. Hence one can expect intra molecular hydrogen bonding in phenylalanine, since it contains NH\(_2\) and CO\(_2\)H groups on the same carbon atom. Such hydrogen bonding is common for molecules having CO\(_2\)H and
NH₂, and CO₂H and OH⁻ groups either on the adjacent carbon atom or on the same carbon atom of the molecule, as found in simple amino acid¹⁶. The moderate values of ΔH* and ΔS* favour electron transfer processes. The ΔH* value was due to release of energy of solution changes in the transition state. The negative ΔS* value within the range found for free radical reactions have been ascribed to the nature of electron pairing and electron unpairing processes, and to the loss of a degree of freedom, formerly available to reactions on the formation of a rigid transition state. The difference in the activation parameters for the catalysed and uncatalysed reaction explains the catalytic effect on the reaction. The catalyst, ruthenium(III), alters the path of the reaction by lowering the energy barrier, that is, it provides an alternate pathway with lower activation parameters for the reaction involving the formation of an intermediate complex as proposed in Scheme 1.

We have calculated the isokinetic temperature as 144K for phenylalanine and other amino acids studied earlier, (r = 0.9987, σ = 0.023). The value of β(144K) is much lower than the experimental temperature (303K). This indicates that the rate is being governed by the entropy of activation.

References
12 Ref 8, p.536; Sathyarayana D N, Electronic absorption spectroscopy and related techniques (Universities Press India Limited, Hyderabad), 2001, p.12.
Ruthenium(III) Catalysed Oxidation of L-Alanine by Alkaline Permanganate: A Kinetic and Mechanistic Approach

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The kinetics of the ruthenium(III) catalysed oxidation of L-alanine by alkaline permanganate was studied spectrophotometrically using a rapid kinetic accessory. The reaction is first order with respect to [oxidant] and [catalyst] with an apparent less than unit order in [substrate] and [alkali] respectively. The results suggest the formation of a complex between the alanine and the hydroxylated species of ruthenium(III). The complex reacts further with the alkaline permanganate species in a rate-determining step, resulting in the formation of a free radical, which again reacts with the alkaline permanganate species in a subsequent fast step to yield the products. The reaction constants involved in the mechanism were calculated. There is a good agreement between observed and calculated rate constants under different experimental conditions. The activation parameters with respect to slow step of the mechanism were calculated and discussed.

Keywords: Oxidation; Kinetics; L-Alanine; Permanganate

INTRODUCTION

Potassium permanganate is widely used as an oxidising agent in synthetic as well as in analytical chemistry, and also as a disinfectant. The permanganate reactions are governed by the pH of the medium. Among the six oxidation states of manganese (+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 provides an important source of information as the manganese intermediates are relatively easy to identify when they have sufficiently long life times. Oxidation states of the intermediates permit useful conclusions to be drawn as to the possible reaction mechanism, including the nature of intermediates. Oxidation by permanganate ion is applied extensively in organic syntheses [1-7] especially since the advent of phase transfer catalysis [3,4,6]. Kinetic studies are important...
sources of mechanistic information on the reactions, as demonstrated by the results referring to unsaturated acids both in aqueous [1,3,7] and non-aqueous media [8]. During the oxidation, it is evident that permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Furthermore, the mechanism by which the multivalent oxidant oxidizes a substrate depends not only on the substrate but also on the medium [1,9] used for the study. In strongly alkaline medium, the stable reduction product [10-13] of the permanganate ion is manganate ion, MnO₄⁻.

No mechanistic information is available to distinguish between a direct one-electron reduction to Mn(VI) and a mechanism, in which a hypomanganate is formed in a two-electron reduction followed by rapid oxidation of the hypomanganate ion [14-17].

Amino acids act not only as the building blocks in protein synthesis but also they play a significant role in metabolism. In metabolism, amino acids are subjected to many reactions and can supply precursors for many endogenous substances, e.g. hemoglobin in blood. Amino acids can undergo many types of reaction, depending on whether a particular amino acid contains non-polar groups or polar substituents. Alanine is present in prostate fluid and it may play a role in supporting prostate health. It is a source of energy for muscle tissue, the brain and the central nervous system. It strengthens the immunosystem by producing antibodies, helps in the metabolism of sugar and organic acids. The oxidation of amino acids is of interest as the products differ depending on the oxidants [18-21].

Ruthenium(III) is known to be an efficient catalyst in several redox reactions, particularly in alkaline medium. The catalysis mechanism 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), RuO₄²⁻, and manganate(VII), i.e., MnO₄⁻ have been studied [22]: the reaction is presumed to proceed via an outer-sphere mechanism. The rapid exchange between MnO₄⁻ and MnO₄⁻ has been studied in detail by various techniques [23]. The uncatalysed reaction between the said amino acid and permanganate in alkaline medium has been studied previously [24]. A microscopic amount of ruthenium(III) is sufficient to catalyze the reaction in the alkaline medium and a variety of mechanisms are possible. Herein we describe the results of the title reaction in order to determine the active species of oxidant: reductant and catalyst in such media and to arrive at a plausible mechanism.

EXPERIMENTAL

Materials

Since the reaction was too fast to monitor by the usual method, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12). Stock solution of Alanine (s.d. fine chemicals) 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 [25]. Potassium manganate solution was prepared as described by Carrington and Symons [26]. The solution was standardized by measuring the absorbance on a Hitachi 150-20 spectrophotometer with a 1 cm quartz cell at 608 nm (ε = 1530 ± 20 dm³ mol⁻¹ cm⁻¹). The ruthenium(III) solution was prepared by dissolving a known weight of RuCl₃ (s.d. fine chemicals) in HClO₄ 0.20 mol dm⁻³. Mercury was added to the ruthenium(III) solution to reduce any ruthenium(IV) formed during the preparation of ruthenium(III) stock solution and was kept for a day. The ruthenium(III) concentration was assayed by EDTA titration [27,28]. All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amount of the samples in double distilled water. NaOH and NaClO₄ were used to provide the required alkalinity and to maintain the ionic strength respectively.

