National conference on Nanomaterials for Environmental [NCNER-2015]
19th & 20th of March 2015

Copper(II) Catalysed Oxidative Deamination of Lysine by Peroxomonosulphate

Paramasivam Suresh Kumar[1], Srinivasalu Kutti Rani[2], Deivanayagam Easwaramoorthy[2]*

[1]Department of Chemistry, NPR College of Engineering and Technology, Natham, Tamil Nadu, India.
[2]Department of Chemistry, B.S. Abdur Rahman University, Chennai, Tamil Nadu, India

Abstract: Catalytic effect of copper (II) ions on the oxidation of lysine present in the waste water by peroxomonosulphate (PMS), an eco friendly oxidant in acetic acid-sodium acetate buffered medium (pH 3.6-4.8) was studied. To propose the reaction mechanism, the reaction was studied with different solvent composition and the rate remained constant ruling out the formation of more polar intermediate. The rate constant was not affected by the variation in the ionic strength of the medium ruling out the interaction between carboxylate group of lysine and SO_5^{2-} of PMS. EPR spectral data confirmed the non involvement of free radical intermediate. The reaction was studied at five different temperatures, the activation and thermodynamic parameters were calculated. The product formed in this reaction was 6-amino-2-oxohexanoic acid .The optimum reaction conditions was determined for the maximum removal of lysine in the waste water.

Keywords: Oxidation of lysine, peroxomonosulphate, copper(II) catalyst, EPR study.

1. Introduction

L-lysine (2, 6-diaminohexanoic acid and α, ε -diaminocaproic acid) is a protein amino acid. It is classified as an essential amino acid for humans and must therefore be supplied in the diet. Certain proteins, such as those found in meat, poultry, and milk are rich in L-lysine. Small amounts of free L-lysine are found in vegetables, vegetable juices, and in such fermented foods as miso and yogurt[1]. L-lysine is a basic amino acid and carries a positive charge under physiological pH conditions. L-lysine, along with other amino acids, participates in biosynthesis of proteins. In the literature, few reports are available for the oxidation of L-lysine by diperiodatocuprate(III) in aqueous alkaline medium[2], hexacyanoferrate(III)[3], alkaline chloramine-T[4], diperiodatoargentate(III) in aqueous alkaline medium[5], diperiodatoargentate(III)[6], osmium(VIII)/ruthenium(III) catalysed oxidation by diperiodatocuprate(III)[7], ruthenium(III) catalysed oxidation by diperiodatoargentate(III) in aqueous alkaline medium[8], Osmium(VIII) catalysed oxidation by ferricyanide[9], Manganese(III) in pyrophosphate solution[10].

Peroxomonosulphate ion (PMS) HSO_5^- is considered to be a monosubstituted derivative of H_2O_2. PMS is available commercially as oxone with the composition $2KHSO_5 \cdot K_2SO_4 \cdot KHSO_4$. The high oxidation potential (~ -1.8 V)[11-13] and the propensity to react via oxygen atom transfer[14] make the HSO_5^- molecule a more favorable oxidant. Oxidation studies of peroxomonosulphate (PMS) with several compounds such as tris(1,10-

phenanthroline)iron(II)[15], nicotinic acid[16], hypophosphorous acid[17], acid red 88[18], nickel(II)lactate[19], tris (2,2'bypy) Iron(II) sulphate[20] etc. were reported. Though we have reported the oxidation of lysine by PMS[21] in acetic acid sodium acetate buffered medium but the effect of copper (II) catalyst on the oxidation has not been reported. Hence the title study was carried out and the results obtained were discussed in this manuscript.

2. Experimental

The kinetics of oxidation of lysine by PMS in presence of copper (II) sulphate in acetic acid–sodium acetate buffered medium was studied under pseudo first order conditions i.e., [lysine] >>[PMS] at various time intervals.

2.1. Materials and Reagents

All the solutions used in this study were prepared using double-distilled water and the solutions of the reagents were prepared afresh everyday before starting the experiments. PMS was from Aldrich, USA and the purity of the sample was tested by iodometric estimation and the purity was found to be 98% and hence used as such. PMS solution was freshly prepared everyday and standardized iodometrically and the PMS was preserved in a blackened vessel to prevent photodecomposition.

