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Mechanistic aspects of oxidation on L-tyrosine by diperiodatocuprate(III) complex in alkali media: a kinetic model

Research Article

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Abstract: Oxidation of an amino acid, L-tyrosine (L-Tyr) by diperiodatocuprate(III) (DPC) in alkaline medium at a constant ionic strength of 0.1 mol dm^{-3} was studied spectrophotometrically at different temperatures (288.1 - 313.1 K). The reaction between DPC and L-Tyr in alkaline medium exhibits 1:4 stoichiometry (L-Tyr:DPC). Intervention of free radicals was observed in the reaction. Based on the observed orders and experimental evidence, a mechanism involving monoperiodatocuprate(III) (MPC) as the reactive oxidant species has been proposed. A suitable mechanism is proposed through the formation of a complex and free radical intermediate. The products were identified by spot test and characterized by spectral studies. The reaction constants involved in the different steps of the mechanism were calculated. The activation parameters with respect to slow step of the mechanism were computed and are discussed. The thermodynamic quantities were determined for different equilibrium steps. Isokinetic temperature was also calculated and found to be 252.3 K.

Keywords: *Kinetics • Mechanism • L-tyrosine • Diperiodatocuprate(III)*

1. Introduction

Amino acids act not only as the building blocks in protein synthesis but they also play a significant role in metabolism and have been oxidized by a variety of oxidizing agents [1]. The study of the oxidation of amino acids is of interest because of their biological significance and selectivity towards the oxidant to yield the different products [2-4].

L-tyrosine [L-Tyr] is a nonessential amino acid that the body synthesizes from phenylalanine. L-Tyr is important to the structure of almost all proteins in the body. It is also the precursor of several neurotransmitters, including L-dopa, dopamine, norepinephrine and epinephrine. L-Tyr, through its effect on neurotransmitters, may affect several health conditions, including Parkinson's disease, depression and other mood disorders.

In recent years, the study of highest oxidation state of transition metals has intrigued many researchers. Transition metals in higher oxidation states can be stabilized by chelation with suitable polydentate ligands. Periodate and tellurate complexes of copper in its trivalent state have been extensively used in the analysis of several organic compounds [5]. The oxidation reaction usually involves the copper(II)-copper(I) couple and such aspects are detailed in different reviews [6,7]. The use of diperiodatocuprate(III) (DPC) 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 media. DPC is a versatile one-electron oxidant for various organic compounds in an alkaline medium. Copper complexes have occupied a major place in oxidation chemistry due to their abundance and relevance in biological chemistry [8]. Since multiple equilibria between different copper(III) species are

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involved, it would be interesting to know which of the species is the active oxidant.

In earlier reports [9] on DPC oxidation, periodate had a retarding effect and the order in [OH^-] was found to be less than unity in most of the reactions. However in the present study we have obtained entirely different kinetic observations. A literature survey reveals that there are no reports on the oxidation of L-tyrosine by diperiodatocuprate(III). The present study deals with the title reaction to investigate the redox chemistry of DPC in alkaline media to arrive at a suitable mechanism on the basis of kinetic and spectral results and to calculate the thermodynamic quantities of various steps.

2. Experimental Procedures

2.1. Chemicals and Materials

All chemicals used were of reagent grade and millipore water was used throughout the work. The copper(III) periodate complex was prepared [10] and standardized by a literature procedure [11]. The UV-vis spectrum with maximum absorption at 415 nm verified existence of a copper(III) complex. The purity of L-Tyr (S.D. Fine Chem.) sample was checked by comparing its melting point 340-343ºC with literature (343ºC). The solution of L-tyrosine and copper sulphate (BDH) was prepared by dissolving known amounts of the samples in millipore water. Periodate solution was prepared and standardized iodometrically. Required alkalinity and ionic strength were maintained by KOH (BDH) and KNO_3 (Analar), respectively, in reaction solutions.

2.2. Kinetic measurements

The kinetic measurements were performed on a Varian CARY 50 Bio UV–Visible Spectrophotometer. The kinetics were followed under pseudo-first order conditions where [L-Tyr] > [DPC] at 298.1 K, unless specified. The reaction was initiated by mixing the DPC to L-Tyr solution which also contained the required concentration of KNO_3, KOH and KIO_4. The progress of the reaction was followed spectrophotometrically at 415 nm by monitoring the decrease in absorbance due to DPC with the molar absorbancy index, 'ε' to be 6235 ± 100 $dm^3\ mol^{-1}\ cm^{-1}$ (in literature ε = 6230 [10]). It was verified that there is negligible interference from other species present in the reaction mixture at this wavelength.