Kinetic Measurements

All kinetic measurements were performed under pseudo-first order conditions with alanine:MnO₄⁻ [10:1 at constant ionic strength (0.50 mol dm⁻³)]. The reaction was initiated by mixing previously
RESULTS

Stoichiometry and Product Analysis

The reaction mixtures containing an excess of permanganate over alanine, and 0.05 mol dm$^{-3}$ sodium hydroxide at a constant ionic strength of 0.50 mol dm$^{-3}$ was allowed to react for 2 h at 25 ± 0.1°C under inert atmosphere. After completion of the reaction, the remaining MnO$_4^-$ was then analysed spectrophotometrically. Some results indicated that two moles of MnO$_4^-$ were consumed by one mole of amino acid each. Other results indicated that four moles of MnO$_4^-$ were consumed by one mole of amino acid each. The reaction products for the first series were identified as acetaldehyde [29], by spot test and ammonia [30] by Nessler's reagent and manganate by its visible spectrum. Carbon dioxide was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through a tube containing limewater [31]. The product aldehyde was quantitatively estimated to about 78%, which is evidenced by its 2,4-DNP derivative [32]. The nature of the aldehyde was confirmed by its I.R. spectrum which showed a carbonyl (C=O) stretch at 1729 cm$^{-1}$ and an OH$^-$ stretch at 2854 cm$^{-1}$. The same type of aldehyde as above was obtained what the product analysis was carried under pseudo-first order conditions, it ms also observed that the aldehyde does not undergo further oxidation under the present kinetic conditions. A test for corresponding acid was negative, so, it is concluded that the stoichiometry of the reaction under kinetic study is,

$$\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + 2\text{MnO}_4^- + 2\text{OH}^- \rightarrow \text{CH}_3\text{CHO} + 2\text{MnO}_2 + \text{NH}_3 + \text{CO}_2 + 2\text{H}_2\text{O} \quad (1)$$
The permanganate in alkaline medium exhibits various oxidation states, such as Mn(VII), Mn(V) and Mn(VI). The solution changed from violet to blue and then to green, excluding the accumulation of hypomanganate. The violet colour originates from the pink of permanganate and blue from hypomanganate. The change of KMnO₄ solution from violet Mn(VII) ion to dark green Mn(VI) ion through the blue Mn(V) ion has been observed. The spectral changes during the reaction are shown (Fig. 1). It is evident that [Mn(VIII)] decreases at 526 nm whereas [Mn(VI)] increases at 608 nm during the reaction.

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

**Reaction Order**

The reaction orders were determined from the slopes of log kₘₐₓ versus log concentration plots, by varying the concentration of reductant, catalyst and alkali, while keeping other constant.

**Effect of Oxidant, Substrate, Alkali and Catalyst**

The oxidant, (potassium permanganate) concentration was varied in the range 0.50 x 10⁻³ to 5.0 x 10⁻³ mol dm⁻³ as shown in Table 1. The plots of log (Aₒ - Aₜₐₐ₉) versus time, for different initial concentrations of MnO₄⁻ are found to be linear (r = 0.9964, σ = 0.021), and the fairly constant kₘₐₓ values indicate that the order with respect to [MnO₄⁻] was unity. This fact was also confirmed by varying [MnO₄⁻] which did not show any change in pseudo-first order.
RUTHENIUM(III) CATALYZED OXIDATION OF L-ALANINE

Effect of Initially Added Reaction Products

The externally added products such as manganese, ammonia and aldehyde did not show any significant effect on the rate of the reaction.

Effect of Ionic Strength and Solvent Polarity

The effect of ionic strength was studied by varying the sodium perchlorate concentration from 0.05 to 0.50 mol dm$^{-3}$ at constant permanganate, amino acids, alkali and catalyst concentrations. It was found that the rate constants increased with increase in concentration of NaClO$_4$ and the plot of log $k_{cat}$ versus log [NaClO$_4$] with unit slope showed unit order (Table I) dependence on NaClO$_4$. Under the conditions used, the uncatalysed reaction rate is negligible compared to the catalysed reaction rate.

### Table I

<table>
<thead>
<tr>
<th>[Ala.] x 10$^3$ mol dm$^{-3}$</th>
<th>[MnO$_4^-$] x 10$^{-4}$ mol dm$^{-3}$</th>
<th>[OH$^-$] mol dm$^{-3}$</th>
<th>[Ru(III)] x 10$^5$ mol dm$^{-3}$</th>
<th>$k_{cat}$ x 10$^2$ s$^{-1}$</th>
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The effect of alkali on the reaction was studied at constant amino acid and potassium permanganate concentrations and at a constant ionic strength of 0.50 mol dm$^{-3}$ at 25$^\circ$C. Keeping all other concentrations and the catalyst concentration constant, the rate constant, $k_{cat}$, increased with increase in concentration of alanine, indicating a less than unit order dependence on substrates concentration. The effect of alkali on the reaction was studied at constant amino acid and potassium permanganate concentrations and at a constant ionic strength of 0.50 mol dm$^{-3}$ at 25$^\circ$C. The rate constants increased with the increase in [alkali], as given in Table I. The ruthenium(III) concentration was varied in 1.0 x 10$^{-4}$ to 1.0 x 10$^{-5}$ mol dm$^{-3}$ range. The linearity of plots, $r = 0.9983$, $\sigma = 0.0341$ for log $k_{cat}$ versus log [Ru(III)] with unit slope showed unit order (Table I) dependence on Ru(III). Under the conditions used, the uncatalysed reaction rate is negligible compared to the catalysed reaction rate.
not successful. However, they were computed from the values of pure liquids as already performed earlier [35]. No reaction of the solvent with the oxidant occurred under the experimental conditions employed. The rate constant increased with decreasing dielectric constant of the medium. The plot of \( \log k_{\text{rxn}} \) versus \( 1/D \) was linear with a positive slope (Fig. 2 \( r=0.9989, \sigma = 0.034 \)).

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.

