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Journal of MOLECULAR STRUCTURE

Journal of Molecular Structure 827 (2007) 137-144

www.elsevier.com/locate/molstruc

Oxidation of threonine by the analytical reagent diperiodatocuprate(III) – An autocatalysed reaction

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Received 9 March 2006; received in revised form 1 May 2006; accepted 10 May 2006 Available online 21 June 2006

Abstract

The kinetics of Cu(II) autocatalysed oxidation of threonine by well-recognized analytical reagent diperiodatocuprate(III) in aqueous alkaline medium at a constant ionic strength of 0.5 mol dm^{-3} was studied spectrophotometrically. The reaction between diperiodatocuprate(III) and threonine in alkaline medium exhibits 2:1 stoichiometry (DPC: threonine). The reaction is of first order in each [DPC] and [threonine] and less than unit order in [alkali]. Periodate has retarding effect on the rate of reaction. Ionic strength has negligible effect on the reaction. Increase in dielectric constant of the medium with decrease in the rate of the reaction was observed. The product, Cu(II), catalyses the reaction with a fractional order. The main products were identified by spot test and I.R. A composite mechanism involving the monoperiodatocuptrate(III) (MPC) as the reactive species of the oxidant in uncatalysed and autocatalysed reaction has been proposed. Activation parameters and the reaction constants involved in the different steps of the mechanisms are calculated.

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Keywords: Kinetics; Oxidation; Autocatalysis; Threonine

1. Introduction

Non-linear chemical phenomena that have been found in various chemical reactions [1-6] in the catalytic autoxidation of various substrates by different oxidants are reported. It has also been reported that the oxidation of certain biological substrates and polyphenols by air oxygen catalysed by copper(II) and iron(II) coordination compounds may exhibit transient oscillations in a batch reactor [7,8].

The periodate and tellurate complexes of copper in its trivalent state have been extensively used in the analysis of several organic compounds. The kinetics of selfdecomposition of these complexes were studied in some detail. Movius [9] reported the reactivity of few alcohols with diperiodatocuprate(III) (DPC). DPC is a versatile

* Corresponding author. *E-mail address:* sureshtuwar@yahoo.co.in (S.M. Tuwar). one-electron oxidant for the oxidation of various organic compounds in alkaline medium and its use as an analytical reagent is now well recognized [10] and also used in the estimation of amino acids. Cu(III) is shown to be an intermediate in the Cu(II)-catalysed oxidation of amino acids by peroxidisulphate [11]. The use of DPC as an oxidant in alkaline medium may not be new but it is restricted to a few cases [12] due to the fact of its limited stability in aqueous medium. Moreover, when the DPC 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 not only act as building blocks in protein synthesis but also play significant role in metabolism. Threonine is one of the 20 different kinds of α -amino acids found in proteins in all living organisms. It is required for synthesis of proteins to maintain normal growth and nitrogen balance in the body. In glycoproteins, the

^{0022-2860/\$ -} see front matter @ 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2006.05.015

carbohydrates are covalently linked by *O*-glycoside bonds to threonine residues of proteins.

Amino acids have been oxidized by a variety of reagents [13], under different experimental conditions. Although several types of organic [14] and inorganic [15,16] substrates are oxidized by DPC in aqueous alkaline medium, only a few reports exist on the oxidation of threonine in aqueous alkaline medium. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants [17,18]. In many cases amino acids undergo oxidative decarboxylation and deamination. Javaprakash Rao et al. [19] suggested that oxidation of ∞ -amino acids by two electron oxidant such as diperiodatoargentate(III) in alkaline medium involves two electron transfer, from the amino acid to the oxidant to give iminoacid intermediate in the rate determining step. This intermediate subsequently undergoes hydrolysis to yield keto acids. One electron oxidants such as ceric sulphate [20], peroxomonosulphate [21] and hexacynoferrate(III) [22] also oxidize amino acids to keto acids. But other studies with amino acids report, the oxidation products as the corresponding aldehydes [23]. Thus, the study of amino acids becomes important because of specificity of their oxidative products, biological significance and selectivity towards the oxidants. There is no report in the literature on the oxidation of threonine by DPC autocatalysed by Cu(II). To understand more about the autocatalysis of Cu(II) in oxidation by DPC and in order to explore the mechanism of oxidation by Cu(III) ion in aqueous alkaline medium, we have selected threonine as a substrate for oxidation. The present study deals with the title reaction to investigate the redox chemistry of Cu(III) and to arrive at a plausible mechanism.