The pseudo-first order rate constants, 'k_{obs}' were determined from the log (absorbance) *versus* time plots. The plots were linear up to 80% completion of reaction under the range of [OH^-] used. The orders for various species were determined from the slopes of plots of log k_{obs} *versus* respective concentration of species except for [DPC] in which non variation of 'k_{obs}' was observed as expected, due to the reaction conditions. During the kinetics a constant concentration *viz*. 5.0×10^{-4} mol dm^{-3} of KIO_4 was used throughout the study unless otherwise stated. Since periodate is present in excess of DPC, the possibility of oxidation of L-tyrosine by periodate in alkaline medium at 298 K 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-tyrosine. The total concentration of periodate and OH^- was calculated by considering the amount present in the DPC solution and that additionally added. Kinetic runs were also carried out under a nitrogen atmosphere in order to understand the effect of dissolved oxygen on the rate of reaction. No significant difference in the results was obtained under a N_2 atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates. The spectral changes during the reaction are shown in Fig. 1. It is evident from the figure that the concentration of DPC decreases at λ_{max} = 415 nm.

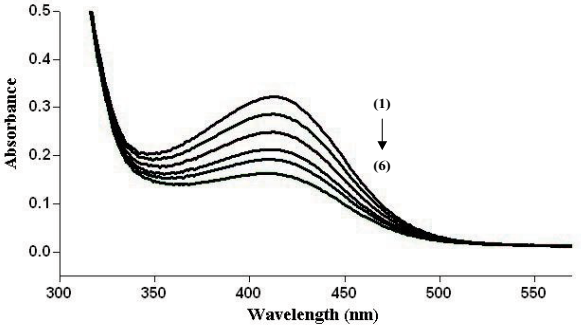
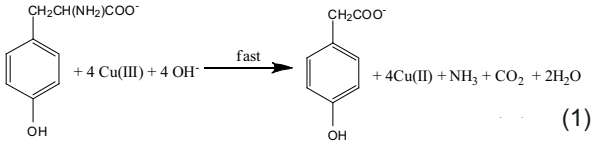


Figure 1. Spectroscopic changes occurring in the oxidation of L-tyrosine by DPC at 298.1 [DPC] = 5.0×10^{-5}, [L-Tyr] = 5.0×10^{-4} mol dm^{-3}, [IO_4^-] = 5.0×10^{-4} mol dm^{-3}, [OH^-] = 0.05 mol dm^{-3} and I = 0.1 mol dm^{-3} with scanning time interval of 30 seconds.

3. Results and Discussion

3.1. Stoichiometry and product analysis

Different sets of reaction mixtures containing an excess of DPC relative to L-Tyr, in the presence of constant amounts of OH^- and KNO_3, were kept for 6 h in a closed vessel under an inert atmosphere. The remaining DPC concentration was estimated spectrophotometrically at λ_{max} = 415 nm. The results indicated 1:4 stoichiometry as given in Eq. 1.



(1)

The main product, 4-hydroxyphenylacetic acid was separated [12] by TLC, using methyl acetate, isopropanol and 20% ammonium hydroxide in the ratio of 35:45:20 (v/v). % yield = 78%; mp 147 to 150ºC; Elemental Analysis: Found % (calcd % for $C_8H_8O_3$) C, 63.15 (63.08); H, 5.30 (5.19).

The IR spectrum of the product showed a broad band at 3387 cm^{-1}, assigned to hydroxyl –OH. An intense sharp band at 1708 cm^{-1} was due to C=O stretching frequencies of the carboxylic group. The product 4-hydroxyphenylacetic acid was further confirmed by its ^1H and ^{13}C NMR spectra. ^1H NMR (300 MHz, DMSO d_6) spectra showed peaks in ppm (1H, s, δ-10.88) carboxylic OH (D_2O exchanged); (1 H, s, δ-4.78) hydroxyl OH (D_2O exchanged); (2Ar H, d, δ-6.91 and 6.91); (2Ar H, t, δ- 6.65 and 6.65); and (1H, s, δ- 2.5). ^{13}C NMR (150 MHz, DMSO d_6) peaks at δ: 173.8 (s, CO); 43.1 (s, CH_2); 152.4-118.2 (Ar carbons). LC-ESI-MS analysis of acidified isolated product indicated the presence of 4-hydroxyphenylacetic acid as molecular ion peak of m/z 152 amu as shown in Fig. 2.

The byproducts were identified as ammonia by Nessler's reagent [11] and CO_2 was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through tube containing limewater. The presence of $Cu(OH)_2$ was confirmed by UV-visible spectroscopic analysis.

Microsoft Excel-2003 was used to perform regression analysis of experimental data to obtain the regression coefficient r and standard deviation S of points from the regression line.

3.2. Reaction orders

The reaction orders were determined from the slope of log (rate constants) *versus* log (concentration) plots by varying the concentrations of L-tyrosine, alkali and periodate, in turn, while keeping all other concentrations and conditions constant.

3.3. Effect of [Diperiodatocuprate (III)]

The oxidant DPC concentration was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} and the fairly constant k_{obs} values indicated the order with respect to [DPC] was unity (Table 1). This was also confirmed by linearity of the plots of log (absorbance) *versus* time ($r \geq 0.986$, $S \leq 0.014$) up to 80% completion of the reaction as shown in Fig. 3.

