



Kinetics and Mechanism of Oxidation of L-proline by Trivalent Copper: A free radical intervention and decarboxylation

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Abstract The kinetics of oxidation of L-proline by diperiodatocuprate(III) (DPC) in aqueous alkaline medium at a constant ionic strength of 0.10 mol dm⁻³ was studied spectrophotometrically. The reaction between DPC and L-proline in alkaline medium exhibits 2:1 stoichiometry (DPC: L-Proline). The reaction is of first order in [DPC], less than unit order in [L-proline] and [alkali]. Periodate has no effect on the rate of reaction. The reaction rate increases with increase in ionic strength and decrease in solvent polarity of the medium. Effect of added products and ionic strength of the reaction medium have been investigated. The main products were identified by spot test and IR spectra. A mechanism involving the DPC as the reactive species of the oxidant and a complex formation with L-proline has been proposed. The reaction constants involved in the different steps of mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also calculated.

Key words Kinetics; Diperiodatocuprate(III); Oxidation; L-proline;

Introduction

The periodate and tellurate complexes of copper in its trivalent state have been extensively used in the analysis of several organic compounds¹. The kinetics of self-decomposition of these complexes were studied in some detail². Diperiodatocuprate (III) (DPC) is a versatile one-electron oxidant for various organic compounds in alkaline medium and its use as an analytical reagent is now well recognized and also used in estimation of amino acids³. Movius⁴ reported the reactivity of some alcohols with DPC. Copper (III) is shown to be an intermediate in the Cu(II) catalysed oxidation of amino acids by peroxdisulphate⁵. The use of diperiodatocuprate (III) as an oxidant in alkaline medium is new and restricted to a few cases due to the fact of its limited solubility and stability in aqueous medium⁶. Moreover, when the copper (III) periodate complex is an 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 oxidising agents⁷. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants^{8,9}. The study of amino acids becomes

important because of their biological significance and selectivity towards the oxidant to yield different products. L-proline is a non-essential amino acid and is an important constituent of collagen. As per recent report¹⁰, L-proline is considered to be the world's smallest natural enzyme and it is used in catalysing the aldol condensation of the acetone to various aldehydes with high stereo-specificity that has the pace. Literature survey reveals that there are no reports on the oxidative mechanism of L-proline by diperiodatoocuprate(III) (DPC) oxidant. The present study deals with the title reaction to investigate the redox chemistry of copper(III) in such media and to arrive at a plausible mechanism of the reaction on the basis of kinetic and spectral results.

The kinetic measurements were performed on a Peltier Accessory (temperature control) attached Varian CARY 50 Bio uv-vis spectrophotometer and IR studies were performed by Nicolet Impact - 410 FTIR.

Materials: Chemicals

All chemicals used were of reagent grade. Double distilled water was used throughout the work. Stock solution of L-proline (sd-fine chem.) was prepared by dissolving the appropriate amount of recrystallised sample in doubly distilled water. The purity of the sample was checked by TLC. The copper(III) periodate complex was prepared by standard procedure¹¹. The purity of the complex was checked by its UV/Visible spectrum, which showed a broad absorption band at 415 nm. The aqueous solution of copper(III) was standardized by back titration¹² method. Dissolving the known amount of copper sulphate (BDH) in distilled water made the Cu(II) solution. Periodate solution was prepared by weighing out the required amount of sample in hot water and it was kept for 24 hours. Its concentration was ascertained iodometrically¹³ at neutral pH by phosphate buffer. KOH and KNO₃ (BDH, AR) were employed to maintain the required alkalinity and ionic strength respectively in reaction solutions.

Kinetic measurements

The oxidation of L-proline by DPC was followed under pseudo-first order conditions where L-proline was excess over [DPC] at $25 \pm 0.1^\circ\text{C}$, unless otherwise stated. The reaction was initiated by mixing the required quantities of previously thermostatted solution of L-proline and [DPC], which also contained definite quantities of KOH, KNO₃ and I₂ 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 1cm quartz cell located in the thermostatted 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 mixture at this wavelength. The obedience of Beer's law was verified that there is negligible interference from other species present in the reaction law by DPC at 415 nm was verified earlier and the molar absorbance coefficient, α was found to be $6213 \pm 310 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at this wavelength (Figure 1). The first order rate constants, k_{obs} , were obtained from the plots of $\log [\text{Absorbance}]$ vs time. The plots were linear up to about 75% completion of the reaction and the rate constants were reproducible within $\pm 5\%$. Since periodate is present in excess in DPC, the possibility of oxidation of L-proline 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-proline.

