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On 18th February 2015

Organized by

Department of Chemistry, Easwari Engineering College (SRM Group of Institutions), Chennai-600089, India.

Mechanistic Investigation of Copper (II) Catalysed Oxidative Deamination and Decarboxylation of Histidine by Peroxomonosulphate in Buffered Medium

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ABSTRACT: A systematic kinetic study on the oxidation of histidine by peroxomonosulphate (PMS) in acetic acid-sodium acetate buffered medium (pH 3.6-4.8) and the catalytic effect of copper(II) was investigated. EPR spectral data ruled out the involvement of free radical intermediate. Formation of copper – histidine – PMS complex was established by cyclic voltammetric and UV –visible absorption studies. NMR studies confirmed that the product formed in this reaction was imidazole -4-acetaldehyde. A suitable mechanism was proposed.

KEYWORDS: Oxidation kinetics, Histidine, Peroxomonosulphate, Copper(II), EPR study, Cyclic voltammetric, NMR studies.

I. INTRODUCTION

Histidine is one of the essential basic amino acids, needed for growth, repair of tissues, production of both red and white blood cells. It helps to protect the body from damage caused due to radiation and to remove heavy metals from the body. Kinetics and mechanism of oxidation of histidine using several oxidants such as dodecatungstocobaltate (III) and trans-cyclohexane-1,2-diamine-N,N,N′,N′-tetraacetato manganate(III) [1], tetra chloroaurate(III) [2], hexacyanoferrate [3], Mn(III) [4] were reported. Peroxomonosulphate ion (HSO_5^-), the anion of caro's acid (H_2SO_5), is an inexpensive and environmentally benign oxidant and has wider applications [5]. In addition to high reactivity, it is quite stable at room temperature and easy to handle compared to hydrogen peroxide. Kinetics and mechanism of oxidation of PMS by several compounds have been reported [6-8]. The presence of an α-amino group in the side chain and a pyridine type nitrogen in the imidazole ring of the histidine molecule, each with a centre of high electron density, facilitating the formation of strong chelates with divalent and trivalent metal ions [9].The role of L-histidine during its interaction with copper(II)–albumin and in the cellular uptake of copper has generated considerable interest to determine the physico-chemical properties and the structure of physiological copper(II)–L-histidine complex [10]. A review on the copper(II)-L-histidine complex was reported recently [11]. The present study is carried out to mimic the oxidation in vitro and also to determine the rate of oxidation, the catalytic effect of Cu(II), identification of product formed and to propose the suitable mechanism as well.

II. EXPERIMENTAL

The kinetics of oxidation of histidine in acetic acid–sodium acetate buffered medium both in presence and absence of copper (II) ions as catalyst by PMS was studied under pseudo first order conditions i.e., [histidine] >> [PMS] and was monitored by following $[PMS]_t$ at various time intervals by iodometric method.

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2.1 Measurement of Rate Constants: The reaction mixture containing histidine in buffer solution (pH 4) was taken in a blackened iodine flask and kept in a thermostat at 308 K. A known volume of PMS solution, thermostatted at the same temperature separately, was pipetted out into the reaction mixture, and simultaneously a timer was started. Consumption of PMS was monitored by iodometric method. The same methodology was followed for copper(II) catalysed reaction as well. The rate of the reaction was studied under pseudo first order conditions

i.e., [histidine] » [PMS]. The rate of the reaction followed first order kinetics (Fig.1) and the rate constants k_{obs} were calculated from the linear plots of log $[PMS]_t$ versus time according to the Equation (1).

$$\log [PMS]_t = \log [PMS]_0 - kt / 2.303 \quad (1)$$

The method of least squares was used to calculate the slope and the intercept in all the cases. The relative standard errors of the above mentioned rate constants for a single run and the relative standard errors of the mean were about 2%. The pH was measured using a DPH 500 global pH meter, calibrated with a buffer solution of pH 4.0