3.4. Effect of [L-tyrosine]

The effect of L-tyrosine on the rate of reaction was studied at constant concentrations of alkali, DPC and periodate and at a constant ionic strength of 0.10 mol dm^{-3}. The substrate, L-Tyr was varied in the range of 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3}. The k_{obs} values increased with increase in concentration of L-tyrosine (Table 1). The order with respect to [L-Tyr] was found to be less than unity ($r \geq 0.991$, $S \leq 0.008$). This was also confirmed by the plot of k_{obs} *versus* $[\text{L-Tyr}]^{0.77}$ which is linear rather than the direct plot of k_{obs} *versus* [L-Tyr] (Fig. 4).

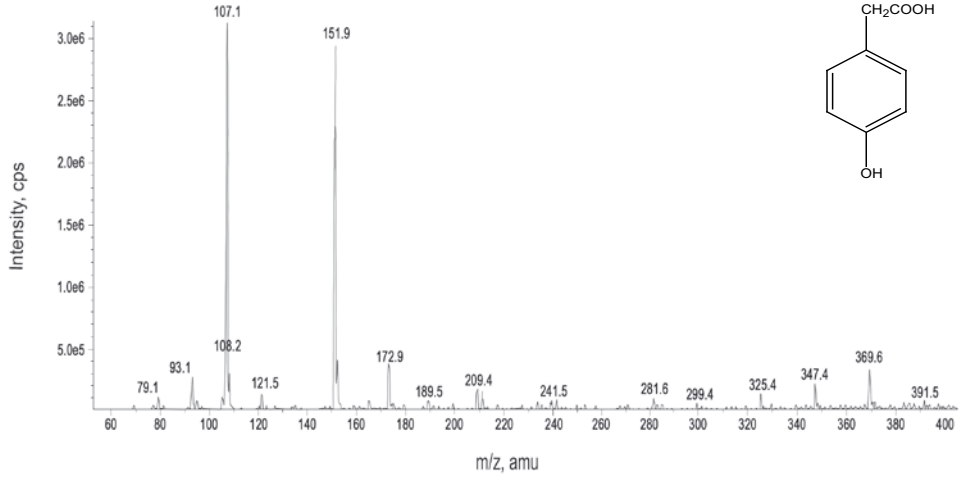


Figure 2. Portion of the LC-MS spectra showing a molecular ion peak (m/z) at 152 amu, confirming the presence of 4-hydroxyphenylacetic acid.

Table 1. Effect of [DPC], [L-Tyr], [IO_4^-] and [OH^-] on diperiodatocuprate(III) oxidation of L-tyrosine in alkaline medium at T = 298.1 K, I = 0.10 mol dm^{-3}.

[DPC]×10^5 (mol dm^{-3})	[L-Tyr]×10^4 (mol dm^{-3})	[IO_4^-]×10^4 (mol dm^{-3})	[OH^-]×10^2 (mol dm^{-3})	k_{obs}×10^3 (s^{-1})	k_{cal}×10^3 (s^{-1})
1.0	5.0	5.0	5.0	3.54	3.58
3.0	5.0	5.0	5.0	3.70	3.58
5.0	5.0	5.0	5.0	3.64	3.58
7.0	5.0	5.0	5.0	3.69	3.58
10.0	5.0	5.0	5.0	3.68	3.58
5.0	1.0	5.0	5.0	0.93	0.94
5.0	3.0	5.0	5.0	2.41	2.44
5.0	5.0	5.0	5.0	3.64	3.58
5.0	8.0	5.0	5.0	4.54	4.86
5.0	10.0	5.0	5.0	5.57	5.52
5.0	5.0	1.0	5.0	6.48	6.27
5.0	5.0	3.0	5.0	4.76	4.54
5.0	5.0	5.0	5.0	3.64	3.58
5.0	5.0	8.0	5.0	2.92	2.73
5.0	5.0	10.0	5.0	2.56	2.42
5.0	5.0	5.0	1.0	5.64	5.42
5.0	5.0	5.0	2.0	4.53	4.80
5.0	5.0	5.0	5.0	3.64	3.58
5.0	5.0	5.0	8.0	2.91	2.86
5.0	5.0	5.0	10.0	2.48	2.51

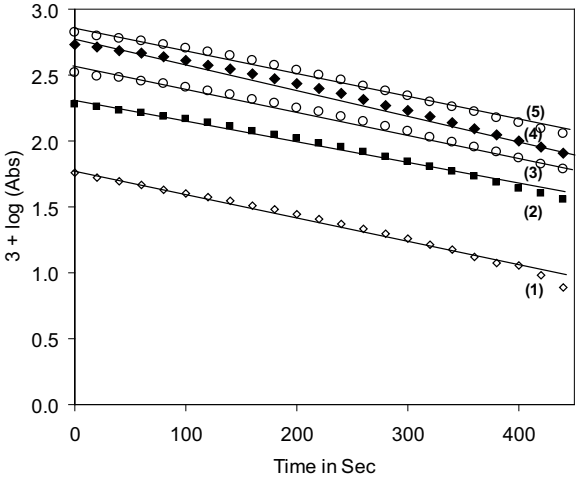


Figure 3. First order plots for the oxidation of L-tyrosine by DPC in aqueous alkaline medium at 298.1 K [DPC] × 10^5 (mol dm^{-3}); (1) 1.0; (2) 3.0; (3) 5.0; (4) 7.0; (5) 10.0.