2. Experimental

2.1. Materials and reagents

All chemicals used were of reagent grade. Double distilled water was used throughout the work. Stock solution of Threonine (Lobo Chemie) was prepared by dissolving the appropriate amount of sample in water. The purity of the sample was checked by TLC and its m.p. 253 °C (Lit. value 256 °C).

2.2. Preparation of DPC

The diperiodatocuprate(III), (DPC) is prepared [24] by oxidizing Cu(II) in the alkaline medium. Copper sulphate (3.54 g), potassium metaperiodate (6.8 g), potassium persulphate (2.2 g) and KOH (9 g) were added in 250 cm³ water. The mixture was heated to boiling for about 20 min on a hot plate with constant stirring. The boiling mixture turned intensely red and the boiling was continued for another 20 min for the completion of the reaction. The mixture was then cooled, filtered through sintered glass crucible (G-4) and diluted to

 250 cm^3 with distilled water. The solution obtained was found fairly stable in room temperature for several months. The complex was characterized by its UV/ Visible spectrum, which exhibits a broad absorption band at 415 nm. The aqueous solution of DPC was standardized by iodometric titration and gravimetrically by thiocynate [25] a method.

The Cu(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 [26] at neutral pH maintained by phosphate buffer. Since periodate is present in excess in DPC, the possibility of oxidation of threonine by periodate in alkaline medium at 25 °C was tested, by following the reaction iodometrically. It was found that there was no significant reaction under the experimental conditions employed compared to the DPC oxidation of threonine. KOH and KNO₃ (BDH, AR) were employed to maintain the required alkalinity and ionic strength, respectively, in reaction solutions.

2.3. Kinetic measurements

The oxidation of thereonine by DPC was followed under pseudo-first order conditions where [thereonine] was excess over [DPC] at 25 ± 0.1 °C. The reaction was initiated by mixing the required quantities of previously thermostatted solution of threonine and DPC, which also contained definite quantities of KOH, KNO₃ and IO₄⁻ to maintain the required alkalinity, ionic strength and periodate, respectively. 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 of a thermostatted compartment of a Hitachi model 150-20 spectrophotometer at its absorbance maximum, 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 absorbance by DPC to Beer's law at 415 nm was verified earlier and the molar absorbance coefficient, 'ɛ', was found to be $6250 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at this wavelength. The first order rate constants, k_{obs} , were obtained from the plots of log (a - x) vs. time, where 'a' and 'x' are the initial concentration and change in concentration of DPC at time 't', respectively. The plots were linear up to about 25% completion of the reaction (non-linearity above 25% was due to the autocatalysis, explained elsewhere) and the rate constants were reproducible within \pm 5%. The spectral changes during the reaction are shown in Fig. 1(A), in which [DPC] decreases at



Fig. 1. (A) Spectroscopic changes of DPC during the reaction period in the Cu(II) autocatalysed oxidation of threonine by diperiodatocuprate(III) at 25 °C (scanning interval 30 s). [DPC] = 1.0×10^{-4} , [TRE] = 1.0×10^{-3} , [OH⁻] = 0.1, [IO₄⁻] = 1.0×10^{-3} , $I = 0.5/\text{mol dm}^{-3}$. (B) Autocatalysis of Cu(II) on oxidation of threonine by alkaline DPC at 25 °C at various [Cu(II)]. [DPC] = 1.3×10^{-4} , [TRE] = 1.0×10^{-3} , [OH⁻] = 0.1, [IO₄⁻] = 1.0×10^{-3} , [OH⁻] = 0.1, [IO₄⁻] = 1.0×10^{-3} , I = 0.5, Cu(II) = 1 (1×10^{-6}), 2 (2×10^{-6}), 3 (4×10^{-6})/mol dm⁻³

415 nm during the reaction. The autocatalysis by Cu(II) is also shown in Fig. 1(B).