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 reaction rate. However, fresh solutions were used during the experiments.

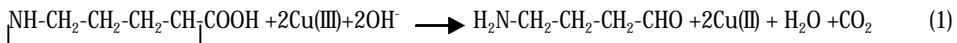
In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have 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 excess DPC than L-proline with constant OH⁻ and KNO₃ were kept for 6 hrs in closed vessel under nitrogen atmosphere. The remaining concentration of DPC was estimated by spectrophotometrically at 415 nm. The results indicated 2:1 stoichiometry as given in Eq(1).

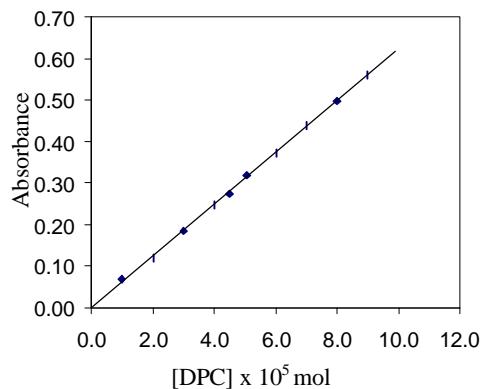


The main reaction products were identified as the aminobutaraldehyde by spot test¹⁴ for amine and aldehyde groups. The product, aminobutaraldehyde was also confirmed by IR spectroscopy¹⁵ which showed bands at 3444 cm⁻¹ for NH stretching, 1773 cm⁻¹ for aldehydic >CO stretching and 2956 cm⁻¹, for aldehydic -CH stretching respectively. The only organic product obtained in the oxidation is aminobutaraldehyde, which is further confirmed by single spot in TLC. However, the other product in alkaline medium is copper(II), identified by spot test¹⁶ and uv-visible spectra. 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 order with respect to [L-proline], [alkali] and [periodate] were found by log k_{obs} vs log concentration plots and the obtained orders were also confirmed by differential method by the plot log(-dc/dt) vs log concentration using the equation log(±dc/dt) = log k + n log c; these orders were obtained by varying the concentration of L-proline, periodate and alkali in turn while keeping others constant.

Figure 1. Verification of Beer's law for [DPC] at 415 nm in 0.02 mol dm⁻³ alkali.



The diperiodatocuprate(III) concentration was varied in the range, 2.0 x 10⁻⁵ to 2.0 x 10⁻⁴ mol dm⁻³ and linearity of plots of log[Abs] vs time ($r>0.9994$, $S\leq 0.026$) up to 75% completion of the reaction (Figure 2) indicate the order in [diperiodatocuprate(III)] as unity. This result was also confirmed by varying the [diperiodatocuprate(III)] which did not show any change in pseudo-first order rate constants (k_{obs}) (Table 1) ($r>0.9994$, $S\leq 0.026$). The substrate, L-proline was varied in the range of 5.0 x 10⁻⁴ to 5.0 x 10⁻³ mol dm⁻³ at 25°C keeping all other reactants concentrations constant. The k_{obs} values increased with increase in concentration of L-proline indicating an apparent less than unit order dependence on [L-proline] (Table 1). The effect of [alkali] on the rate of reaction was studied at constant concentrations of L-Proline, DPC and ionic strength at 0.10 mol dm⁻³. The rate constants increased with increase in [alkali] and the order was found to be less than unity (Table 1).

Effect of relative permittivity and ionic strength

The effect of relative permittivity (ϵ_r) was studied by varying the t-butanol-water content in the reaction mixture with all other conditions being maintained constant. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquids¹⁷.

The solvent did not react with the oxidant under the experimental conditions. The rate constant, k_{obs} increased with decreasing dielectric constant of the medium. The plot of $\log k_{\text{obs}}$ versus $1/\epsilon_T$ was linear with a positive slope (Figure 3). The effect of ionic strength was studied by varying the KNO_3 concentration in the reaction medium. The ionic strength was varied from 0.05 to 0.25 mol dm^{-3} at constant concentrations of diperiodatocuprate(III), L-proline and alkali. It was found that the rate constant increased with increasing concentration of KNO_3 ; the plot of $\log k_{\text{obs}}$ versus $I^{1/2}$ was linear with a positive slope (Figure 3) ($r>0.9978$, $S\leq 0.018$).