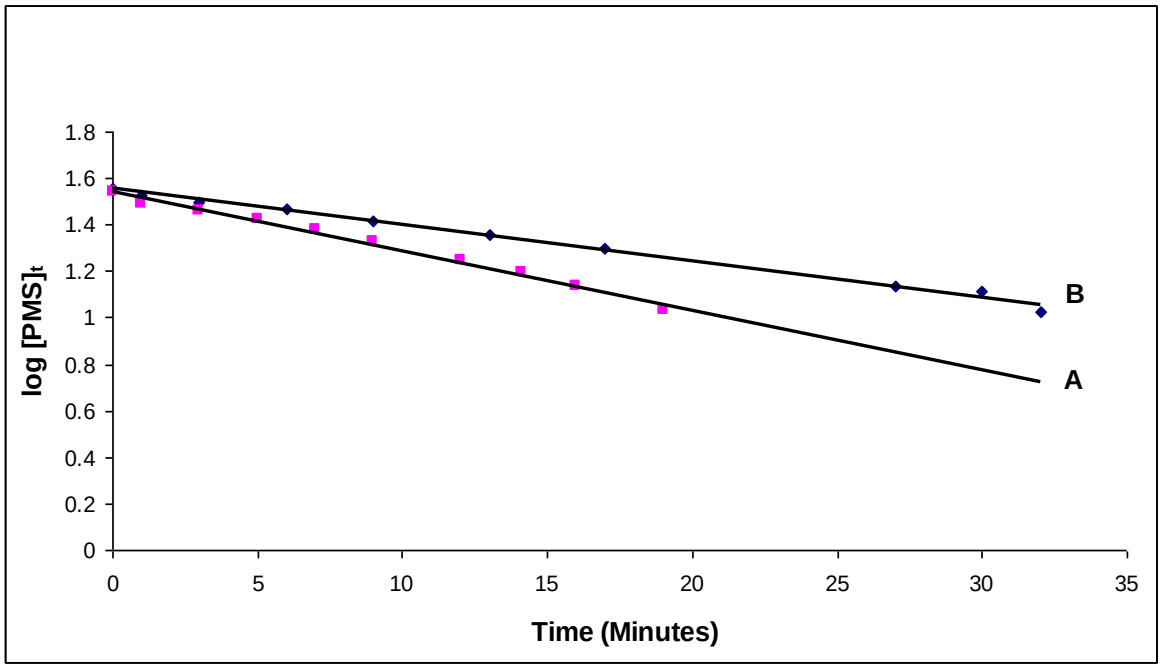

Fig. 1 Plot of log $[PMS]_t$ vs time both in the presence and absence of copper(II) at 308 K
A: In the presence of copper(II)
[histidine]= 0.05 mol dm^{-3}; [sodium acetate] = 0.085 mol dm^{-3}; [Cu(II)] = 2.5 x 10^{-3} mol dm^{-3}; pH = 4.0 ± 0.1; [PMS] = 3.86 x 10^{-3} mol dm^{-3}
B: In the absence of copper(II)
[histidine] = 0.05 mol dm^{-3}; [sodium acetate] = 0.085 mol dm^{-3}; pH = 4.0 ± 0.1; [PMS] = 3.86 x 10^{-3} mol dm^{-3}

2.2 Catalytic system: Copper sulphate pentahydrate was used as a homogeneous catalyst. The catalytic effect of copper(II) was well pronounced at 2.5 x 10^{-3} mol dm^{-3} and hence the concentration of Cu(II) in the reaction mixture was kept at 2.5 x 10^{-3} mol dm^{-3} except for copper variations.

2.3 Spectral Analysis: The reaction mixture was scanned in the ultraviolet and visible regions on a Perkin Elmer LS 25 UV spectrophotometer to unravel the intermediate formed if any during the course of the reaction. The reaction mixture was prepared by adding PMS to histidine in acetic acid - sodium acetate buffer. The same method was followed for the

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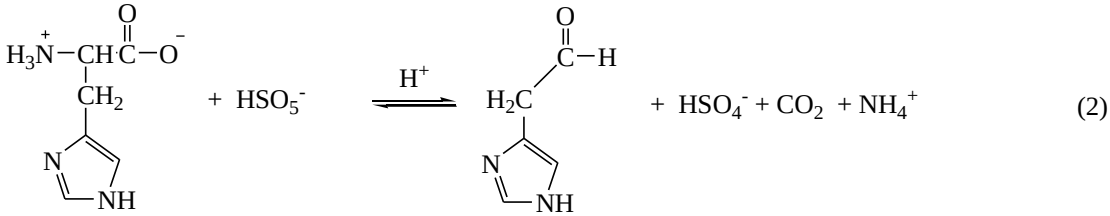
copper(II) catalysed reaction as well. The spectral studies were carried out immediately after preparing the reaction mixture in the 1 cm cell at room temperature (298 K). Time history of the absorption spectra was also recorded.