Lysine was obtained from Merck, India and used as such. The chemicals such as sodium acetate and sodium perchlorate were of analar grade and used as such. Acetic acid was distilled and used to make the buffer solution. Analar grade solvents like acetonitrile and 2-methyl-2-propanol were distilled and used for the reactions.

2.2. Measurement of Rate Constant

The reaction mixture except PMS was taken in a 250 ml 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 rate of the reaction was studied under pseudo first order condition i.e., [lysine] » [PMS]. The rate of the reaction followed first order kinetics (Figure 1) and the rate constant k_{obs} were calculated from the linear plots of log $[PMS]_t$ versus time according to the Equation (1).

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

The method of linear squares was used to calculate the slope and the intercept in all the cases. All the statistical analysis was carried out with Microsoft Excel Version, Windows 98 operating system. 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%.
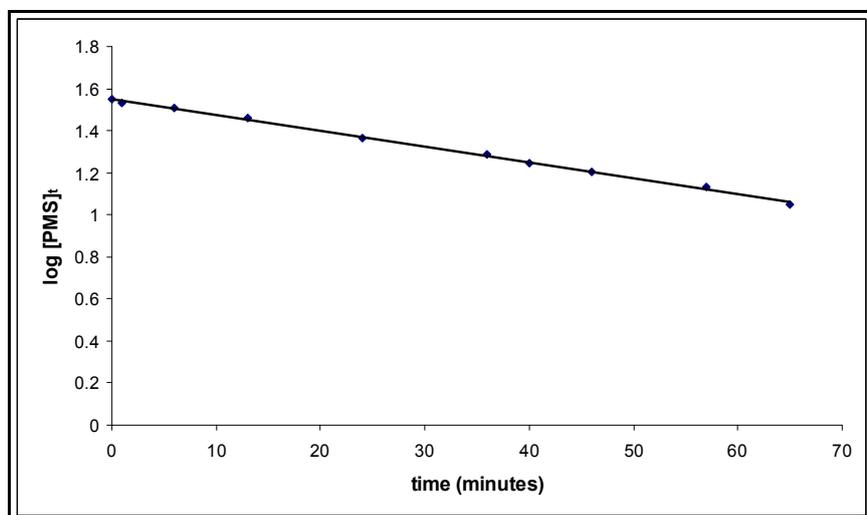

Figure 1. Plot of log $[PMS]_t$ vs time in presence copper(II) ions at 308 K
[lysine] = 5 x 10^{-2} mol dm^{-3}; pH = 4.0 ± 0.1; [sodium acetate] = 8.5 x 10^{-2} mol dm^{-3}
[Cu(II)] = 2.5 x10^{-3} mol dm^{-3}; [PMS] = 3.90 x 10^{-3} mol dm^{-3}

Table 1. Effect of varying concentrations on the reaction rate at 308K

10^3 x [PMS] (mol dm^{-3})	10^2 x [Lysine] (mol dm^{-3})	10^2 x [sodium acetate] (mol dm^{-3})	pH 4.0 $\pm$ 0.1	10^3 x [Cu(II)] mol dm^{-3}	With [Cu(II)] 10^4 x k_{obs} (s^{-1})	Temperature (K)
1.95	5.00	8.50	4.0	2.50	2.99	308
3.90	5.00	8.50	4.0	2.50	2.88	308
5.85	5.00	8.50	4.0	2.50	2.72	308
7.80	5.00	8.50	4.0	2.50	2.57	308
9.75	5.00	8.50	4.0	2.50	2.53	308
3.90	2.50	8.50	4.0	2.50	1.61	308
3.90	5.00	8.50	4.0	2.50	2.88	308
3.90	7.50	8.50	4.0	2.50	3.95	308
3.90	10.00	8.50	4.0	2.50	4.79	308
3.90	12.50	8.50	4.0	2.50	5.68	308
3.90	5.00	2.13	4.0	2.50	3.91	308
3.90	5.00	4.25	4.0	2.50	3.60	308
3.90	5.00	6.38	4.0	2.50	3.30	308
3.90	5.00	8.50	4.0	2.50	2.88	308
3.90	5.00	10.63	4.0	2.50	2.57	308
3.90	5.00	8.50	3.6	2.50	1.34	308
3.90	5.00	8.50	4.0	2.50	2.88	308
3.80	5.00	8.50	4.4	2.50	6.67	308
3.80	5.00	8.50	4.6	2.50	9.44	308
3.80	5.00	8.50	4.8	2.50	14.82	308
3.80	5.00	8.50	4.0	2.50	2.88	308
3.80	5.00	8.50	4.0	5.00	3.30	308
3.80	5.00	8.50	4.0	7.50	3.49	308
3.80	5.00	8.50	4.0	10.00	3.68	308
3.80	5.00	8.50	4.0	12.50	3.80	308
3.80	5.00	8.50	4.0	2.50	1.84	303
3.80	5.00	8.50	4.0	2.50	2.88	308
3.80	5.00	8.50	4.0	2.50	4.53	313
3.80	5.00	8.50	4.0	2.50	6.83	318
3.80	5.00	8.50	4.0	2.50	10.67	323