Figure 2. First order plots of oxidation of diperiodatocuprate(III) by L-proline in aqueous alkaline medium at 25°C.

[DPC] $\times 10^4$ (mol dm^{-3}): (1) 0.2 (2) 0.5 (3) 1.0 (4) 1.5 (5) 2.0

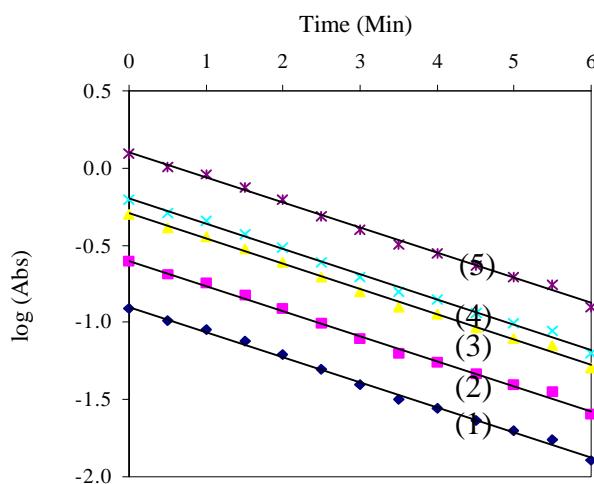
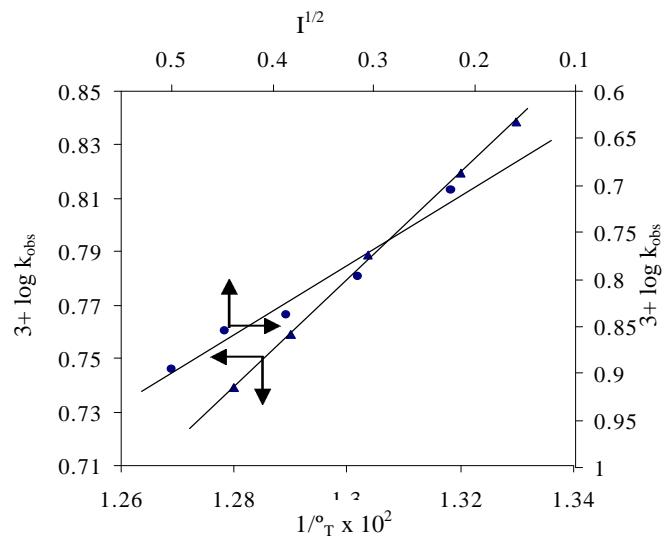


Figure 3. Effect of ionic strength (I) and relative permitivity (ϵ_T) on the DPC oxidation of L-proline in aqueous alkaline medium at 25 °C.



Effect of initially added products

The externally added products, Cu(II) in the form of copper sulphate and another product aminobutaraldehyde did not have 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 hours 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-proline in which acrylonitrile alone did not induce polymerization 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 earlier work¹⁸.

Effect of periodate

The effect of $[IO_4^-]$ was observed by varying the concentration from 1.0×10^{-5} to 1.0×10^{-4} mol dm⁻³ keeping all other reactants concentrations constant. It was found that the added periodate has no effect on the rate of reaction.

Effect of temperature

The rate of reaction was measured at different temperatures under varying L-proline 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 $1/k_{obs}$ vs $1/[L\text{-proline}]$ ($r>0.9978$, $S\leq 0.0162$) at different temperatures 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 $\log k$ vs $1/T$ ($r>0.9989$, $S\leq 0.0135$) and are tabulated in table 2.

Table 1. Effect of variation of [DPC], [SAL], [OH⁻], and $[IO_4^-]$ on oxidation of L-Proline by DPC at 25°C, I = 0.10 mol dm⁻³.