2.3.1 EPR spectral analysis: The reaction mixture was scanned on a Varian E-112 EPR Spectrometer, Microwave power: 20 micro Watt (DPPH: 'g' Value = 2.00232, Magnetic field strength: 3300 G) to detect the formation of free radical intermediate during the course of the reaction. The reaction mixture was prepared in acetic acid- sodium acetate buffered medium by adding PMS (3.86×10^{-3} mol dm^{-3}) to histidine (5×10^{-2} mol dm^{-3}) both in presence of copper(II) sulphate, (2.5×10^{-3} mol dm^{-3}) and absence of copper(II) sulphate. The spectra were taken immediately after preparing the reaction mixture and also at different time intervals.

2.3.2 Cyclic voltammetric studies: Electrochemical studies were carried out with a CHI 760C – CH Instrument Inc., USA. Cyclic voltammetric measurements were made at room temperature in an undivided cell (C-3 cell stand) with a glassy carbon, platinum counter electrode and a calomel reference electrode. All potentials were reported with respect to calomel electrode (SCE). The solutions were deoxygenated by passing dry nitrogen through the solution for 15 minutes prior to the experiments, and during the experiments the flow was maintained over the solution.

III. RESULTS AND DISCUSSION

3.1 Stoichiometry and Product Analysis: The stoichiometry of the reactions was determined for both copper(II) catalysed and uncatalysed reactions for the reaction mixtures containing a large excess of [PMS] over [histidine]. Then the reaction mixture was allowed to stand for 48 h and the unconsumed PMS was estimated iodometrically. Corrections for the self-decomposition of PMS were made from the values obtained from the control experiments. The observed stoichiometry of the reaction in both copper(II) catalysed and uncatalysed reaction (histidine: PMS = 1: 1) when [PMS] > [histidine] was represented by the following equation.



(2)

The product analysis was done as given below. The reaction mixture containing a large excess of PMS over histidine was allowed to stand for 48 h in a blackened vessel at room temperature. Excess PMS present in the reaction mixture was destroyed by adding sodium bisulphite and then the mixture was extracted with dichloromethane. The organic layer was separated, dried and given for IR analysis. From the IR data, absorption at 3427 cm^{-1} due to amine, 2900 cm^{-1} CH stretching and 1645 cm^{-1} due to C=O of carboxyl group. The product was further confirmed by ^1H NMR studies. ^1HNMR studies were carried out with a JEOL AL 300 MHz. The NMR data was given below δ 3.27 (CH_2, 2H, s), δ 7.72 (Imidazole CH, 1H, s), δ 8.46 (imidazole, CH, 1H, s), δ 9.69 (CHO, 1H, s) which confirmed the formation of imidazole-4- acetaldehyde (Fig. 2). The yield of imidazole-4- acetaldehyde is 80 %.

3.2 Effect of [PMS] on k_{obs}: The values of k_{obs} were calculated for different concentrations of PMS by maintaining the other parameters at constant values. The results showed that the rate constant decreased with increase in [PMS] both in presence and absence of copper(II) catalyst. The plots of k_{obs}^{-1} versus [PMS] were straight lines with positive intercepts. This might be due to the dimerization of the active complex formed between histidine and PMS.

3.3 Effect of [histidine] on k_{obs}: The values of k_{obs} were calculated for different concentrations of histidine both in presence and absence of copper(II) ions by keeping other parameters at constant values. Perusal of the kinetic results showed that the rate constant increased with increase in [histidine] and the plots of k_{obs} versus [histidine] were linear, irrespective of the presence and absence of Cu(II) ion catalyst. The positive intercept obtained in the above plots revealed that the reaction proceeded by two steps, one dependent on [histidine] and the other independent of [histidine].

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The histidine independent step was due to the self-decomposition of PMS under the experimental conditions employed in this study. The evolution of oxygen during the self decomposition of PMS was confirmed by the colour change with alkaline sodium dithionite activated by indigo carmine [12].