2.3. Stoichiometry and Product Analysis

The stoichiometry of the reaction was determined for copper (II) catalysed reaction by allowing the reaction mixtures containing a large excess of [PMS] over [lysine]. Simultaneously, a blank solution of the reaction mixture was also prepared, by adding all the solutions as above without lysine. Both the reaction mixtures were allowed to stand for 48 hours and the excess of PMS present 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 is [lysine]: [PMS] = 1:1 as represented by the following equation.
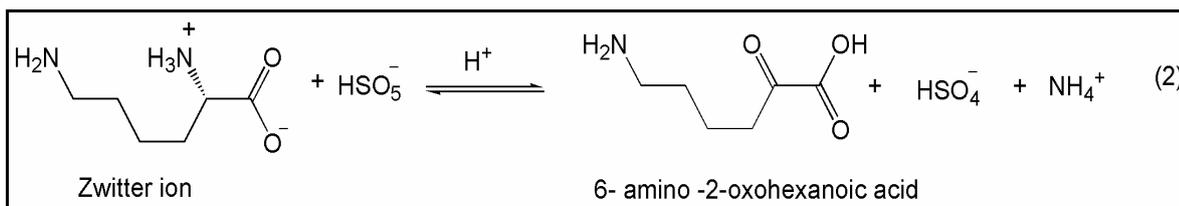
The reaction mixture containing a large excess of PMS over lysine in the presence of Cu(II) ions in a blackened vessel was allowed to stand for 48 h at room temperature. Excess PMS present in the reaction mixture was destroyed by adding sodium bisulphite and then the mixture was extracted with dichloromethane. The organic layer was separated, dried and IR spectrum was taken. From the IR data, absorption at 3434 cm^{-1} and 3293 cm^{-1} due to N-H stretching, 1706 cm^{-1} due to carboxylic C=O stretching, 1179 cm^{-1} due to C–N stretching, 1640 cm^{-1} due to ketonic C=O stretching confirmed the formation of . 6-amino-2-oxohexanoic acid.

2.4. UV-Visible 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 during the course of the reaction. The reaction mixture was prepared by adding PMS (~3.98 x 10^{-3} mol dm^{-3}) to lysine in the presence of copper(II) sulphate, (~2.5 x 10^{-5} mol dm^{-3}) in acetic acid - sodium acetate buffer. The concentration of lysine and PMS in the spectral solution was kept in the ratio 1:13. The spectra were taken immediately after preparing the reaction mixture in 1 cm cell at room temperature (298 K). Time history of the absorption spectra was also done at different time intervals.

2.5. EPR spectral analysis

The reaction mixture was scanned in the electron paramagnetic resonance spectrometer on a Varian E-112 EPR Spectrometer, Microwave power: 20 micro Watt (DPPH: 'g' Value = 2.00232, Magnetic field strength: 3300 G) to unravel the free radical intermediate formed during the course of the reaction. The reaction mixture was prepared by adding PMS (~3.86 x 10^{-3} mol dm^{-3}) to lysine in the presence of copper(II) sulphate, (2.5 x 10^{-3} mol dm^{-3}) in acetic acid- sodium acetate buffer. The spectra were taken immediately after preparing the reaction mixture and also at different time intervals.