3.5. Effect of [Alkali]

The effect of increase in concentration of alkali on the reaction was studied at constant concentrations of L-tyrosine, DPC and periodate and at a constant ionic strength of 0.10 mol dm^{-3} at 298.1 K. The rate constants decreased with increase in alkali concentration (Table 1), indicating negative fractional order dependence of rate on alkali concentration ($r \geq 0.988$, $S \leq 0.007$).

3.6. Effect of [Periodate]

The effect of increasing concentration of periodate was studied by varying the periodate concentration from 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} keeping all other reactant concentrations constant. It was found that the added periodate had a retarding effect on the rate of reaction. The order with respect to periodate concentration was negative less than unity ($r \geq 0.9984$, $S \leq 0.004$) (Table 1).

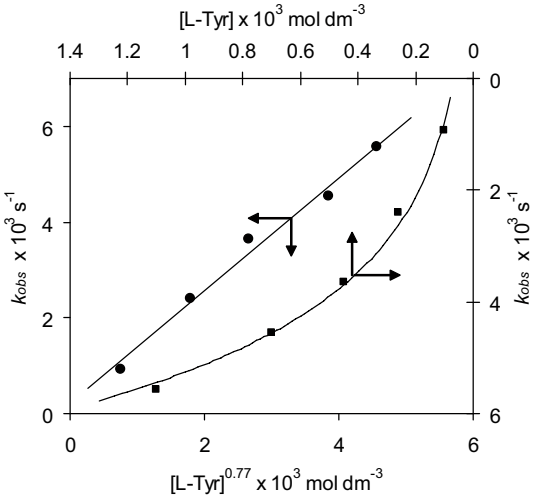


Figure 4. Plots of k_{obs} *versus* [L-Tyr]$^{0.77}$ and k_{obs} *versus* [L-Tyr] (Conditions outlined in Table 1).

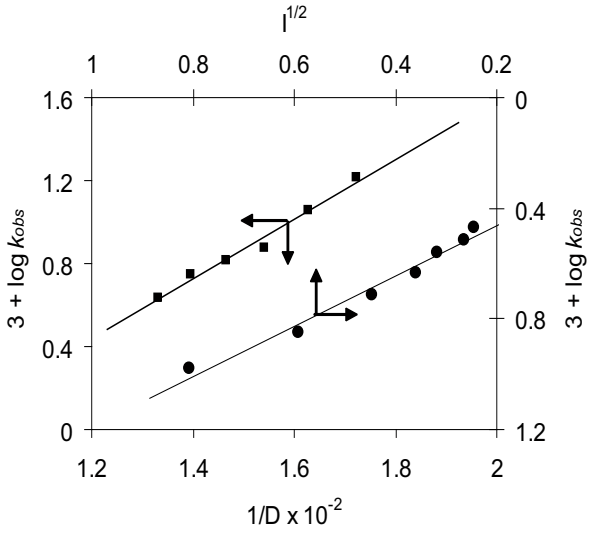


Figure 5. Effect of ionic strength and dielectric constant of the medium on oxidation of L-tyrosine by DPC at 298.1 K.

Under the experimental conditions, the rate law is given as

Rate = k_{obs} [DPC] [L-Tyr]$^{0.77}$[OH$^-$]$^{-0.34}$ [IO$_4^-$]$^{-0.40}$ (Here k_{obs} refers to the observed rate constant under the experimental conditions).

3.7. Effect of Ionic Strength (I) and Dielectric Constant of the Medium (D)

The ionic strength of the reaction medium was varied by using different amounts of KNO_3 from I = 0.06 to 0.65 mol dm^{-3}, while the concentrations of all other reactants were held constant. The rate constants increased with an increase in the ionic strength of the reaction medium. The plot of log k_{obs} *versus* $\sqrt{I}$ was linear with a positive slope (0.92) (Fig. 5).

The effect of polarity of the solvent medium on the rate of the reaction was studied by decreasing the solvent polarity using *t*-butyl alcohol + water mixture as the reaction medium. The Dielectric constants of the medium with various ratios (u/u) of *t*-butyl alcohol and water were calculated by a known method [13]. The decrease in dielectric constant of the reaction medium increased the rate of the reaction. Under our experimental conditions the *t*-butyl alcohol-water mixture of solvents did not undergo oxidation by DPC. The plot of log k_{obs} *versus 1/D* was linear with a positive slope (145.2) (Fig. 5).