Effect of temperature

The reaction rate was measured at four different temperatures with separately varying [Substrate], and [alkali] keeping other conditions constant. The rate was found to increase with increasing temperature. The rate constants, \( k \) of the slow step of Scheme 1 were obtained from the intercept of the plots of \( [\text{Rut(III)}]/k_{\text{rxn}} \) versus \( 1/[\text{Ala}] \) for different temperatures. The energy of activation corresponding to these constants was evaluated from the plot of \( \log k \) versus \( 1/T \), from which the activation parameters were calculated (Table II a).

The thermodynamic quantities of the first step of Scheme 1 can be evaluated as follows. The hydroxyl ion concentration (as in Table I) was varied at
(a) Activation parameters with respect to slow step of Scheme 1

<table>
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<tr>
<th>Activation Parameters</th>
<th>Values</th>
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<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>20.2 ± 2.0</td>
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<tr>
<td>$\log A$</td>
<td>9.33 ± 1.5</td>
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<tr>
<td>$\Delta H^\circ$ (kJ mol$^{-1}$)</td>
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<tr>
<td>$\Delta S^\circ$ (JK$^{-1}$ mol$^{-1}$)</td>
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</tr>
<tr>
<td>$\Delta G^\circ$ (kJ mol$^{-1}$)</td>
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(b) Thermodynamic quantities with respect to first step of Scheme 1

<table>
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<td>$\Delta H$ (kJ mol$^{-1}$)</td>
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<tr>
<td>$\Delta S$ (JK$^{-1}$ mol$^{-1}$)</td>
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</tr>
<tr>
<td>$\Delta G$ (kJ mol$^{-1}$)</td>
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</table>

(c) Thermodynamic quantities with respect to second step of Scheme 1

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<tr>
<td>$\Delta S$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>73 ± 5.0</td>
</tr>
<tr>
<td>$\Delta G$ (kJ mol$^{-1}$)</td>
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</tr>
</tbody>
</table>

TABLE II
Effect of temperature

several temperatures, and values of $K_2$ were determined at each temperature. The values for $K_1$ (dm$^3$mol$^{-1}$) at 298K, 303K, 308K and 313K are 6.51, 7.80, 9.62 and 11.7 respectively. The thermodynamic quantities of the second step of Scheme 1 can also be evaluated as follows. The alanine concentration (as in Table 1) was varied at several temperatures, and values of $K_2$ were determined at each temperature. The values for $K_2$, (dm$^3$mol$^{-1}$) at 298K, 303K, 308K and 313K are 160, 174, 182 and 191 respectively. The van't Hoff's plots were drawn for the variation of $K_1$ and $K_2$ with temperature (log$K_1$ versus $1/T$; $r = 0.9972$, $\sigma = 0.0231$) and (log $K_2$ versus $1/T$; $r = 0.9983$, $\sigma = 0.0245$). The values of thermodynamic quantities are given in Table II b and II c. A comparison of these values with those obtained for the slow step shows that the reactions before the rate determining step are fairly fast.
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 manganese(VII) is stable and further reduction of manganese (VI) might be stopped [14-19]. Diode Army Rapid Scan Spectrophotometric (DARSS) studies have shown that at pH $> 12$, the product of manganese(VII) is manganese(VI) and no further reduction was observed as reported [14-19] by Shimandl et al. However, on prolonged standing, green manganese(VI) is reduced to manganese(IV) under our experimental conditions. It is known that in aqueous solution, amino acid exists as zwitterionic [36] form whereas in aqueous alkaline medium it exists as anionic form according to the following equilibria.

$$\text{RCH}(\text{NH})\text{COOH} \rightleftharpoons \text{RCH}(\text{NH})\text{COO}^-$$  
(\text{Zwitterion})

$$\text{RCH}(\text{NH})\text{COOH} + \text{OH}^- \rightleftharpoons \text{RCH}(\text{NH})\text{COO}^- + \text{H}_2\text{O}$$

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

It is interesting to identify the probable ruthenium(III) chloride species in alkaline medium. In the present study it is quite probable that the species $[\text{Ru}(\text{H}_2\text{O})_3\text{OH}]^{3+}$ might assume the general form $[\text{Ru(III)}\text{OH}]^{x-}$ and the hydroxylated species, $[\text{Ru}(\text{H}_2\text{O})_3\text{OH}]^{3+}$. Increase in rate with increase in [OH$^-$] indicates the presence of the hydroxylated species of ruthenium (III) as a reactive species, which is shown by the following equilibrium in accordance with the earlier work [41-44].

$$\text{RuH}_2\text{O}_6^{3+} + \text{OH}^- \rightleftharpoons \text{RuH}_2\text{O}_5\text{OH}^{2+} + \text{H}_2\text{O}$$

The results suggest the formation of a complex between the amino acid and the hydroxylated ruthenium(III) species. Such complex formation between substrate and catalyst has also been observed in earlier work [45-49]. Evidence is provided by the fractional order found in [alanine]. The spectral evidence for complex formation between catalyst and substrate was obtained from the uv-vis spectra of the catalyst and a mixture of catalyst and alanine in the alkaline medium. A bathochromic shift of 10 nm from 230 to 240 nm is observed for alanine. The formation of the complex was also proved kinetically by the non-zero intercept of the plot of $[\text{Ru(III)}]/k_{\text{obs}}$ versus 1/1[Alanine]. The existence of two isosbestic points in the uv-vis spectrum of permanganate in alkaline medium (Fig. 1) indicates the presence of two equilibrium steps before the slow step of the mechanism [50,51]. The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as a higher rate constant for the slow step, indicate that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observation [52-54]. Since Scheme 1 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in sequence of one electron steps, the reaction between the substrate and oxidant would afford 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 on the alkaline permanganate oxidation of amino acids [55-57]. It is also known that permanganate ion in alkaline medium [58] exists as $[\text{MnO}_4^- \text{OH}]^2$. The complex formed reacts further with the oxidant species of permanganate in a rate determining step, resulting in the formation of a free radical, which again reacts...
RUHENIUM(III) CATALYSED OXIDATION OF L-ALANINE