3.4 Effect of pH on k_{obs}: By keeping other parameters at constant values, the effect of pH on the rate constants were studied by varying the pH values (3.6 - 4.8) both in the presence and absence of copper(II) ions. The rate constant, k_{obs} values, increased with increase in pH values in both the cases. The rate of the reaction was very fast above a pH value of 4.8 and hence the study was restricted to pH value below 4.8. The plot of k_{obs} x $[H^+]$ versus $[H^+]$ was a straight line in both the cases.

3.5 Effect of Temperature on k_{obs}: The reaction was carried out at five different temperatures, viz, 303, 308, 313, 318 and 323 K by keeping all other parameters constant. The k_{obs} increased with increase in the temperature. The plot of log k_{obs} versus (1/T) was a straight line (Arrhenius plot) and the plot of log (k_{obs}/T) versus (1/T) was also linear (Eyring's plot). From the slope and the intercept of the straight line, the thermodynamic parameters were calculated which are shown in Table 1. The high positive values of free energy of activation ($\Delta G^{\ddagger}$) and enthalpy of activation ($\Delta H^{\ddagger}$) indicated that transition state was highly solvated while the negative values of entropy of activation ($\Delta S^{\ddagger}$) suggested the formation of rigid transition state with reduction in degree of freedom of molecules.

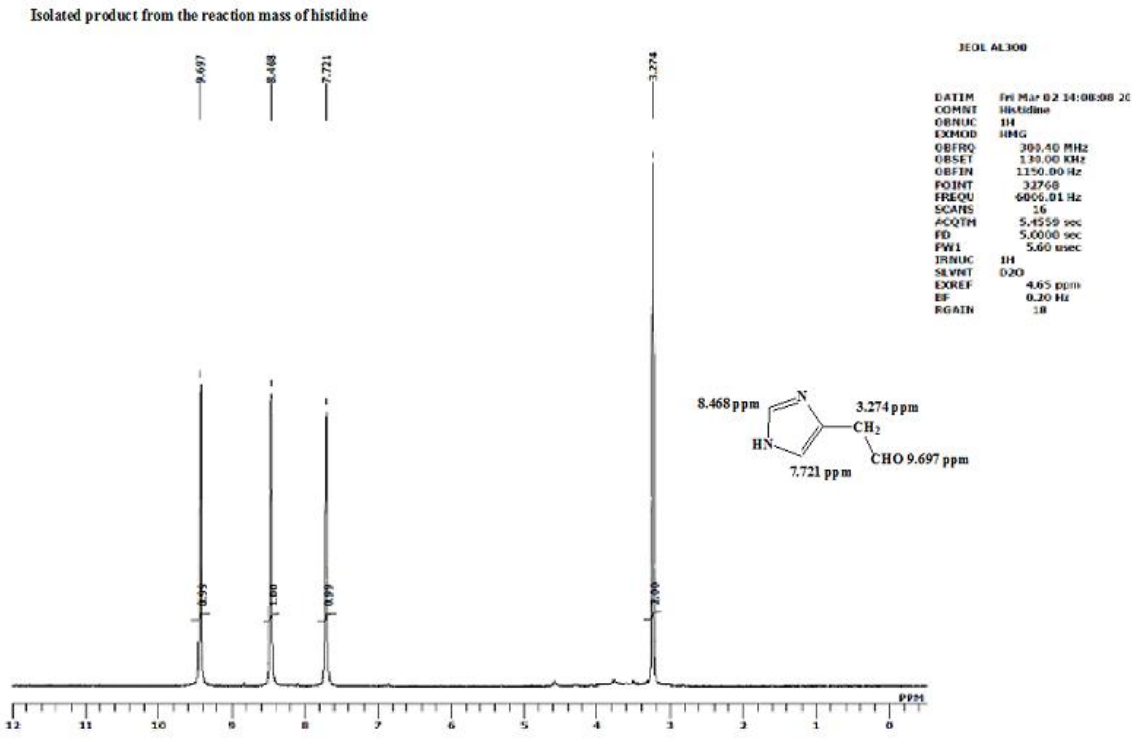

Fig. 2 NMR spectrum of the product [histidine] = 2.5 x 10^{-2} mol dm^{-3}; pH =4.0 ± 0.1; [sodium acetate] = 8.5 x 10^{-2} mol dm^{-3}; [PMS] = 8.0 x 10^{-2} mol dm^{-3}