3.8. Effect of Initially Added Products

The externally added products, 4-hydroxyphenylacetic acid and copper(II) ($CuSO_4$) in the concentration range of 1.0×10^{-5} to 1.0×10^{-4}, did not have any significant effect on the rate of the reaction.

3.9. Polymerization Study

The intervention of free radicals generated during the oxidation of L-tyrosine with a single equivalent of oxidant, DPC, was expected as it is a non-complimentary reaction. This possibility was tested by adding a free radical scavenger, acrylonitrile, while the reaction was in progress. On diluting the reaction mixture with methanol after the reaction was complete, a copious precipitate resulted, indicating that the oxidation occurred *via* the intervention of a free radical [14,15]. Earlier, it was ascertained that no precipitate formed with either the oxidant or reductant alone.

3.10. Effect of Temperature (T)

The kinetics was studied at six different temperatures (288.1, 293.1, 298.1, 303.1, 308.1 and 313.1) K under varying concentrations of L-tyrosine, alkali and periodate, keeping other conditions constant. The rate constants were found to increase with increase in temperature. The rate constants (k) of the slow step of Scheme 1 were obtained from the slopes and intercepts of 1/k_{obs} *versus* 1/[L-Tyr] plots at six different temperatures and were used to calculate the activation parameters. The energy of activation corresponding to these constants was evaluated from the Arrhenius plot of log *k versus 1/T* ($r \geq 0.996$, $S \leq 0.006$) and other activation parameters obtained are tabulated in Supplementary Table 1 (Supplementary material).

The water–soluble copper(III) periodate complex is reported [10] to be [Cu(HIO$_6$)$_2$(OH)$_2$]$^{7-}$. However, in an aqueous alkaline medium and at a high pH range 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 equilibria [16] (2)-(4), depending on the pH of the solution.

$$H_5IO_6 \overset{K_1}{\rightleftharpoons} H_4IO_6^- + H^+ \qquad K_1 = 5.1 \times 10^{-4} \qquad (2)$$

$$H_4IO_6^- \overset{K_2}{\rightleftharpoons} H_3IO_6^{2-} + H^+ \qquad K_2 = 4.9 \times 10^{-9} \qquad (3)$$

$$H_3IO_6^{2-} \overset{K_3}{\rightleftharpoons} H_2IO_6^{3-} + H^+ \qquad K_3 = 2.5 \times 10^{-12} \qquad (4)$$

Periodic acid exists as H_5IO_6 in acid medium and as $H_4IO^-_6$ near pH 7. Hence, under alkaline conditions as employed in this study, the main species are expected to be $H_3IO_6^{2-}$and $H_2IO_6^{3-}$. Thus, at the pH employed in this study, the soluble copper(III) periodate complex might be $[Cu(OH)_2(H_3IO_6)_2]^{3-}$, a conclusion also supported by earlier work [9,10].

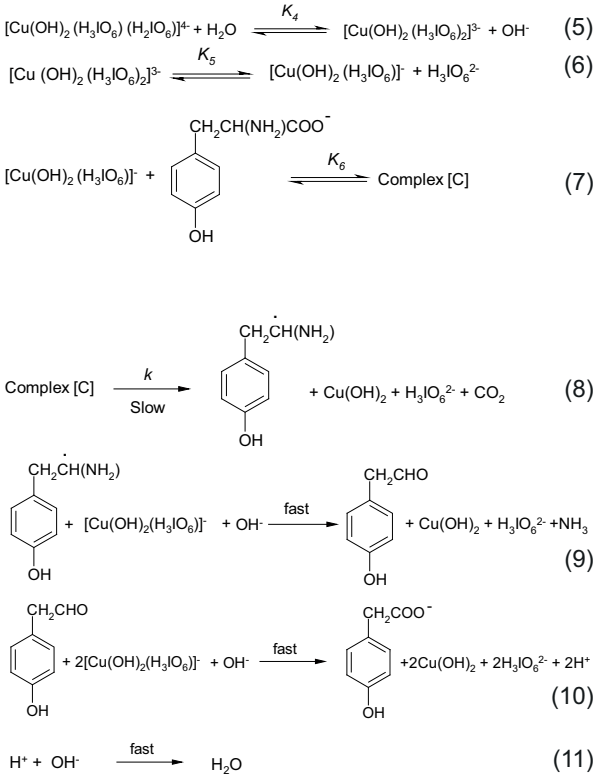
The reaction between the diperiodatocuprate(III) complex and L-tyrosine in alkaline medium has the stoichiometry 1:4 (L-Tyr: DPC) with a first order dependence on [DPC] and an apparent order of less than unit order in [L-Tyr], a negative fractional order dependence both on the [periodate] and [alkali]. No effect of added products was observed. Based on the experimental results, a mechanism is proposed for which all the observed orders in each constituent such as [oxidant], [reductant], $[OH^-]$ and $[IO_4^-]$ may be well accommodated. It is known that in alkali media L-tyrosine exists completely as the anionic form [17].