Scheme 1

The above equation (2) can be rearranged to the following form which is used for the verification of the rate law.

\[
\begin{align*}
\text{[Ru(III)]} &\quad \frac{1}{k_{\text{obs}}} = \frac{1}{k} \frac{1}{k K_d[Ala][OH]} + \\
&\quad \frac{1}{k K_d[Ala]} + \frac{1}{k} + \\
&\quad \frac{1}{k K_d[Ala][OH] + k K_d[Ala][OH]} [Ala]
\end{align*}
\]

Scheme 1 leads to rate law (2) as follows

\[
\begin{align*}
\frac{k_{\text{obs}}}{[\text{MnO}_4^-]} = k_{\text{obs}} = &\quad k K_d[\text{Ala}] [\text{Ru(III)}][\text{OH}^+] \\
&\quad (1+K_d[\text{OH}^+] + K_d[\text{Ala}]+k K_d[\text{OH}^+][\text{Ala}])
\end{align*}
\]

with the alkaline species of permanganate in a subsequent fast step to yield the products. In agreement with the experimental results obtained, a mechanism, as set out below, may be envisaged.

The probable structure of complex (C) is

\[
\text{Ru} = \text{RuCl}_3 \quad \text{C} = \text{RuCl}_3
\]

According to equation (3), the plots of $[\text{Ru(III)}]/K_d$ versus $1/[\text{Ala}]$ ($r = 0.9988, \sigma = 0.045$) and $[\text{Ru(III)}]/K_d$ versus $1/[\text{OH}^-]$ ($r = 0.9928, \sigma = 0.052$) should be linear, which is verified. (Fig. 3). From the slopes and intercepts of such plots, $K_p$, the equilibrium constant for the formation of alkaline species of the oxidant, $K_d$, 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 $6.51 \pm 0.2 \text{ dm}^3\text{ mol}^{-1}\text{s}^{-1}$, $1.60 \pm 0.1 \times 10^5 \text{ dm}^3\text{ mol}^{-1}\text{s}^{-1}$, and $6.21 \pm 0.05 \times 10^5 \text{ dm}^3\text{ mol}^{-1}\text{s}^{-1}$ respectively at 298K. 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 1. The $K_r$ value is in the neighborhood of the earlier work [58].

The effect of ionic strength on the rate can be understood essentially on the basis of ionic species as in Scheme 1. The effect of solvent on the reaction kinetics has been described in the literature [59-62]. For the limiting case of a zero angle approach between two dipoles or an ion-dipole system, Amis [63] has shown that a plot of log $k_{obs}$ versus $1/D$ is linear with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and with a positive slope for a positive ion and dipole interaction. In the present study, an increase in the rate with a decrease in the dielectric constant of the medium was observed, which cannot be explained by the Amis
Amino acid | \( k \times 10^2 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) (298 K) | \( k \times 10^3 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) (303 K) | \( \Delta G^* \) (JK mol\(^{-1}\)) | \( \Delta H^* \) (kJ mol\(^{-1}\)) | \( \Delta S^* \) (kJ mol\(^{-1}\)) | Reference
---|---|---|---|---|---|---
L-arginine | 5.80 | 3.00 | -13.1 | 29.4 | 33.4 | [58]
Rac-serine | 1.06 | 1.27 | -17.1 | 28.6 | 36.4 | [69]
L-lysine | 1.53 | 1.96 | -62.0 | 30.7 | 49.2 | [70]
L-isoleucine | 1.10 | 1.39 | -71.0 | 28.8 | 49.3 | [70]
L-Alanine | 62.1 | 73.8 | -75.1 | 17.6 | 40.6 | In this issue

TABLE III
Activation parameters for some amino acids (for isokinetic temperature).

The moderate values of \( \Delta H^* \) and \( \Delta S^* \) both favour electron transfer processes. The \( \Delta H^* \) value was due to release of energy of solution changes in the transition state. The negative \( \Delta S^* \) value within the range found for free radical reactions have been ascribed to the nature of electron pairing and electron unpairing processes, and to the loss of a degree of freedom, formally available to reactions on the formation of a rigid transition state. The difference in the activation parameters for the catalysed and uncatalysed reaction [246] explains the catalytic effect on the reaction. The catalyst, Ru(III), alters the path of the reaction by lowering the energy barrier, that is, it provides an alternate pathway with lower activation parameters for the reaction involving the formation of an intermediate complex as proposed in Scheme I.

The activation parameters for the oxidation of some amino acids by MnO\(\text{V}^\text{II}\) are summarized (Table III). The entropy of activation for the title reaction falls within the observed range. Variation in the rate within a reaction series may be caused by changes in the enthalpy and/or entropy of activation. Changes in rate are caused by changes in both \( \Delta H^* \) and \( \Delta S^* \), but these quantities vary extensively in a parallel fashion. A plot of \( \Delta H^* \) versus \( \Delta S^* \) is linear according to equation.

\[
\ln k = \ln k^* + \frac{\Delta H^*}{2D RT} \left(1 - \frac{1}{r^*}ight) 
\]

where \( k \) is the rate constant in a medium of infinite dielectric constant and \( r \) and \( r^* \) refer to radius of the reacting species and the activated complex, respectively. It can be seen from the equation that the rate should be greater in a medium of lower dielectric constant when \( r^* > r \). Intramolecular hydrogen bonding that could stabilise the transition, increasing the size of activated complex by attracting solvent molecules due to a solvation effect is possible. It is likely that \( r^* > r \) for alanine, thus explaining the experimental observation. Hence one can expect intra molecular hydrogen bonding in alanine since it contains NH and CO-H groups on the same carbon atom. Such hydrogen bonding is common for molecules having CO-H and NH and CO-H and OH groups either on the adjacent carbon atom or on the same carbon atom of the molecule, as found in simple amino acid [64].
β is called the isokinetic temperature; it has been asserted that apparently linear correlation of $\Delta H^0$ with $\Delta S^0$ are sometimes misleading and the evaluation of $\beta$ by means of the above equation lacks statistical validity [66]. Exner [67] advocates an alternative method for the treatment of experimental data. If the rates of the several reactions in a series have been measured at two temperatures and $\log k_1$ (at $T_1$) is linearly related to $\log k_2$ (at $T_2$) i.e. $\log k_1 = a + b \log k_2$, he proposes that $\beta$ can be evaluated from the equation,

$$\beta = \frac{T_1 b - T_2 b}{T_1 - T_2}$$

We have calculated the isokinetic temperature as 75K by plotting $\log k_1$ at 298K versus $\log k_2$ at 303K (Fig. 4, $r = 0.9987, \sigma = 0.032$). The value of $\beta$ (75K) is much lower than the experimental temperature (303K). This indicates that the rate is being governed by the entropy of activation [68]. The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow a similar mechanism, as previously suggested.