3.6 Effect of [copper(II)] on k_{obs}: The effect of [copper(II)] on k_{obs} was studied by determining the values of k_{obs} at different concentrations of [Cu(II)], by keeping other parameters at pre-determined values. The kinetic results showed that the rate increased with increase in [Cu(II)] and the plot of k_{obs} versus [Cu(II)] was linear with a positive intercept which revealed that the reaction proceeded by two steps, one of which was catalysed by copper(II) ions.

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3.7 Effect of Dielectric Constant on k_{obs}: The effect of dielectric constant (ε) of the reaction mixture both in presence and absence of copper(II) catalyst on the reaction rate was studied by using two different solvents, such as 2-methlylpropan-2-ol and acetonitrile. The k_{obs} remained unaffected with the increase in composition of the solvents in both the cases which ruled out the formation of polar intermediate.

3.8 Effect of ionic strength on k_{obs}: The effect of ionic strength on the reaction rate was studied by varying the ionic strength of the medium and maintaining the other parameters at constant values. The increase in the ionic strength of the medium had no effect on the k_{obs} value. This result suggested that HSO_5^- may attack amino group of histidine rather than the carboxylate group of histidine.

3.9 Catalytic activity: According to Moelwyn-Hughes [13] the catalytic constant was calculated from the following equation.

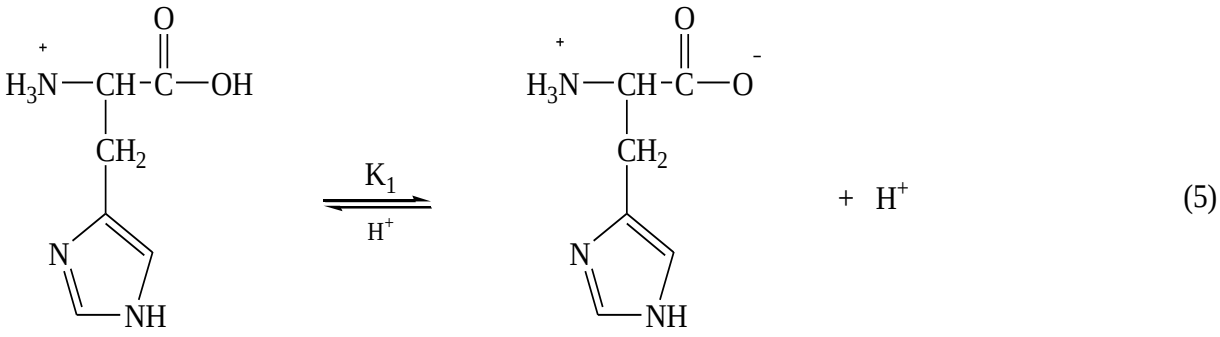
$$k_T = k_U + k_c [Cu(II)]^x \qquad (3)$$

Where
k_T is the observed pseudo first order rate constant in the presence of Cu(II) catalyst
k_U is pseudo first order rate constant for the uncatalysed reaction
k_c is catalytic constant
x is the order of the reaction with respect to copper(II) catalyst
In the present investigation 'x' value was found to be unity, since the rate was first order with respect to [Cu(II)].

$$k_c = \frac{k_T - k_U}{[Cu(II)]^X} \qquad (4)$$

The values of k_c were calculated from the equation 4. The values of k_c were evaluated for copper(II) catalysed reaction at different temperatures and were found to increase with increase in temperature. Further log k_c versus 1/T and log (k_c/T) versus 1/T were linear. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were also calculated and are presented in Table 1.

3.10 Test for free radical intermediates: In this kinetics study, the reaction failed to initiate the polymerisation of added acrylonitrile, which ruled out the involvement of free radical intermediates. Further EPR spectral measurement confirmed the non-involvement of free radicals in this reaction.