3. Results and discussions

3.1. Stoichiometry and product analysis

Different sets of reaction mixtures containing different concentrations of threonine 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 [threonine], the unreacted DPC was estimated spectrophotometrically by measuring the absorbance at 415 nm. The results indicated that two moles of DPC consumed one mole of threonine as in Eq. (1).

The main reaction products were identified as aldehyde [27] by a spot test, ammonia [25(b)] by Nessler's reagent and Cu(II) by its spot test [28]. The CO₂ evolved is tested by bubbling nitrogen gas through a tube containing lime water [29] after acidification. The quantitative estimation of aldehyde as its 2,4-DNP derivative was nearly 80% and it also was confirmed by its I.R. spectrum which showed [30] a band at 2919 cm⁻¹ due to aldehydic C–H stretching. It was further observed that the aldehyde does not undergo further oxidation under the prevailing kinetic conditions. Tests for the corresponding acid were negative.

3.2. Reaction order

The order with respect to [threonine], [alkali] and [periodate] was determined by $\log k_{obs}$ vs. log concentration plots and the obtained orders were also confirmed by differential method by the plot log (initial rate) vs. log concentration using the equation log(rate) = $\log k + n \log c$; these orders were obtained by varying the concentration of DPC, threonine, periodate and alkali in turn while keeping others constant.

The concentration of DPC was varied in the range, $2.0 \times 10^{-5} - 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ at fixed [threenine], $[OH^-]$, $[IO_4^-]$ and ionic strength. The non-variation in the pseudo-first order rate constants at various concentrations of DPC indicates the order in [DPC] as unity (Table 1). This was also confirmed from the linearity of plots of log absorbance vs. time (r > 0.9994, $S \leq 0.026$) up to 25% completion of the reaction. The substrate, [threonine], was varied in the range of 5.0×10^{-4} - 5.0×10^{-3} mol dm⁻³ at 25 °C keeping all other reactant concentrations constant (Table 1). The k_{obs} values were increased with increase in concentration of threonine and its order was found to be unity (Table 1). The effect of [alkali] on the rate of reaction was studied at constant concentrations of threonine, DPC, IO4- and ionic strength at 0.5 mol dm^{-3} . The rate constants were increased with increase in [alkali] and the order was found to be less than unity (Table 1).

3.3. Effect of periodate

The effect of $[IO_4^{-1}]$ was observed by varying the concentration from 5.0×10^{-4} to 5.0×10^{-3} mol dm⁻³ at constant concentrations of DPC, threonine, alkali and constant ionic strength (Table 1). It was found that the added periodate retarded the rate, and order in periodate was inverse fractional.



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Table 1

Effect of variation of [DPC], [TRE], [OH⁻] and $[IO_4^-]$ on autocatalysed oxidation of threonine by [DPC] at 25 °C, I = 0.5 mol dm⁻³

$[DPC] \times 10^4$ (mol dm ⁻³)	$[TRE] \times 10^{3}$ (mol dm ⁻³)	$[OH^{-}] \times 10$ (mol dm ⁻³)	$[IO_4^{-}] \times 10^3$ (mol dm ⁻³)	$k_{\rm obs} \times 10^2 ({\rm s}^{-1})$	
				Exptl. ^a	Calc. ^a
0.2	1.0	1.0	1.0	1.84	1.91
0.4	1.0	1.0	1.0	1.87	1.91
0.8	1.0	1.0	1.0	1.84	1.91
1.0	1.0	1.0	1.0	1.85	1.91
2.0	1.0	1.0	1.0	1.85	1.91
3.0	1.0	1.0	1.0	1.86	1.91
1.0	0.5	1.0	1.0	0.99	0.96
1.0	0.8	1.0	1.0	1.53	1.53
1.0	1.0	1.0	1.0	1.85	1.91
1.0	2.0	1.0	1.0	3.75	3.82
1.0	4.0	1.0	1.0	7.67	7.65
1.0	5.0	1.0	1.0	9.41	9.56
1.0	1.0	0.5	1.0	1.29	1.27
1.0	1.0	0.8	1.0	1.69	1.70
1.0	1.0	1.0	1.0	1.85	1.91
1.0	1.0	2.0	1.0	2.51	2.54
1.0	1.0	4.0	1.0	3.07	3.04
1.0	1.0	5.0	1.0	3.16	3.17
1.0	1.0	1.0	0.5	2.62	2.55
1.0	1.0	1.0	0.8	2.29	2.12
1.0	1.0	1.0	1.0	1.85	1.91
1.0	1.0	1.0	2.0	1.36	1.28
1.0	1.0	1.0	4.0	0.75	0.77
1.0	1.0	1.0	5.0	0.69	0.64