| [DPC] x10 ⁴ (mol dm ⁻³) | [L-Poline] x 10 ³ (mol dm ⁻³) | [OH ⁻] (mol dm ⁻³) | $[IO_4^-] \times 10^5$ (mol dm ⁻³) | $k_{obs} \times 10^3$ (s ⁻¹) | |
|---|---|---|---|--|-------|
| | | | | Found. Found | Calc. |
| 0.2 | 1.0 | 0.02 | 1.0 | 6.23 | 6.50 |
| 0.4 | 1.0 | 0.02 | 1.0 | 6.24 | 6.50 |
| 0.8 | 1.0 | 0.02 | 1.0 | 6.20 | 6.50 |
| 1.0 | 1.0 | 0.02 | 1.0 | 6.25 | 6.50 |
| 2.0 | 1.0 | 0.02 | 1.0 | 6.19 | 6.50 |
| 1.0 | 0.5 | 0.02 | 1.0 | 3.80 | 3.75 |
| 1.0 | 1.0 | 0.02 | 1.0 | 6.25 | 6.50 |
| 1.0 | 2.0 | 0.02 | 1.0 | 10.3 | 10.50 |
| 1.0 | 3.0 | 0.02 | 1.0 | 15.0 | 14.90 |
| 1.0 | 5.0 | 0.02 | 1.0 | 18.5 | 16.50 |
| 1.0 | 1.0 | 0.01 | 1.0 | 3.90 | 3.86 |
| 1.0 | 1.0 | 0.02 | 1.0 | 6.25 | 6.50 |
| 1.0 | 1.0 | 0.04 | 1.0 | 10.0 | 9.98 |
| 1.0 | 1.0 | 0.08 | 1.0 | 14.4 | 14.3 |
| 1.0 | 1.0 | 0.10 | 1.0 | 16.8 | 15.6 |
| 1.0 | 1.0 | 0.02 | 1.0 | 6.25 | 6.50 |
| 1.0 | 1.0 | 0.02 | 2.0 | 6.03 | 6.50 |
| 1.0 | 1.0 | 0.02 | 4.0 | 6.13 | 6.50 |
| 1.0 | 1.0 | 0.02 | 8.0 | 6.23 | 6.50 |
| 1.0 | 1.0 | 0.02 | 10.0 | 6.31 | 6.50 |

Table 2. Thermodynamic activation parameters for the oxidation of diperiodatocuprate(III) by L-proline in alkaline medium with respect to the slow step of **Scheme 1**

(A) Effect of temperature

| Temp. (K) | $k \times 10^{-2}(\text{s}^{-1})$ |
|-----------|-----------------------------------|
| 298 | 2.66 |
| 303 | 3.16 |
| 308 | 3.92 |
| 313 | 4.78 |

(B) Effect of temperature to calculate K_4 and K_5 on oxidation of DPC by L-proline in alkaline medium.

| Temp. (K) | $K_4 (\text{dm}^3 \text{ mol}^{-1})$ | $K_5 \times 10^3 (\text{dm}^3 \text{ mol}^{-1})$ |
|-----------|--------------------------------------|--|
| 298 | 2.64 | 8.58 |
| 303 | 3.21 | 5.63 |
| 308 | 4.26 | 3.31 |
| 313 | 5.63 | 2.32 |

(C) Activation parameters

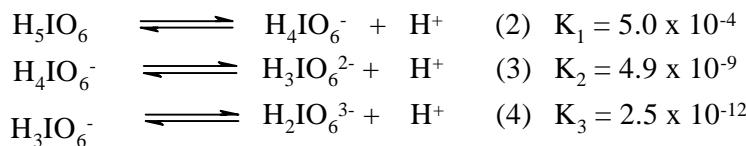
| Parameters | Values |
|---|---------------|
| $H^\# (\text{kJ mol}^{-1})$ | 29 ± 1 |
| $\log A$ | 9.0 ± 0.3 |
| $S^\# (\text{J K}^{-1} \text{ mol}^{-1})$ | -181 ± 10 |
| $G^\# (\text{kJ mol}^{-1})$ | 55 ± 4 |

(D) Thermodynamic quantities

| Thermodynamic quantities | Values |
|--|----------------|
| $\ddot{A}H (\text{kJ mol}^{-1})$ | 39 ± 1 |
| $\ddot{A}S (\text{J K}^{-1} \text{ mol}^{-1})$ | 140 ± 8 |
| $\ddot{A}G (\text{kJ mol}^{-1})$ | -2.3 ± 0.2 |

Discussion

The water soluble Cu(III) periodate complex is reported¹⁹ to be $[\text{Cu}(\text{HIO}_6)_2(\text{OH})_2]^{7-}$. However, in an aqueous alkaline medium and at a high pH range as employed in the study, periodate is unlikely to exist as HIO_6^{4-} (as present in the complex) as is evident from its involvement in the multiple equilibria²⁰(2)-(4) depending on the pH of the solution.