CONCLUSIONS

It is interesting that the oxidant species $\text{MnO}_4^-$ requires pH $\geq 12$, below which the system becomes disturbed and the reaction proceeds further to give a reduced oxidation product as manganese(IV), which slowly develops a yellow turbidity. Hence, it becomes apparent that, in carrying out this reaction, the role of pH in the reaction medium is crucial. Ruthenium(III) is found to be an efficient catalyst, (especially in alkaline medium) which catalyses the reaction with a measurable velocity at a concentration of $10^{-4}$ mol dm$^{-3}$. It is also noteworthy that, under the conditions studied, the reaction occurs in two successive one-
electron reduction (Scheme 1) steps rather than a two-electron reduction in a single step.

REFERENCES

KINETIC AND MECHANISTIC STUDY OF OXIDATION OF L-ASPARTIC ACID BY DIPEROXATOCUPRATE(III) IN AQUEOUS ALKALINE MEDIUM

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P. G. Department of Studies in Chemistry, Karnataka University, 580 003 Dharwad, India
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ABSTRACT
The kinetics of oxidation of L-aspartic acid (L-ASPA) by diperoxatocuprate(III) (DPC) in aqueous alkaline medium at a constant ionic strength of 0.5 mol dm$^{-3}$ was studied spectrophotometrically. The reaction between diperoxatocuprate(III) and L-aspartic acid in alkaline medium exhibits 2:1 stoichiometry (DPC: L-ASPA). The reaction is of first order in [DPC], less than unit order in [L-ASPA] and [alkali]. Periodate has a retarding effect on the rate of the reaction. Dielectric constant of the medium has no effect on the rate of reaction. Effect of added products and ionic strength of the reaction medium has been investigated. A mechanism involving the monoperoxatocuprate(III) (MPC) as the reactive species of the oxidant has been proposed. In complex equilibrium step L-ASPA binds to MPC species to form a complex (C). Then this complex (C) decomposes in a slow step to form an intermediate free radical species, which reacts with another molecule of MPC species in a fast step to yield the products. The activation parameters with respect to slow step of the reaction are computed and discussed.

Keywords: diperoxatocuprate(III), L-aspartic acid, kinetics, mechanism.

AIMS AND BACKGROUND
The periodate and tellurate complexes of copper in their trivalent state have been extensively used in the analysis of several organic compounds. The kinetics of self-decomposition of these complexes was studied in some detail. Movius reported the reactivity of some alcohols with diperoxatocuprate (III) (DPC). DPC is a versatile one-electron oxidant for various organic compounds in alkaline medium and its use as an analytical reagent is now well recognised, and also used in the estimation of amino acids. Copper(III) is shown to be an intermediate in the copper(II)-catalysed...
oxidation of amino acids by peroxodisulphate. The use of DPC as an oxidant in alkaline medium is new and restricted to a few cases due to its limited solubility and stability in aqueous medium. The kinetics and mechanism of oxidation of some organic substrates by DPC have been studied. Moreover, when the copper(III) periodate complex is oxidant, since multiple equilibria between the different copper(III) species are involved, it needs to be known which of species is the active oxidant. Amino acids have been oxidised by a variety of oxidants yielding different products. The kinetic investigation of the oxidation of amino acids has been carried out under different experimental conditions. In many cases it was reported that amino acids undergo oxidative decarboxylation and deamination. Thus, the study of amino acids oxidants is important due to their biological significance and selectivity. In view of multiple equilibria embracing the different copper(III) periodate species and the complexity of the title reaction, a detailed study of the reaction is undertaken. L-ASPA is a non-essential amino acid. It aids in the exclusion of harmful ammonia from the body. Recent studies have shown that L-ASPA may increase resistance to fatigue and increase endurance. The literature survey reveals that there are no reports on the kinetics of oxidation of L-ASPA by DPC. The oxidation of L-ASPA is of interest as the product of oxidation differs with different oxidants and media. In view of multiple equilibria embracing the different copper(III) periodate species and the complexity of the title reaction, a detailed study of the reaction is undertaken.