^a Experimental and calculated.

3.4. 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 0.5 mol dm⁻³ at constant [DPC], [threonine], $[IO_4^{-1}]$ and [alkali]. It was found that the ionic strength has negligible effect on the rate of the reaction.

The relative permittivity (ε_T) 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 [31]. It was also found that there was no reaction of the solvent with the oxidant under the experimental conditions used. The k_{obs} values were decreased with the increase in the dielectric constant of the medium (Table 2(A)). The plot of log k_{obs} vs. $1/\varepsilon_T$ was linear ($r \ge 0.9989$, $S \le 0.0122$) (Fig. 2) with positive slope.

3.5. Effect of initially added products

Effect of initially added product Cu(II) was studied in the [Cu(II)] range 1.0×10^{-6} - 1.0×10^{-5} mol dm⁻³, when all other reactant concentrations were kept constant. The initially added Cu(II) enhanced the rate of reaction (Table 2(B)) with an order ≈ 0.25 . However, the other product, 2-hydroxy propanal, did not affect the rate of the reaction.

Table 2		
% *	D	$k_{\rm obs} \times 10^2 ({\rm s}^{-1})$
(A) Effect of solvent polarity	on the oxidation of threonir	e by DPC at 25 °C
5.0	74.9	1.86
10.0	71.3	2.00
15.0	67.7	2.14
20.0	64.0	2.26
25.0	60.4	2.60
$[Cu(II)] \times 10^6 \text{ (mol dm}^{-3}\text{)}$	$k_{\text{obs(autocat)}} \times 10^2 (\text{s}^{-1})$	$k_{\rm cal} \times 10^2 ({\rm s}^{-1})$
(B) Effect of added product	, $Cu(II)$, on oxidation of th	reonine by alkaline
DPC		
1.0	2.01	2.07
2.0	2.26	2.23
4.0	2.66	2.55
6.0	2.95	2.87
8.0	3.21	3.19

 $[DPC] = 1.0 \times 10^{-4};$ $[TRE] = 1.0 \times 10^{-3};$ $[OH^{-}] = 0.1;$ $[IO_4^{-}] = 1.0 \times 10^{-3};$ $I = 0.5/mol dm^{-3}.$

3.51

3.47

* % of *t*-butyl alcohol and water



Fig. 2. Verification of rate law (Eq. (5)) in the form of Eq. (4) for Scheme 1, on oxidation of threonine by DPC at 25 °C (Conditions as in Table 1).

3.6. 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 intervention of free radicals in the reaction. The blank experiment of either DPC or threonine in acrylonitrile alone did not induce polymerization under the same condition as those induced with reaction mixture. Initially added acrylonitrile decreases the rate indicating the free radical intervention, which is the case in earlier work [32].

3.7. Effect of temperature

The rate of reaction was measured at different temperatures at constant concentrations of reactants and other conditions being constant. The rate of reaction increased with the increase of temperature. The activation energy was calculated from the slope of the plot of log k_{obs} vs. 1/T ($r \ge 0.9948$) and used to calculate other activation parameters (Table 3).