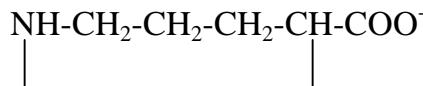


Periodic acid (H_5IO_6) exists in acid medium and also as H_4IO_6^- at pH 7. Thus, under alkaline conditions, the main species are expected to be $\text{H}_3\text{IO}_6^{2-}$ and $\text{H}_2\text{IO}_6^{3-}$. At higher concentrations, periodate also tends to dimerise. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III), $[\text{Cu}(\text{H}_3\text{IO}_6)_2(\text{OH})_2]^{3-}$ in aqueous alkaline medium, a conclusion also supported by earlier work⁴.

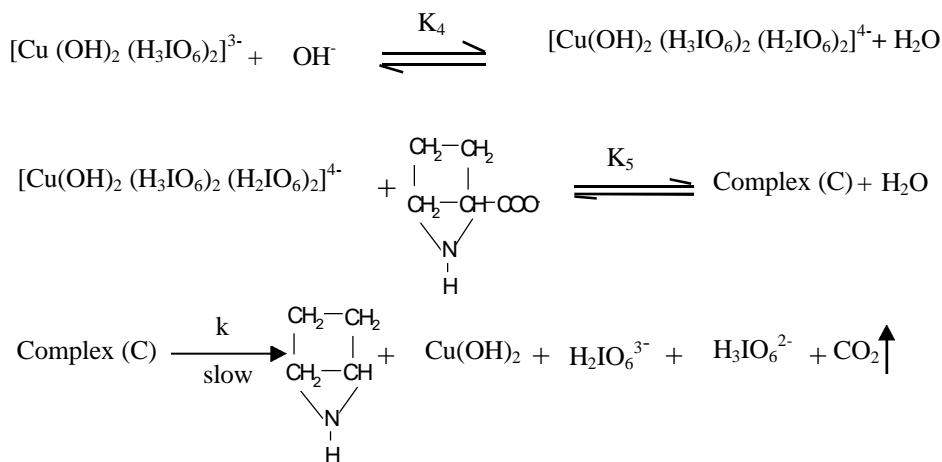
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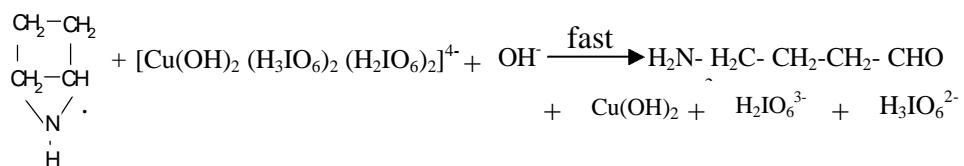
The reaction between the L-proline and diperiodatocuprate(III) complex in alkaline medium has the stoichiometry 1:2 with a first order dependence on the [DPC] and a less than unit order dependence on the [alkali] and [substrate]. In most of the reports⁴ on DPC oxidation, periodate had retarding effect and order in the $[\text{OH}]$ was found to be less than unity and monoperiodatocuprate(III) is considered to be the active species. However, in the present kinetic study, different observations have been obtained i.e., periodate has totally no effect on the rate of the reaction. Accordingly, the DPC is considered to be the active species. No effect of added product such as copper (II) was observed.

It is known that L-proline exists in the form of Zwitter ion²¹ in aqueous medium. In highly acidic medium, it exists in the protonated form, whereas in highly basic medium, it is in the fully deprotonated form²¹. The observed fractional order in $[\text{OH}]$ indicate that first alkali combines with Cu^{3+}