(5)

3.11 EPR spectral analysis: Peroxomonosulphate ion (HSO_5^-) is a weak acid with pK_a 9.4. PMS exist as HSO_5^- in acidic condition [15]. EPR spectrum was taken for the oxidation of histidine by PMS in presence and absence of copper(II) catalyst at pH (4.0 ± 0.1).No EPR signal was obtained for the reaction mixture in the absence of copper (II), however EPR signal was obtained for the reaction mixture in the presence of copper (II) ions. EPR spectrum of copper(II) in water showed only one signal, however copper (II) in acetate buffer showed four signals revealing the formation of copper-acetate complex. EPR spectrum of the mixture containing histidine in buffered medium in presence and absence of copper(II) were taken. No signal was obtained for histidine molecular species, but in presence of copper(II)

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showed signal which corresponds to the formation of copper(II)-histidine complex. Spectra taken at various time intervals revealed that the position (g value) and nature of signal did not get altered which confirmed that the structure and oxidation state of Cu(II) remained unchanged throughout the reaction.

3.12 UV- visible spectral analysis: UV- visible spectrum of the mixture containing histidine and PMS in acetic acid and sodium acetate buffered medium showed an absorption maximum at 235 nm. Analysis of the spectrum at various time intervals showed an increase of absorbance due to the formation of the intermediate imine. The absorption spectra of the reaction mixture in presence of copper(II) catalyst (2.5 x10^{-3} mol dm^{-3}) also showed absorption peak at 235 nm. The time history of the plot revealed that the absorption at 235 nm increased. The absorption band due to copper(II) ions was absent in this absorption spectra. The d-d transition ($^2E_g \rightarrow {}^2T_{2g}$) specific for Cu(II) complexes gave very weak signals which were not visible at lower concentrations. However the absorption spectra recorded at higher concentration of copper(II) ions (1.5x10^{-2} mol dm^{-3}) showed an absorption peak at 647 nm.

To ascertain the peak due to copper(II) ions in the reaction mixture, the spectrum was recorded with higher concentration of copper(II) ions (1.5 x 10^{-2} mol dm^{-3}). λ_{max} values of copper (II) ions in water was at 804 nm. When acetate buffer was added to this solution, the λ_{max} was shifted to 761 nm indicating the formation of copper acetate complex. After the addition of histidine to the reaction mixture, λ_{max} was shifted to 667 nm revealing the formation copper acetate-histidine complex. When the reaction mixture reacted with PMS, λ_{max} was further lowered to 647 nm revealing the formation of copper acetate-histidine-PMS complex. A. hypso chromic shift observed in all these cases revealed the formation of different copper(II) complexes.

3.13 Cyclic voltammetric studies: The cyclic voltammogram of Cu(II) ions and acetate buffer system was recorded. The peak potential corresponding to reduction of Cu(II) ions was -0.71 V. The cyclic voltammogram of histidine in buffered medium showed the peak potential at -0.33 V. The cyclic voltammogram of PMS in buffered medium has peak potential for reduction at -0.80 V. The interaction between Cu(II) ions and histidine showed three different reduction peak potentials: -0.25, -0.71 and -0.87 V. Comparing these peak potentials with those of free copper(II) ions in buffer, histidine in buffer and PMS in buffer, it was observed that a new peak -0.25 V has appeared. This could be assigned to reduction of 1:1 Cu(II) histidine complex. Since, the value was lower than that of free histidine (-0.33 V), it is confirmed that histidine in the Cu(II) complex has more tendency to undergo reduction than the free histidine.