The water soluble Cu(III) periodate is to be existed [33] in the form of $Na_7KH(Cu(IO_6)_2)$. However, periodate under pH >12 has not been existing as IO_6^{5-} ; its form [34] is purely depending on the pH of the medium. There are H_5IO_6 and $H_4IO_6^-$ at pH below 7, $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$ of pH above 7, in addition to these polymeric forms at higher $[IO_4^{-}]$. Thus, in the present study, the periodate may be in the form of $H_3IO_6^{2-}$ or $H_2IO_6^{3-}$ and may be both as pH > 11. On incorporating the periodate species in the copper(III) periodate, it can be written $[Cu(H_3IO_6)_2]^-$. However, Lister [35] proposed as the copper(III) periodate into three forms in alkaline medium diperiodatocuprate(III) (DPC), monoperiodatocuprate(III) (MPC) and tetrahydroxocuprate(III). The latter is ruled out [36] as its equilibrium constant [35] is 8.0×10^{-11} at 40 °C. Hence, in the present study DPC and MPC are to be considered as active forms of cop-

Table 3

Effect of temperature on Cu(II) autocatalysed oxidation of threonine by alkaline diperiodatocuprate(III)

Temp. (K)		$k_{\rm obs} \times 10^2 ({\rm s}^{-1})$
(A) Effect of temperature		
298		1.85
303		2.59
308		3.59
313		4.84
(B) Activation parameters		
$Ea (kJ mol^{-1})$		48.7 ± 0.5
$\Delta H^{\#}$ (kJ mol ⁻¹)		46.2 ± 0.5
$\Delta S^{\#} (\mathbf{J} \mathbf{K}^{-1} \operatorname{mol}^{-1})$		-122 ± 2
$\Delta G^{\#} (\text{kJ mol}^{-1})$		83 ± 2
Log A		6.8 ± 0.2
$[DPC] = 1.0 \times 10^{-4}; [TRE] = 1.0 \times 10^{-3};$	$[OH^{-}] = 0.1;$	$[{\rm IO_4}^-] = 1.0 \times$

 10^{-3} ; $I = 0.5 \text{ /mol dm}^{-3}$.

per(III) periodate complex. However, the reports reveal that the actual molecular formulae of DPC and MPC are not known. Based on the active form of periodate, enhancing effect of $[OH^-]$ and retarding effect of $[IO_4^-]$, the plausible forms of MPC and DPC are given in Eqs. (2) and (3).

$$[\operatorname{Cu}(\operatorname{H}_{3}\operatorname{IO}_{6})_{2}]^{-} + \operatorname{OH}^{-} \stackrel{\kappa_{1}}{\rightleftharpoons} [\operatorname{Cu}(\operatorname{H}_{2}\operatorname{IO}_{6})(\operatorname{H}_{3}\operatorname{IO}_{6})]^{2-} + \operatorname{H}_{2}\operatorname{O}$$

$$(2)$$

$$\begin{aligned} \left[\operatorname{Cu}(\operatorname{H}_{2}\operatorname{IO}_{6})(\operatorname{H}_{3}\operatorname{IO}_{6})\right]^{2-} + 2\operatorname{H}_{2}\operatorname{O} &\stackrel{\operatorname{A}_{2}}{\rightleftharpoons} \operatorname{Cu}(\operatorname{H}_{2}\operatorname{IO}_{6})(\operatorname{H}_{2}\operatorname{O})_{2}\right] \\ &+ \left[\operatorname{H}_{3}\operatorname{IO}_{6}\right]^{2-} \end{aligned} (3)$$

In Eq. (3), bidentate ligand, $H_3IO_6^{2-}$, has been replaced by water molecules to give diaquomonoperiodato copper(III) complex (MPC). The similar forms of complexes have been reported for Nickel(IV) periodate [37] and silver(III) periodate [38] complexes.

The test for intervention of free radicals during the reaction and first order each in oxidant, DPC and reductant, threonine is a simple second order reaction, determined from the k_{obs} values at the initial state of reaction and by considering the active species of Cu(III) as MPC, the results can be accommodated as in Scheme 1.