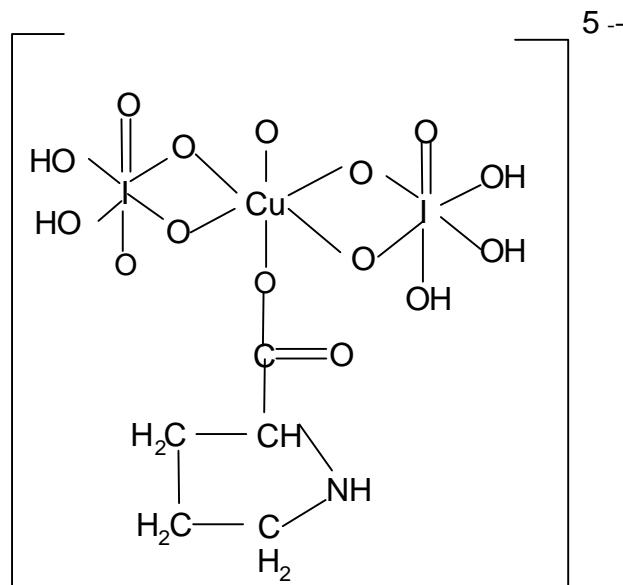
to form an alkali-DPC species $[\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{4-}$ in a pre-equilibrium step²², which is also supported by the Michaelis-Menten plot (Figure 4) which is linear with a positive intercept. L-proline in the deprotonated form reacts with alkali $[\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{4-}$ to form a complex C. This complex C decomposes in a slow step to give a free radical derived from decarboxylated L-proline. This radical in turn reacts with another molecule of DPC species in a fast step to yield the products (Scheme 1).





Scheme - 1

The probable structure of the complex (C) is given below



Spectral evidence of such a complex was obtained from the uv-vis spectra of, DPC, alkali and a mixture of L-proline,alkali and DPC. A hypochromic shift, ϵ_{\max} of ca.about 6 nm 416 to 410 nm is observed together with hyperchromicity at 410 nm. Such complex formation between the oxidant and substrate has been observed earlier²³. Further, the evidence for complex formation is also proved by kinetic studies (i.e., from the Michaelis-Menten plot) by the non-zero intercept (Figure 4) ($r>0.9989$, $S\leq0.0135$) of the plot of $1/k_{\text{obs}}$ vs $1/[L\text{-proline}]$. The mechanism is also supported by moderate values of activation parameters (Table 2). A high negative value of $\Delta S^\#$ suggests that the intermediate complex is more ordered than the reactants. The observed modest enthalpy of activation and a relatively high rate constant of the slow step indicated that the oxidation presumably occurs via inner-sphere mechanism. This conclusion is supported by earlier observation²⁴. Spectral evidence of such a complex was obtained from the uv-vis spectra of, DPC, alkali and a mixture of L-proline,alkali and DPC. A hypochromic shift, ϵ_{\max} of ca.about 6 nm 416 to 410 nm is observed together with hyperchromicity at 410 nm. Such complex formation between the oxidant and substrate has been observed earlier²³. Further, the evidence for complex formation is also proved by kinetic studies (i.e., from the Michaelis-Menten plot) by the non-zero intercept (Figure 4) ($r>0.9989$, $S\leq0.0135$) of the plot of $1/k_{\text{obs}}$ vs $1/[L\text{-proline}]$. The mechanism is also supported by moderate values of activation parameters (Table 2). A high negative value of $\Delta S^\#$ suggests that the intermediate complex is more ordered than the reactants. The observed modest enthalpy of activation and a relatively high rate constant of the slow step indicated that the oxidation presumably occurs via inner-sphere mechanism. This conclusion is supported by earlier observation²⁴.

Since Scheme 1 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in sequences of one-electron steps, the reaction would involve a radical intermediate. A free radical scavenging experiment revealed such a possibility (vide infra). This type of radical intermediate has also been observed in earlier work²⁵ on alkaline-DPC oxidations of amino acids. Scheme 1 leads to the rate law given in Eq. (5).

$$\text{rate} = -\frac{d[\text{DPC}]}{dt} = \frac{kK_4K_5[\text{L-proline}][\text{OH}^*][\text{DPC}]}{(1+K_4[\text{OH}^*] + K_4K_5[\text{OH}^*][\text{L-proline}])}$$

$$x \frac{1}{(1+K_4K_5[\text{DPC}][\text{OH}^*])(1+K_4[\text{DPC}]+K_4K_5[\text{L-proline}][\text{DPC}])} \quad (5)$$

The terms $(1+K_4K_5[\text{DPC}][\text{OH}^*])$ and $(1+K_4[\text{DPC}] + K_4K_5[\text{L-proline}][\text{DPC}])$ in the denominator of Eq.(2) approximate to unity in view of the low concentration of DPC used ($K_1=2.64$ and $K_2=8588$). Therefore, Eq.(5) becomes

Eq (6) can be rearranged to the following form (7), which is suitable for the verification of the rate law:

$$\text{Rate} = kK_4K_5[\text{L-proline}][\text{OH}^*] \quad (6)$$

$$\frac{k_{\text{obs}}}{1} = \frac{1}{[\text{DPC}]} = \frac{1}{1+K_4[\text{OH}^*] + K_4K_5[\text{OH}^*][\text{L-proline}]} \quad (7)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k K_4K_5[\text{L-proline}][\text{OH}^*]} + \frac{1}{k K_5[\text{L-proline}]} + \frac{1}{k}$$