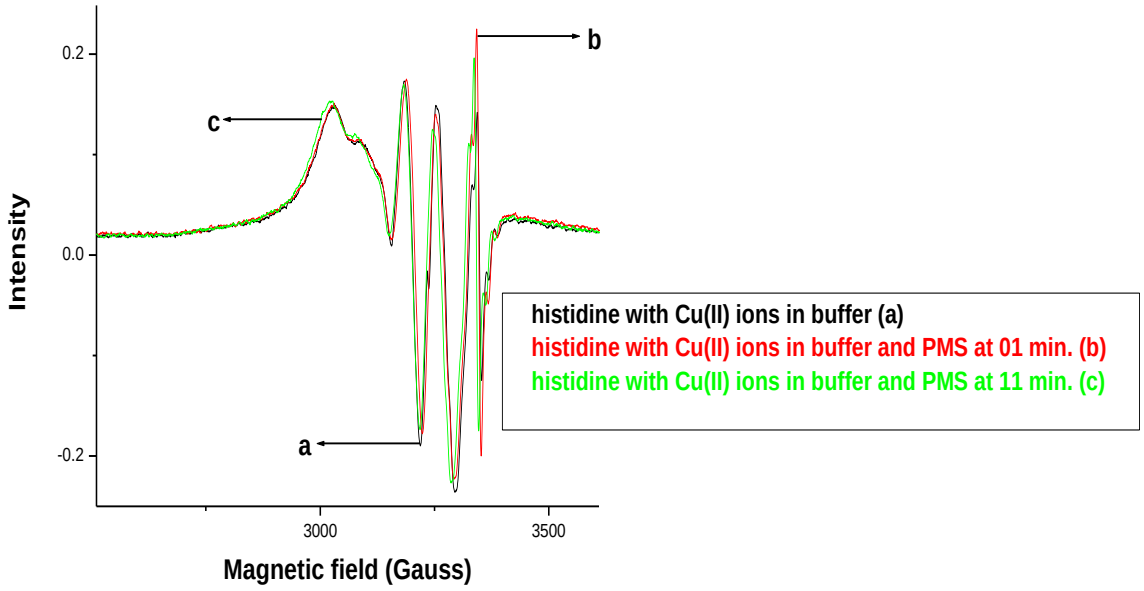

Fig. 3 EPR spectra of the histidine reaction mixture in the presence of copper(II) ions
[histidine] = 5 x 10^{-2} mol dm^{-3} ; [copper(II)] = 2.5 x 10^{-3} mol dm^{-3} ; pH = 4.0 ± 0.1 ; [PMS] = 4.0 x 10^{-3} mol dm^{-3}

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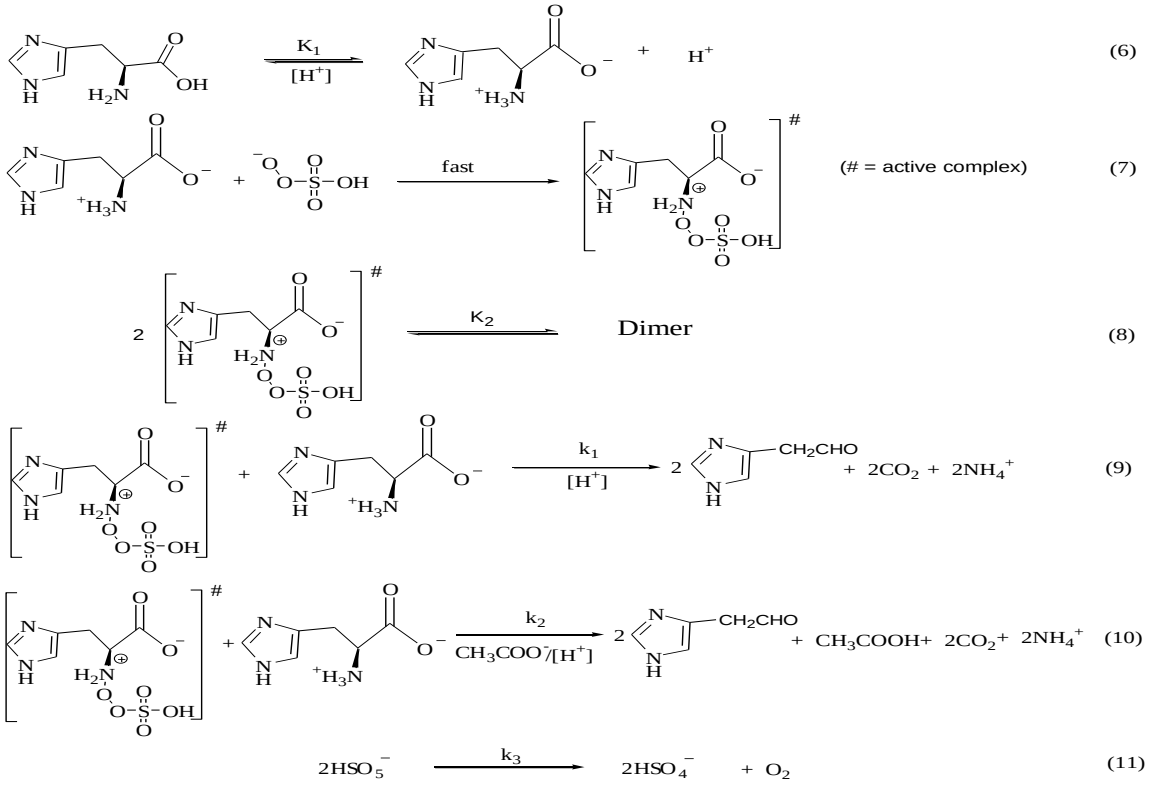
The cyclic voltammogram of Cu(II)- histidine - PMS system showed two peaks at -0.45 V and -0.79 V. The peak potential of Cu(II) ions in Cu(II) – histidine complex was shifted to a low value (-0.45 V and -0.79 V) compared to those of Cu(II)-histidine complex (-0.71 V and -0.87 V). So, from the study of cyclic voltammetry it was established that Cu(II) form complex with histidine and PMS form complex with Cu(II) – histidine complex. The PMS complexation was observed to lower reduction potential of Cu(II) - histidine complex. Though PMS can donate electrons to form complex with Cu(II), electron might be donated back predominantly, in order to decrease the reduction potential of Cu(II). Hence PMS might also be interacting with free histidine forms histidine – PMS complex, thus establishing existence of Cu(II) – histidine – PMS complex and histidine – PMS complex. ESR spectral data also confirmed distorted octahedron complex.