In Scheme 1, the active form of Cu(III) periodate, the monoperiodatocuprate(III), reacts with threonine in a slow step to give a free radical by the cleavage of α -hydrogen atom of threonine. This free radical reacts with another molecule of MPC in a fast step to give products. Scheme 1 leads to the following rate law (4):

$$-\frac{d[DPC]}{dt} = rate_{1}$$

$$= \frac{k_{u}K_{1}K_{2}[Cu(III)]_{T}[OH^{-}][TRE]_{T}}{[H_{3}IO_{6}^{2-}] + K_{1}[OH^{-}][H_{3}IO_{6}^{2-}] + K_{1}K_{2}[OH^{-}]}$$

$$k_{obs} = \frac{k_{u}K_{1}K_{2}[TRE][OH^{-}]_{T}}{[H_{3}IO_{6}^{2-}] + K_{1}[OH^{-}][H_{3}IO_{6}^{2-}] + K_{1}K_{2}[OH^{-}]}$$
(5)

Eq. (5) can be verified in the following form:

$$\begin{bmatrix} Cu(H_{3}IO_{6})_{2}]^{-} + OH^{-} & \underbrace{K_{1}} & [Cu(H_{2}IO_{6})(H_{3}IO_{6})]^{2} + H_{2}O \\ \begin{bmatrix} Cu(H_{2}IO_{6})(H_{3}IO_{6})]^{2} + 2H_{2}O & \underbrace{K_{2}} & Cu(H_{2}IO_{6})(H_{2}O)_{2}] + [H_{3}IO_{6}]^{2} \\ \begin{bmatrix} Cu(H_{2}IO_{6})(H_{2}O)_{2}] & + H_{3}C - CH & \underbrace{C}_{H} & \underbrace{C}_{H} & -CH & \underbrace{C}_{H} & H_{3}C - CH & \underbrace{C}_{H} & H_{3}C - CH & \underbrace{C}_{H} & H_{3}C - CH & \underbrace{C}_{H} & H_{3}C + Cu^{2} \\ & + H_{2}IO_{6}^{3} + CO_{2} \\ & + H_{2}IO_{6}^{3} + CO_{2} \\ & + H_{2}IO_{6}^{3} + Cu^{2} + 2H_{2}O \\ & + H_{2}IO_{6}^{3} + CU^{2} + 2H_{2}O$$

Scheme 1. Mechanism with respect to reactive species.

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$$\frac{1}{k_{\rm obs}} = \frac{[{\rm H}_3 {\rm IO}_6^{2-}]}{k_u K_1 K_2 [{\rm TRE}] [{\rm OH}^-]} + \frac{[{\rm H}_3 {\rm IO}_6^{2-}]}{k_u K_2 [{\rm TRE}]} + \frac{1}{k_u [{\rm TRE}]}$$
(6)

The plot of $1/k_{obs}$ versus $[H_3IO_6]^{2-}$, 1/[TRE] and $1/[OH^-]$ should be linear and found so as in Fig. 2. The slopes and intercepts of such plots give the k_u , K_1 and K_2 as $38.1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $0.2 \text{ dm}^3 \text{ mol}^{-1}$ and 5.05×10^{-2} mol dm⁻³, respectively. These data are used to reproduce the k_{obs} for different experimental conditions. The 'k'



calculated and k_{obs} are reasonably in agreement with each other, which fortifies the mechanism (Table 1).

The autocatalysis by one of the products, Cu(II), and first order each in DPC and threonine may be depicted as in Scheme 2.

Scheme 2 is in accordance with the fractional order in [Cu(II)] and kinetic evidence for complex formation between threonine and Cu²⁺ from the Michaelis-Menten plot of $1/k_{obs}$ vs. 1/[Cu(II)]. The complexes between mono and bivalent states of copper and amines and amino acids are quite common examples. The complexes of copper in trivalent state with amines and amino acids are rare [39] and appearing only as a transient species. Such complexes have been proposed as intermediates in Cu(II) catalysed oxidation of amines by hydrogen peroxide. Hence, in the present study, the complex between Cu(II) and the amino acid, threonine, is in expected direction and it is also evidenced by the hypsochromic shift of Cu(II) from 670 to 617 nm in presence of threonine. This may be more active than the threonine alone where there is unit order each in DPC and threonine for an outersphere mechanism for the transfer of electrons from reductant to oxidant (Scheme 1). The higher rate observed for autocatalysis of Cu(II) is

also due to -I effect of -OH group present in threonine which induces a greater positive charge on the nitrogen atom facilitating complex formation. Autocatalysis in DPC oxidations has not been reported so far. It may be a first of its kind in Cu(III) oxidations.