According to Eq (7), other conditions being constant, the plots of $1/k_{\text{obs}}$ vs $1/[\text{L-proline}]$ ($r>0.9734$, $s\leq 0.0138$), $1/[\text{OH}^*]$ ($r>0.875$, $s\leq 0.0217$) should be linear (Figure 4). From the slopes and intercepts, the values of K_4 , K_5 and k could be derived as $2.64\pm 1.0 \text{ dm}^3 \text{ mol}^{-1}$, $8.58\pm 0.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$, and $2.66\pm 0.10 \times 10^{-2} \text{ s}^{-1}$ respectively. Using these constants, the rate constants were calculated over different experimental conditions and there is a reasonable agreement between the calculated and experimental values Table 1, which fortifies the proposed mechanism.

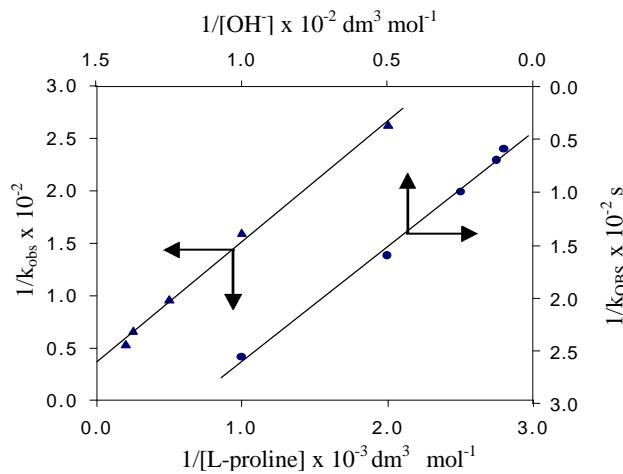


Figure 4. Verification of rate law (7) DPC oxidation of L-proline in aqueous alkaline medium at 25° C. (Conditions as in Table 1)

The thermodynamic quantities for the first equilibrium steps in Scheme 1 can be evaluated as follows: The hydroxyl ion concentration and L-proline concentration as in Table 1 were varied at four different temperatures and the K_4 and K_5 were determined at and are given in Table (2B). A Vant Hoff's plot was made for the variation of K_4 with temperature (*i.e.*, $\log K_4$ vs $1/T$) ($r \geq 0.9781$, $s \leq 0.0108$) and the corresponding thermodynamic quantities are given in Table (2D). A comparison of the latter 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 high activation energy²⁶.

The effect of increasing ionic strength on the rate explains qualitatively the reaction between two negatively charged ions, as seen in Scheme 1. However, increasing the content of t-butyl alcohol in the reaction medium leads to the increase in the reaction rate, contrary to the expected slower reaction between like ions in the media of lower relative permittivity. Perhaps the effect is countered substantially by the formation of active reactive species to a greater extent in low relative permittivity media leading to the net increase in rate²⁷. The activation parameters for the oxidation of some amino acids by Diperiodatocuprate(III) are summarized in Table 3. The entropy of the activation for the title reaction falls within the observed range. Variation in the rate within a reaction series may be caused by change in the enthalpy and / or entropy of activation. Changes in the 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, β is called the isokinetic temperature;

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

We have calculated the isokinetic temperature as 247.80 K by plotting $\Delta H^\#$ versus $\Delta S^\#$ (Figure 5) ($r \geq 0.979$ & $s \leq 0.0051$). The value of β (247.80 K) is lower than experimental temperature range (298–313K). This indicates that the entropy of activation²⁸ governs the rate. The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow similar mechanism, as previously suggested.