EXPERIMENTAL

Materials and reagents. All chemicals used were of reagent grade. Doubly distilled water was used throughout the work. Stock solution of L-ASPA (s.d. Fine chemicals) was prepared by dissolving the appropriate amount of sample in water. The purity of the sample was checked by TLC. The copper(III) periodate complex was prepared by standard procedure. The purity of the complex was checked by its UV-vis. spectrum, which shows broad absorption band at 415 nm. The aqueous solution of copper(III) was standardised by back titration method. The copper(II) solution was made by dissolving the known amount of copper sulphate (BDH) in distilled water. Periodate solution was prepared by weighing out the required amount of sample in hot water and it was kept for 24 h. Its concentration was ascertained iodometrically at neutral pH by phosphate buffer. Since periodate is present in excess in DPC, the possibility of oxidation of L-ASPA by periodate in alkaline medium at 25°C was tested. The progress of the reaction was followed iodometrically. However, it was found that there was no significant reaction under the experimental conditions employed compared to the DPC oxidation of L-ASPA. Potassium hydroxide and potassium nitrite (BDH, AR) were employed to maintain the required alkalinity and ionic strength, respectively, in reaction solutions.
Kinetic studies. The oxidation of L-ASPA by DPC was followed under pseudo-first order conditions where L-ASPA was in excess over [DPC] at 25 ± 0.1°C, unless otherwise stated. The reaction was initiated by mixing the required quantities of previously thermostated solution of L-ASPA and DPC, which also contained definite quantities of KOH, KNO₃, and IO₃⁻ to maintain the required alkalinity, ionic strength and periodate. Here the total concentration of hydroxide ion was calculated considering the KOH in DPC as well as the KOH additionally added. Similarly, the total metaperiodate concentration was calculated by considering metaperiodate present in solution of DPC and additionally added. The course of reaction was followed by measuring the absorbance of unreacted DPC in the reaction mixture in a 1-cm quartz cell located in the thermostated compartment of a Peltier Accessory (temperature control) attached Varian CARY 50 Bio UV-vis. spectrophotometer at its maximum absorption wavelength of 415 nm as a function of time. Earlier it was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength. The obedience of the Beer’s law by DPC at 415 nm was verified earlier and the molar absorbance coefficient, "ε" was found to be 6231.311 dm³ mol⁻¹ cm⁻¹ at this wavelength. The first order rate constants, k, were obtained from the plots of Ig (a – x) versus time, where 'a' and 'x' being the initial concentration and change in concentration of DPC at time 't', respectively. The plots were linear up to about 85% completion of the reaction and the rate constants were reproducible within ±5%. The spectral changes during the reaction are shown in Fig. 1. It is evident from the figure that the concentration of
DPC decreases at 415 nm. The effect of dissolved oxygen on the rate of reaction was studied by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results 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 during the experiments. In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface 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-IV personal computer.

RESULTS

Stoichiometry and product analysis. Different sets of reaction mixtures containing different concentrations of L-ASPA and DPC at constant ionic strength and alkali were kept for ca. 6 h at 25 ± 0.1°C in an inert atmosphere and in a closed vessel. When [DPC] was higher than [L-ASPA], the unreacted DPC was found by measuring the absorbance at 415 nm spectrophotometrically. The results indicated that 2 mol of DPC consumed 1 mol of L-ASPA as in equation (1).

$$\text{HOOC-CH}_{2}-\text{CH-COOH} + 2\text{Cu(III)} + \text{OH}^{-} \rightarrow \text{CH}_{2}-\text{CHO} + 2\text{CO}_2 + \text{N}_2\text{H}_4+2\text{Cu(II)}$$  \hspace{1cm} (1)

$\text{H}_2\text{N}$

The reaction products were extracted with ether. The main reaction product was identified as acetaldehyde by spot test. The product acetaldehyde was quantitatively estimated to about 78%, which is evidenced by its 2,4-DNP derivative. The nature of the aldehyde was confirmed by its IR spectrum carbonyl stretching at 1729 cm$^{-1}$ and a band at 2928 cm$^{-1}$ due to the aldehydic stretching. Other products like ammonia were identified by the Nessler's reagent, CO$_2$ was qualitatively detected by bubbling gas through the acidified reaction mixture and passing through a tube containing lime-water. The reaction products do not undergo further oxidation under the present kinetic conditions.

Reaction order. The order with respect to [L-ASPA], [alkali] and [periodate] were found from $\lg k$ versus $\lg$ (concentration) plots and the obtained orders were also confirmed by differential method by the plot of $\lg (-dC/dt)$ versus $\lg$ (concentration) using the equation $\lg (-dC/dt) = \lg k + n \lg C$; these orders were obtained by varying the concentration of L-ASPA, periodate and alkali in turn while keeping others constant. The concentration of DPC was varied in the range of 0.25×10$^{-3}$ to 2.0×10$^{-4}$ mol dm$^{-3}$ at fixed [L-ASPA], [OH$^-$], [IO$_4^-$] and ionic strength. The non-
variation in the pseudo-first order rate constants at various concentrations of DPC indicates the order in \([\text{DPC}]\) as unity (Table 1). This was also confirmed by the linearity of the plots of \(\log(\text{absorbance})\) versus time \((r > 0.9994, S \leq 0.026)\) up to 85% completion of the reaction. The substrate, L-ASPA was varied in the range of \(5 \times 10^{-4}\) to \(5.0 \times 10^{-3}\) mol dm\(^{-3}\) at 25°C keeping all other reactants concentrations constant (Table 1). The \(k_{\text{obs}}\) values increased with increase in concentration of L-ASPA indicating an apparent less than unit order dependence on \([\text{L-ASPA}]\) (Table 1). The effect of [alkali] on the rate of the reaction was studied at constant concentrations of L-aspartic acid, DPC and ionic strength at 0.5 mol dm\(^{-3}\). The rate constants increased with increase in [alkali] and the order was found to be less than unity (Table 1).

Table 1. Effect of variation of \([\text{DPC}], [\text{L-ASPA}], [\text{OH}^+], \) and \([\text{IO}_4^-]\) on oxidation of L-ASPA by DPC at 25°C, \(I = 0.50\) mol dm\(^{-3}\)

<table>
<thead>
<tr>
<th>([\text{DPC}] \times 10^4) (mol dm(^{-3}))</th>
<th>([\text{L-ASPA}] \times 10^5) (mol dm(^{-3}))</th>
<th>([\text{OH}^+]) (mol dm(^{-3}))</th>
<th>([\text{IO}_4^-] \times 10^5) (mol dm(^{-3}))</th>
<th>(k_{\text{obs}} \times 10^5) (s(^{-1}))</th>
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</tr>
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</tr>
<tr>
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<td>0.05</td>
<td>8.0</td>
<td>1.90</td>
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<td>0.05</td>
<td>1.5</td>
<td>1.50</td>
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</table>

Effect of periodate. The effect of \([\text{IO}_4^-]\) was observed by varying its concentration from \(1 \times 10^{-5}\) to \(2 \times 10^{-4}\) mol dm\(^{-3}\) at constant concentrations of DPC, L-ASPA, alkali
and constant ionic strength (Table 1). It was found that the added periodate retarded the rate, and order in periodate was inverse fractional.