The diamagnetic, dsp^2 , square planar structure of copper(III) periodate in the form of DPC, MPC and paramagnetic dsp^2 complex of Cu(II) and threonine can be shown below.



Rate law for Scheme 2 is derived by using Eqs. (2) and (3) for active form of copper(III) periodate as in Eq. (7),

$$-\frac{d[DPC]}{dt} = rate_{2}$$

$$= \frac{k_{a}K_{1}K_{2}K_{3}[Cu(III)]_{T}[TRE]_{T}[OH^{-}][Cu(II)]}{[H_{3}IO_{6}^{2-}] + K_{1}[OH^{-}][H_{3}IO_{6}^{2-}] + K_{1}K_{2}[OH^{-}]}$$
(7)

The composite rate law for Schemes 1 and 2 using Eqs. (4) and (7) leads to Eq. (8).

$$Rate_{total} = rate_{1} + rate_{2}$$

$$= \frac{K_{1}K_{2}[Cu(III)]_{T}[TRE]_{T}[OH^{-}]}{[H_{3}IO_{6}^{2-}] + K_{1}[OH^{-}][H_{3}IO_{6}^{2-}] + K_{1}K_{2}[OH^{-}]} \times [k_{u} + K_{3}k_{a}[Cu(II)]]$$

$$k_{obs(autocat)} = \frac{K_{1}K_{2}[TRE]_{T}[OH^{-}]}{[H_{3}IO_{6}^{2-}] + K_{1}[OH^{-}][H_{3}IO_{6}^{2-}] + K_{1}K_{2}[OH^{-}]} \times [k_{u} + K_{3}k_{a}[Cu(II)]]$$
(8)
(8)
(9)

Scheme 2. Mechanism with species including autocatalysis.

Eq. (9) is verified (Fig. 2) and the $k_a K_3$ calculated from the graph of $k_{obs(autocat)}$ vs. [Cu(II)]. $k_a K_3$ value is found to be 3.17×10^6 dm⁶ mol⁻² s⁻¹. Using the data K_1 , K_2 , $k_a K_3$ and k_u , the experimental rate constants are regenerated for [Cu(II)] variation, compared with the $k_{obs(autocat)}$, and were found to be in good agreement with each other (Table 2(B)).

Non-variation of rate of reaction with increase in ionic strength [40] is due to the involvement of non-ionic species or ionic and neutral species in the rate determining step. It supports the mechanisms of Schemes 1 and 2 as non-ionic species like MPC and negatively charged threonine are involved.

Increase in rate with decreasing of the dielectric constant [41] of the media is due to the interaction of a negatively charged threonine and a polar molecule, monoperiodatocuprate(III), to give a less solvating activated complex in a polar solvent than the reactants alone. It may be due to the loss of degree of freedom in the activated complex to give a rigid sphere. Dealing with the activation parameters for the reaction is complicated as it involves autocatalysis by Cu(II). However, the large negative value of entropy activation [42] (Table 3) and high positive value of $\Delta G^{\#}$ explain the loss of degree of freedom in the activated complex which might be a rigid sphere.

The large negative value of entropy of activation, enhancing the rate in lower dielectric medium and non-variation of rate with ionic strength variation, clearly envisages the transfer of electron from substrate to oxidant in an outer sphere mechanism. It is also supported by the fact that the derived small rate constant, $k_u = 38.1$ dm³ mol⁻¹ s⁻¹, entrenches the outer sphere mechanism.

4. Summary

Among various species of DPC in alkaline medium, monoperiodatocuprate (MPC) is considered as active species for the title reaction. One of the products Cu(II) catalyses the reaction. The reaction proceeds through the intervention free radicals. Equilibrium constants involved in the mechanism and activation parameters of the reaction were evaluated. The overall mechanistic sequence described here is consistent with product studies, mechanistic studies and kinetic studies.

Acknowledgements

One of the authors S.M. Tuwar thanks the UGC, Regional Office Bangalore, for providing financial assistance.

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