In most of the reports [9] on DPC oxidation, periodate had a retarding effect and OH^- had an increasing effect on the rate of the reaction. However in the present kinetic study, different kinetic results have been obtained. In this study both OH^- and periodate retarded the rate of the reaction. The result of decrease in rate of reaction with increase in alkalinity (Table 1) can be explained in terms of prevailing equilibrium of formation of $[Cu(OH)_2(H_3IO_6)]^{3-}$ from $[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-}$ hydrolysis as given in the Eq. 5.

Also, the decrease in rate with increase in $[H_3IO_6^{2-}]$ (Table 1) suggests the displacement of periodate species to form monoperiodatocuprate(III) (MPC) species as given in Eq. 6.

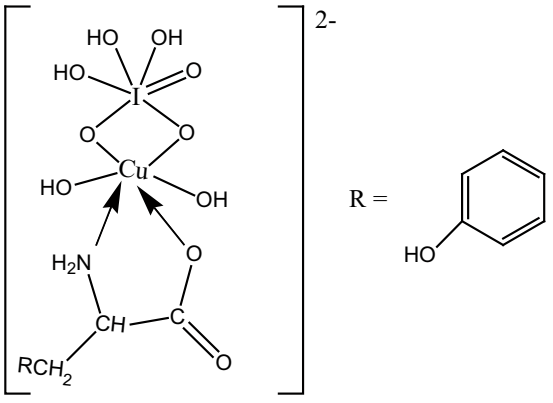
Such types of equilibria (5) and (6) have been well noted in the literature [9,10]. It may be expected that a lower periodate complex such as monoperiodatocuptrate(III) (MPC) is more important in the reaction than the DPC in view of its participation in the reaction as given in Scheme 1. The inverse fractional order in $[H_3IO_6^{2-}]$ might also be due to this reason. Therefore, MPC might be the main reactive form of the oxidant.

The less than unit order in [L-Tyr] presumably results from formation of a complex (C) between the MPC species and L-tyrosine prior to the formation of the products. This complex (C) decomposes in a slow step to form a free radical derived from L-tyrosine. This free radical species further reacts with another molecule of MPC in a fast step to form 4-hydroxyphenylacetal intermediate. The 4-hydroxyphenylacetal then reacts with two more molecules of MPC in a further fast step to form the products such as 4-hydroxyphenylacetic acid, Cu(II) and periodate, as given Scheme 1.



Scheme 1. Detailed Scheme for the oxidation of L-tyrosine by alkaline diperiodatocuprate(III).

Here, K_4, K_5 and K_6 are the equilibrium constants of the reaction Scheme and k is rate constant for slow step of the reaction. 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 (see infra). This type of radical intermediate has also been observed in earlier work [2]. The direct plot of k_{obs} *versus* [L-Tyr] was drawn to discover the presence of a parallel reaction, if one existed, along with the interaction of oxidant and reductant. However the plot of k_{obs} *versus* [L-Tyr] was not linear. Thus, in Scheme 1, the parallel reaction and involvement of two molecules of L-Tyr in the complex are excluded. The probable structure of the complex is given in Scheme 2.



Scheme 2. The probable structure of the complex [C].

Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-Vis spectra of L-tyrosine (5.0×10^{-4} mol dm^{-3}), DPC (5.0×10^{-5} mol dm^{-3}), [OH^-] = 0.05 mol dm^{-3}) and a mixture of DPC, L-Tyr and alkali. A bathochromic shift of about 7 nm from 254 to 261 nm in the spectra of DPC was observed (Fig. 6). The Michaelis-Menten plot (Fig. 7a) also proved the complex formation between DPC and L-tyrosine, which explains the less than unit order dependence on [L-Tyr]. Scheme 1 leads to the rate law (12).

$$\text{rate} = -\frac{d[DPC]}{dt} = \frac{k K_4 K_5 K_6 [\text{L-Tyr}][DPC]}{[OH^-][H_3IO_6^{2-}] + K_4[H_3IO_6^{2-}] + K_4K_5 + K_4K_5K_6[\text{L-Tyr}]} \quad (12)$$

$$k_{obs} = \frac{\text{Rate}}{[DPC]} = \frac{kK_4K_5K_6[\text{L-Tyr}]}{[OH^-][H_3IO_6^{2-}] + K_4[H_3IO_6^{2-}] + K_4K_5 + K_4K_5K_6[\text{L-Tyr}]} \quad (13)$$

This explains all the observed kinetic orders of different species. The rate law (13) can be rearranged in to the following form, which is suitable for verification

$$\frac{1}{k_{obs}} = -\frac{[OH^-][H_3IO_6^{2-}]}{kK_4K_5K_6[\text{L-Tyr}]} + \frac{[H_3IO_6^{2-}]}{kK_5K_6[\text{L-Tyr}]} + \frac{1}{kK_6[\text{L-Tyr}]} + \frac{1}{k} \quad (14)$$