Table 1: Kinetic and thermodynamic parameters for the oxidation of Histidine at 308 K

Histidine	E_a kJ/mol	$\Delta H^{\ddagger}$ kJ/mol	$\Delta S^{\ddagger}$ J/K/mol	$\Delta G^{\ddagger}$ kJ/mol	$10^4 \times k_1K_1 mol^{-1} dm^3 s^{-1}$	$10^2 \times k_2K_1 Mol^{-1} dm^3 s^{-1}$	$10^4 \times k_3 Mol^{-1} dm^3 s^{-1}$
without Cu(II) catalyst	30.79	29.55	- 151.86	76.33	18.21	2.28	0.56
with Cu(II) catalyst	28.80	27.46	- 154.02	74.89		226.8	
Catalytic constant k_c	25.42	25.04	-143.66	69.29			

Based on the above discussion, the detailed mechanism of the uncatalyzed reaction pathway is given in Scheme 1.



(Scheme 1)

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k_{obs} was derived as

$$k_{obs} = \frac{2k_1K_1\,[\text{Histidine}]+2k_2K_1\,[\text{Histidine}]\,[OAc^-] + 2k_3[H^+]}{[H^+]\,\{1 + K_2\,[HSO_5^-]} \quad (12)$$

From the eq.(12) k_1K_1, k_2K_1 & k_3 were calculated from different plots and the average values are given in Table 1.

Similarly k_{obs} was derived for the copper(II) catalysed reaction as

Substituting $[HSO_5^-]_f$

$$k_{obs} = \frac{2k_1K_1\,[\text{Histidine}]+2\,k_2K_1[\text{Histidine}]\,[Cu^{2+}] + k_3[H^+]}{[H^+]\,\{1 + K_2'\,[HSO_5^-]} \quad (13)$$

From eq. (13) values of k_1K_1, k_2K_1 & k_3 were calculated from different plots and average values are given in Table 1

V. CONCLUSION

Kinetics of the oxidation of histidine by peroxomonosulphate in acetic acid-sodium acetate buffered medium (pH 3.6-5.2) in presence and absence of copper(II) ions was investigated. Catalytic constant k_c has been calculated as 0.15 $mol^{-1}dm^3s^{-1}$, when the [Cu (II)] catalyst was 2.5 $x10^{-3}$ mol dm^{-3} .The effect of ionic strength on the rate revealed that PMS attack the amino group of histidine rather than the carboxylate group of histidine. ESR spectra taken for the reaction mixture at various time intervals, confirmed the reaction proceeding through molecular intermediate. Cyclic voltammetric studies and UV-Visible absorption studies established the formation of copper(II) – histidine – PMS complex. A suitable reaction mechanism was proposed to explain the experimental observation.

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