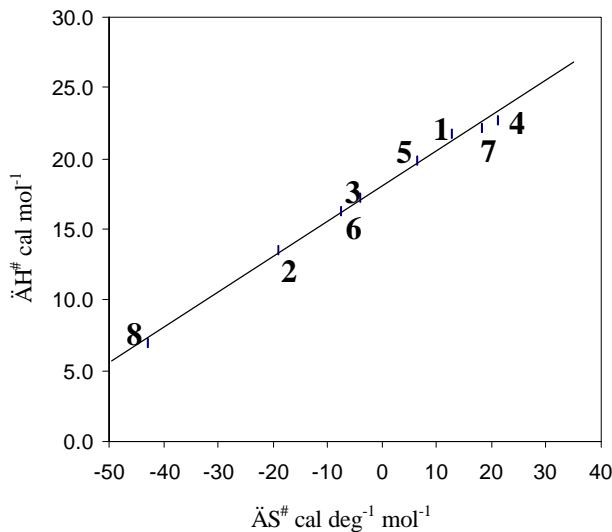


Figure 5. Isokinetic relation ship of $\Delta H^\#$ versus $\Delta S^\#$ plot for oxidations of some amino acids by Diperiodatocuprate(III).

1=Glycine ,2 = α-Alanine, 3 = α-Alanine, 4 =Phenylalanine, 5= Leucine, 6= Valine, 7 = Serine , 8= L-proline.

Table 3. Activation parameters for some amino acids (for isokinetic temperature)

| Amino acid | ΔS^\ddagger (cal deg ⁻¹ mol ⁻¹) | ΔH^\ddagger (k cal mol ⁻¹) | ΔG^\ddagger (k cal mol ⁻¹) | References |
|-------------------|---|---|---|--------------|
| Glycine | 12.6 | 21.8 | 18.0 | 29 |
| | | | 19.21 | |
| α -Alanine | -19.0 | 13.5 | 19.2 | 29 |
| β -Alanine | -4.10 | 17.2 | 18.4 | 29 |
| Phenylalanine | 21.0 | 22.7 | 16.3 | 29 |
| L-Leucine | 6.30 | 19.9 | 18.0 | 29 |
| L-Valine | -7.70 | 16.3 | 18.6 | 29 |
| Serine | 18.10 | 22.2 | 16.9 | 29 |
| L-Proline | -43 | 7.0 | 13.2 | Present Work |

Conclusion

Among various species of DPC in alkaline medium, $[(\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^4$ 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. The overall mechanistic sequence described here is consistent with product studies, mechanistic studies and kinetic studies.

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APPENDIX

According to Scheme 1,

$$\begin{aligned} \text{Rate} &= k[\text{C}] = k K_5[\text{L-proline}]_f [\text{Cu}^{4+}]_f \\ &= k K_4 K_5 [\text{Cu}^{3+}] [\text{OH}^-] [\text{L-proline}] \quad \text{Now,} \\ [\text{DPC}]_T &= [\text{Cu}(\text{OH})_2 (\text{H}_3\text{IO})_6]^{3-} + [\text{Cu}^{4+}] + \text{C} \\ &= [\text{Cu}^{3+}]_f + K_4 [\text{Cu}^{3+}]_f [\text{OH}^-] + K_5 \text{Cu}^{4+} [\text{L-proline}] \\ &= [\text{Cu}^{3+}]_f + K_4 [\text{Cu}^{3+}]_f [\text{OH}^-] + K_4 K_5 [\text{Cu}^{3+}] [\text{L-proline}] [\text{OH}^-] \\ &= [\text{Cu}^{3+}]_f (1 + K_4 [\text{OH}^-] + K_4 K_5 [\text{L-proline}] [\text{OH}^-]) \end{aligned} \quad (\text{I})$$

Where T and f stand for total and free,

$$[\text{DPC}]_T = \frac{[\text{DPC}]_T}{1 + K_4 [\text{OH}^-] + K_4 K_5 [\text{L-proline}] [\text{OH}^-]} \quad (\text{II})$$

Similarly, and

$$[\text{OH}^-]_f = \frac{[\text{OH}^-]_T}{1 + K_4 [\text{Cu}^{3+}] + K_4 K_5 [\text{L-proline}] [\text{DPC}]} \quad (\text{III})$$

$$[\text{L-proline}]_f = \frac{[\text{L-proline}]_T}{1 + K_4 K_5 [\text{Cu}^{3+}] [\text{OH}^-]} \quad (\text{IV})$$

Substituting the values of equation (II), (III) and (IV) in equation (I) and omitting subscripts T and f, we get

$$\frac{\text{Rate}}{[\text{DPC}]} = \frac{k K_4 K_5 [\text{L-proline}] [\text{OH}^-]}{1 + K_4 [\text{OH}^-] + K_4 K_5 [\text{L-proline}] [\text{OH}^-]} \quad (\text{V})$$