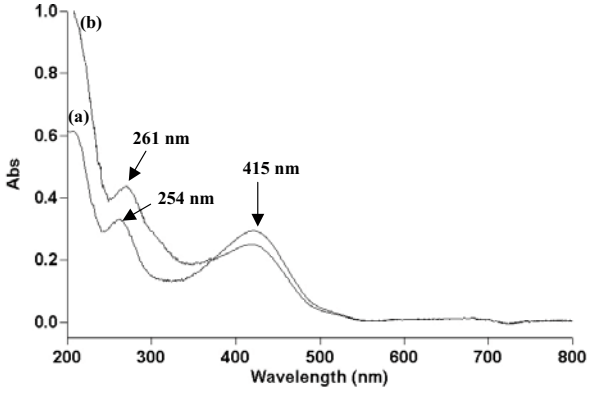


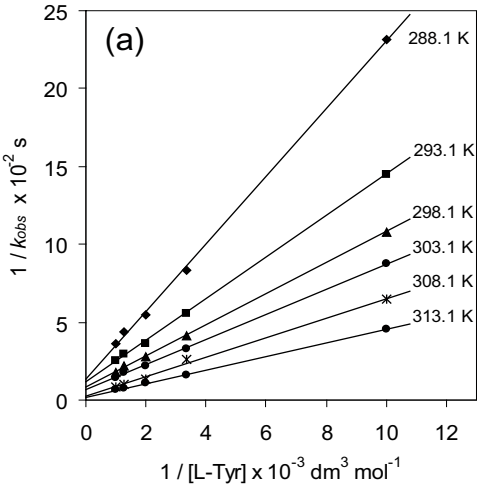
Figure 6. Spectroscopic evidence for the complex formation between DPC and L-Tyr. (a) UV-vis spectra of DPC (254 nm); (b) UV-vis spectra of mixture of DPC and L-Tyr (261 nm).

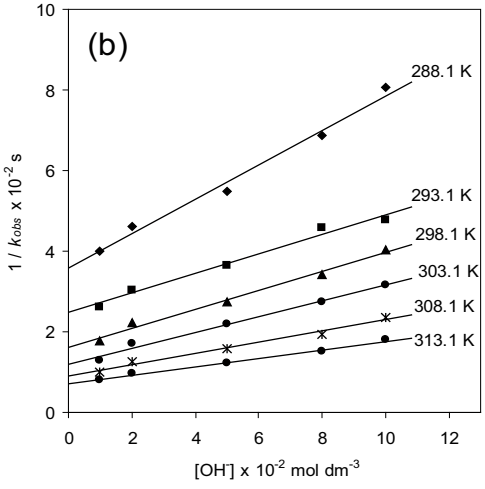
According to Eq. 14, other conditions being constant, plots of $1/k_{obs}$ *versus* [OH^-] ($r \geq 0.991$, $S \leq 0.012$), $1/k_{obs}$ *versus* 1/[L-Tyr] ($r \geq 0.999$, $S \leq 0.014$) and $1/k_{obs}$ *versus* [$H_3IO_6^{2-}$] ($r \geq 0.995$, $S \leq 0.018$) should be linear and were found to be so (Figs. 7a-c). The slopes and intercepts of such plots lead to the values of K_4, K_5, K_6 and k as $(1.2 \pm 0.1)\times10^{-2}$ mol dm^{-3}, $(8.8 \pm 0.4)\times10^{-4}$ mol dm^{-3}, $(3.4 \pm 0.2)\times10^{3}$ dm^3 mol^{-1} and $(1.2 \pm 0.02)\times10^{-2}$ s^{-1}, respectively. These constants were used to calculate the rate constants and compared with the experimental values and found to be in reasonable agreement with each other (Table 1), which further supports Scheme 1. The equilibrium constant K_4 is far greater than K_5. This may be attributed to the greater tendency of DPC to undergo hydrolysis compared to the dissociation of hydrolyzed species in an alkaline medium. The effect of ionic strength and dielectric constant of the medium on the rate qualitatively explains the reaction between two negatively charged ions, as seen in Scheme 1.

The thermodynamic quantities for the first, second and third equilibrium steps of Scheme 1 can be evaluated as follows. The [$H_3IO_6^{2-}$], [L-Tyr] and [OH^-] (as in Table 1) were varied at six different temperatures. The plots of $1/k_{obs}$ *versus* [OH^-], $1/k_{obs}$ *versus* 1/[L-Tyr] and $1/k_{obs}$ *versus* [$H_3IO_6^{2-}$] should be linear (Figs. 7a-c). From the slopes and intercepts, the values of K_4, K_5 and K_6 were calculated in terms of concentration ratios at different temperatures. The equilibrium constants (in terms of concentration ratios) K_4, K_5 and K_6 were divided by the activity coefficient to obtain the true equilibrium constant. The activity coefficient was calculated from the Debye-Huckel limiting law [18].