**Effect of ionic strength and solvent polarity.** The effect of ionic strength was studied by varying the potassium nitrate concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.05 to 0.50 mol dm$^{-3}$ at constant [DPC], [L-ASPA], [IO$_4^-$] and [alkali]. It was found that the rate constants increased with increase in concentration of potassium nitrate and the plot of $\lg k_{\text{obs}}$ versus $I$ was a linear with positive slope (Fig. 2, $r = 0.9989, S = 0.031$). The relative permittivity ($\epsilon$) effect was studied by varying the t-butyl alcohol-water content in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivities of the mixture of t-butyl alcohol-water were not successful. However, they were computed from the values of pure liquids. It was also found that there was no reaction of the solvent with the oxidant under the experimental conditions used. The $k_{\text{obs}}$ values remain constant with the decrease in the dielectric constant of the medium.

![Figure 2](image.png)

**Effect of initially added products.** The initially added products such as copper(II) and acetaldehyde did not show any significant effect on the rate of the reaction.

**Test for free radicals.** To test the intervention of free radicals, the reaction mixture was mixed with acrylonitrile monomer and kept for 24 h under nitrogen atmosphere. On dilution with methanol, white precipitate of polymer was formed, indicating the presence of intervention of free radicals in the reaction. The blank experiment of either DPC or L-ASPA with acrylonitrile alone did not induce polymerisation under the same condition as those induce with reaction mixture. Initially added acrylonitrile decreases the rate indicating the free radical intervention, which is the case in an earlier work.
Effect of temperature. The rate of the reaction was measured at different temperatures under varying L-ASPA concentration. The rate of reaction increased with the increase of temperature. The rate constants, \( k \), of slow step of Scheme 1 were obtained from intercepts of the plots of \( 1/k_{on} \) versus \( 1/[\text{L-ASPA}] \) (\( r > 0.9998, S \leq 0.0152 \)) and used to calculate the activation parameters. The values of \( k \) (s\(^{-1}\)) are given in Table 2. The activation parameters corresponding to these constants were evaluated from the plot of \( \ln k \) versus \( 1/T \) (\( r > 0.9989, S \leq 0.0135 \)) and are tabulated in Table 2.

Table 2. Thermodynamic activation parameters for the oxidation of L-ASPA by DPC in alkaline medium with respect to the slow step of Scheme 1

(A) Effect of temperature

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( k \times 10^2 ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.25</td>
</tr>
<tr>
<td>303</td>
<td>1.60</td>
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<tr>
<td>308</td>
<td>2.20</td>
</tr>
<tr>
<td>313</td>
<td>2.90</td>
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</table>

(B) Activation parameters for the slow step of Scheme 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a ) (kJ mol(^{-1}))</td>
<td>44.1 ± 1.6</td>
</tr>
<tr>
<td>( \lg A )</td>
<td>5.8 ± 0.2</td>
</tr>
<tr>
<td>( \Delta H^\circ ) (kJ mol(^{-1}))</td>
<td>41.5 ± 1.4</td>
</tr>
<tr>
<td>( \Delta S^\circ ) (J K(^{-1}) mol(^{-1}))</td>
<td>-142 ± 9</td>
</tr>
<tr>
<td>( \Delta G^\circ ) (kJ mol(^{-1}))</td>
<td>75 ± 4</td>
</tr>
</tbody>
</table>

DISCUSSION

The water soluble copper(II) periodate complex is reported\(^{6,18}\) to be \([\text{Cu}([\text{HIO}_4]^4)^{-})(\text{OH}]^\text{°}\). However, in an aqueous alkaline medium and at a high pH range as employed in the study, periodate is unlikely to exist as \([\text{HIO}_4]^4-\) (as present in the complex) as is evident from its involvement in the multiple equilibria\(^{1,2} \) (2) to (4) depending on the pH of the solution.

\[
\begin{align*}
\text{H}_2\text{IO}_5^- & \rightleftharpoons \text{H}_2\text{IO}_4^- + \text{H}^+ , K_1 = 5 \times 10^{-4} \quad \text{(2)} \\
\text{H}_2\text{IO}_4^- & \rightleftharpoons \text{H}_2\text{IO}_3^- + \text{H}^+ , K_2 = 4.9 \times 10^{-4} \quad \text{(3)} \\
\text{H}_2\text{IO}_3^- & \rightleftharpoons \text{H}_2\text{IO}_2^- + \text{H}^+ , K_3 = 5 \times 10^{-4} \quad \text{(4)}
\end{align*}
\]

Periodic acid (\( \text{H}_2\text{IO}_5^- \)) exists in acid medium and also as (\( \text{H}_2\text{IO}_3^- \)) at pH 7. Thus, under alkaline conditions, the main species are expected to be \( \text{H}_2\text{IO}_3^- \) and \( \text{H}_2\text{IO}_2^- \).
At higher concentrations, periodate also tends to dimerise. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as DPC, \([\text{Cu(OH)}_2(HIO_6)]^3^-\) in aqueous alkaline medium, a conclusion also supported by earlier work.

The results of rate increase with increase in alkalinity and the rate decrease with increase in [periodate] (Table 1) suggest that equilibria of different copper(III) periodate complexes as in equations (5) and (6) are possible. It may be expected that monoperiodatocuprate(III) (MPC) is more important in the reaction than the DPC:

\[
\begin{align*}
[\text{Cu(OH)}_2(HIO_6)]^3^- + [\text{OH}^-] &\rightleftharpoons [\text{Cu(OH)}_2(HIO_6)_2]^4^- + \text{H}_2\text{O} \quad (5) \\
[\text{Cu(OH)}_2(HIO_6)_2]^4^- &\rightleftharpoons [\text{Cu(OH)}_2(HIO_6)]^3^- + \text{H}_2\text{O}^+ \quad (6)
\end{align*}
\]

than the diperiodatocuprate(III) (DPC). The inverse fractional order in [IO_4^-] might also be due to this reason. Added acrylonitrile monomer undergoes polymerisation under inert atmosphere indicating the presence of free radical formation in the mixture.