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

where, γ = activity coefficient, A = 0.509 for an aqueous solution at 25°C, I is the dimensionless ionic strength of the solution and z is the charge number of an ion. Thermodynamic values were calculated using true equilibrium constants, given in Supplementary Table 1 (Supplementary Material). The vant Hoff's plots were made for variation of K_4, K_5 and K_6 with temperature (log K_4 *versus* 1/T ($r \geq 0.994$, $S \leq 0.005$), log K_5 *versus* 1/T ($r \geq 0.987$, $s \leq 0.006$) and (log K_6 *versus* 1/T ($r \geq 0.997$, $S \leq 0.009$) and the values of enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG, were calculated for the first, second and third equilibrium steps. These values are given in Supplementary Table 1 (Supplementary Material). A comparison of the thermodynamic quantities of first step of Scheme 1 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 fast and involves low activation energy [19].





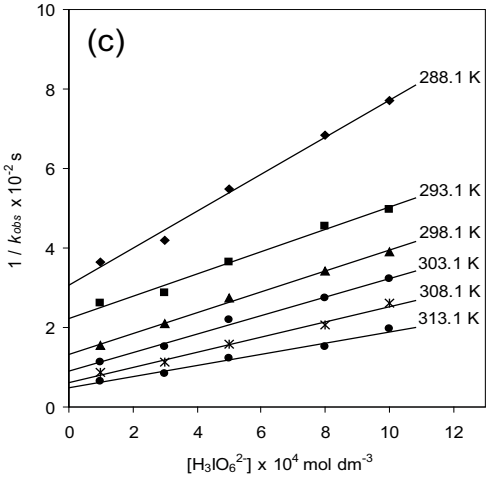


Figure 7. Plots of $1/k_{obs}$ *versus* (a) 1/[L-Tyr], (b) [OH^-] and (c) [$H_3IO_6^{2-}$] at six different temperatures (conditions outlined in Table 1).

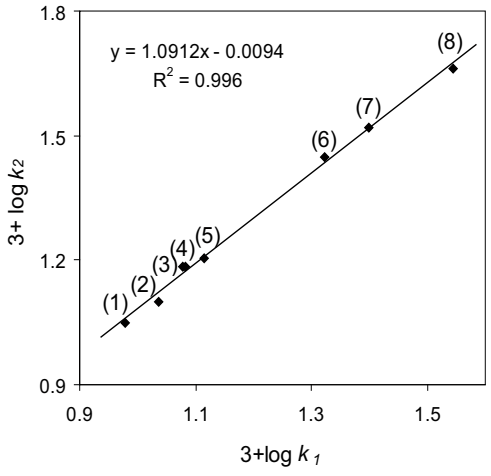


Figure 8. Plot of log k_2 at 303.1 K *versus* log k_1 at 298.1 K for the Isokinetic temperature (Table 1) (1) L-Glutamic acid; (2) L-Tryptophan; (3) L-Tyrosine; (4) L-Valine; (5) L-Aspartic acid; (6) L-Lysine; (7) L-Proline; (8) L-Vanilline.

The value of $\Delta S^{\#}$ is within the range for a radical reaction and has been ascribed to the nature of electron pairing and unpairing processes and to the loss of degrees of freedom formerly available to the reactants upon the formation of rigid transition state [20]. The negative value of $\Delta S^{\#}$ indicates that the complex(C) is more ordered than the reactants [21]. The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as higher rate constant of the slow step, indicate that the oxidation presumably occurs *via* inner-sphere mechanism [22].

3.11. Isokinetic Relationship

The activation parameters for the oxidation of some amino acids by DPC are summarized in Supplementary Table 2 (Supplementary Material). 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 change in the enthalpy 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 the following equation.

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

β is called the Isokinetic temperature; it has been asserted that apparently linear correlations of $\Delta H^{\#}$ with $\Delta S^{\#}$ are sometimes misleading and the evaluation of β by means of the above equation lacks statistical validity [23]. Exner, [24] advocates an alternative method for the treatment of experimental data. If the rates of several reactions in a series have been measured at two temperatures and log k_2 (at T_2) is linearly related to log k_1

(at T1), *i.e.*, log k_2 = a + b log k_1, he proposes that β can be evaluated from the equation.

$$\beta = T_1T_2\,(b\text{-}1)/T_2b\text{-}T_1$$

We have calculated the isokinetic temperature to be 252.3 K by plotting log k_2 at 298 K *versus* log k_1 at 303K ($r \geq 0.997$, $S \leq 0.006$) as in Fig. 8, b is the slope and is found to be 1.09. The value of β (252.3 K) is lower than experimental temperature (298 K). This indicates that the rate is governed by the entropy of activation [25]. The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follows a similar mechanism, as previously suggested.

4. Conclusions

Among various species of DPC in alkaline medium, monoperiodatocuprate(III) (MPC) $[Cu(OH)_2(H_3IO_6)]^-$ is considered as active species for the title reaction. The results indicate that, the role of pH in the reaction medium is crucial. The rate constant of the slow step and other equilibrium constants involved in the mechanism were evaluated and activation parameters with respect to slow step of reaction were computed. The overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.

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