The reaction between DPC complex and L-ASPA in alkaline medium has a 1:2 stoichiometry of oxidant to reductant with first order dependence on [DPC], apparent less than unit order in [OH^-] and [L-ASPA] and inverse fractional order in [IO_4^-]. The less than unit order in [L-ASPA] presumably results from a complex (C) formation between the oxidant and substrate prior to the formation of the products. \(K_s\) is the composite equilibrium constant comprising the equilibrium to bind L-ASPA anion to MPC species to form a complex (C). Then this complex (C) reacts in a slow step to form an intermediate free radical species of L-asparatic acid. This intermediate species further reacts with another molecule of MPC species in a fast step to yield the products. All the results indicate a mechanism as given in Scheme I.

**Scheme 1**

\[
\begin{align*}
[\text{Cu(OH)}_2(HIO_6)]^3^- + [\text{OH}^-] &\rightleftharpoons [\text{Cu(OH)}_2(HIO_6)_2]^4^- + \text{H}_2\text{O} \\
&\quad \overset{K_s}{\longrightarrow} [\text{Cu(OH)}_2(HIO_6)_2]^4^- + \text{H}_2\text{O}^+ \\
\text{[complex (C)]} &\overset{K_s}{\longrightarrow} \text{OOC-CH}_2-\text{CO} - \text{H}_2\text{O} + \text{Cu(OH)}_2 + \text{H}_2\text{O}^+ \\
\text{[complex (C)]} &\overset{K_r}{\longrightarrow} \text{OOC-CH}_2-\text{CO} - \text{H}_2\text{O} + \text{Cu(OH)}_2 + \text{H}_2\text{O}^+ \\
\text{[OOC-CH}_2-\text{CO} - \text{H}_2\text{O} + \text{Cu(OH)}_2 + \text{H}_2\text{O}^+] &\overset{\text{fast}}{\longrightarrow} \text{L-ASPA} + \text{Cu(OH)}_2 + \text{H}_2\text{O}^+ \\
\text{[L-ASPA]} &\overset{\text{fast}}{\longrightarrow} \text{CO}_2 + \text{CH}_2\text{CHO}
\end{align*}
\]
The probable structure of the complex might be given as follows:

\[
\begin{array}{c}
| \text{O} \\
| \text{OH} \\
\hline
| \text{O} \\
| \text{NH} \\
\hline
| \text{HO} \quad \text{I} \quad \text{O} \\
| \text{OH} \\
\end{array}
\]

The spectral evidence for the complex (C) formation between oxidant and substrate was obtained from UV-vis. spectra of the oxidant and mixtures of substrate and oxidant. A bathochromic shift of about 6 nm from 420 to 426 nm is observed, and hyperchromicity is also observed at \( \lambda_{\text{max}} \) of about 426 nm. Analogous effects upon complex (C) formation between a substrate and an oxidant have been observed earlier. The formation of the complex (C) is proved kinetically by the non-zero intercept of the plot of \( 1/k_{\text{obs}} \) versus \( 1/[L-\text{ASPA}] \) (\( r > 0.9998, S \leq 0.0152 \)) (Fig. 3). The observed modest enthalpy of activation and a relatively low value of the entropy of activation as well as a higher rate constant of the slow step indicate that the oxidation presumably occurs via inner-sphere mechanism. This conclusion is supported by earlier observation. Since Scheme 1 is in accordance with the generally well-accepted principle of non-complementary oxidations taking place in sequence of

Fig. 3. Verification of rate law (8) in the form of equation (9) (conditions as in Table I)
one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in earlier work

Scheme 1 leads to the rate law (equation (7)),

\[
\text{rate} = - \frac{d[DPC]}{dt} = \frac{k K_s K_a[DPC][ASPA][OH]}{[\text{II}_2\text{IO}_6^{5-}] + K_s[\text{OH}][\text{II}_2\text{IO}_6^{5-}] + K_s K_a[\text{OH}] + K_s K_a[\text{ASPA}][\text{OH}]} \tag{7}
\]

The rate law (8) may be verified by rearranging it in the form of equation (9)

\[
\frac{1}{k_{\text{obs}}} = \frac{[\text{II}_2\text{IO}_6^{5-}]}{k K_s K_a[\text{OH}][\text{ASPA}]} + \frac{[\text{II}_2\text{IO}_6^{5-}]}{k K_s [\text{ASPA}]} + \frac{1}{k_s} + \frac{1}{k} \tag{9}
\]

According to equation (9), the plots of \(1/k_{\text{obs}}\) versus \(1/[\text{ASPA}]\) (\(r > 0.9998, S \leq 0.0152\)), \(1/k_{\text{obs}}\) versus \(1/[\text{OH}]\) (\(r > 0.9989, S \leq 0.0121\)) and \(1/k_{\text{obs}}\) versus \([\text{II}_2\text{IO}_6^{5-}]\) (\(r > 0.9978, S \leq 0.0186\)) should be linear as shown in the figure. From the slopes and intercepts, the values of \(K_s\) and \(k\) could be derived as \(4.07 \times 10^5\) dm\(^3\)mol\(^{-1}\)s\(^{-1}\) and \(1.25 \pm 0.05 \times 10^2\) dm\(^3\)mol\(^{-1}\)s\(^{-1}\), respectively.

The moderate values of \(\Delta H^\circ\) and \(\Delta S^\circ\) were both favourable for electron transfer processes. The negative value of \(\Delta S^\circ\) indicates that the complex (C) is more ordered than the reactants.

CONCLUSIONS

Among various species of DPC in alkaline medium, monoperiodatocuprate (MPC) is considered as active species for the title reaction. It becomes apparent that in carrying out this reaction, the role of pH in the reaction medium is crucial. Rate constant of slow step and other equilibrium constants involved in the mechanism are evaluated and activation parameters with respect to slow step of the reaction were computed. The overall mechanistic sequence described is consistent with product studies, mechanistic and kinetic studies.
REFERENCES


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