2.6 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 nitrogen through the solution for 30 min prior to the experiments, and during the experiments the flow was maintained over the solution. Cyclic voltammogram was taken for copper(II) ions in buffer, lysine in buffer, PMS in buffer and the reaction mixture as well.

3. Results and discussion

3.1. 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 was unafffected with increase in [PMS] even by five fold times which revealed that the rate was first order in [PMS]. This result ruled out the dimerization of PMS or reaction between PMS and copper. If PMS dimerised, this would have resulted in second order and hence dimerization of PMS is ruled out.

3.2. Effect of [lysine] on k$_{obs}$

The values of k$_{obs}$ were calculated for different concentrations of lysine by keeping other parameters at constant values. Perusal of the kinetic results showed that the rate constant increased with increase in [lysine]. Further, the plots of k$_{obs}$ versus [lysine] were linear. The positive intercept obtained in the above plots revealed

that the reaction proceeded by two steps, one dependent on [lysine] and the other independent of [lysine]. The lysine independent step was due to the self-decomposition of PMS under the experimental conditions employed in this study.

3.3. Effect of pH on k_{obs}

By keeping other parameters at constant values, the effect of pH on the rate constants was studied by varying the pH values of the reaction mixture. The rate constant, k_{obs} values, increased with increase in pH values. Moreover, the plot of k_{obs} versus pH gave a parabola. When k_{obs} x $[H^+]$ versus $[H^+]$ was plotted, a perfect straight line was obtained with a high correlation coefficient.

3.4. Effect of [Sodium Acetate] on k_{obs}

The effect of [sodium acetate] on k_{obs} was studied by determining the values of k_{obs} at different [sodium acetate] by keeping other parameters at constant values and further the ratio of acetic acid/sodium acetate was maintained at constant value as well. In the presence of copper(II) the values of k_{obs} decreased with increase in [sodium acetate] and the plot of k_{obs}^{-1} versus [sodium acetate] was linear with a positive intercept. This observation suggested that the reaction was inhibited by acetate ion.

3.5. 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 [copper(II)], by keeping other parameters at pre-determined values. The kinetic results showed that the rate increased with increase in [copper (II)]. Further the plot of k_{obs} versus [copper(II)] was linear with a positive intercept.

3.6. Effect of Temperature on k_{obs}

The reaction was carried out at five different temperatures, namely, 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 (Table 2). The high positive values of free energy of activation ($\Delta G^{\#}$) and enthalpy of activation ($\Delta H^{\#}$) indicated that transition state was highly solvated while the negative values of entropy of activation ($\Delta S^{\#}$) suggested the formation of rigid transition state with reduction of degree of freedom of molecules.

Table 2. Kinetic and thermodynamic parameters for the oxidation of lysine catalysed by copper (II) ions at 308 K

Lysine	E_a kJ/mol	$\Delta H^{\ddagger}$ kJ/mol	$\Delta S^{\ddagger}$ J/K/mol	$\Delta G^{\ddagger}$ kJ/mol	$10^3 \times k_1 K_1$ Ms^{-1}	$10^4 \times k_2$ s^{-1}	$10^2 \times k_3 K_1 K_2$ $M^{-1} s^{-1}$
With copper(II) catalyst	31.02	29.88	-150.63	76.28	1.07	2.38	5.90

3.7. Effect of Dielectric Constant on k_{obs}

The effect of dielectric constant (ε) of the reaction mixture on the reaction rate was studied by using two different solvents, such as 2-methlyl propan-2- ol and acetonitrile. The k_{obs} remained unaffected with the increase in composition of the solvents ruling out the formation of more polar intermediate than the reactants.

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, by adding sodium perchlorate (0.01-0.04 M) and maintaining the other parameters at constant values. The increase in the ionic strength of the medium had negligible effect on the k_{obs} value. This result ruled out the interaction between the carboxylate group of lysine and SO_5^{2-} of PMS.

3.9. 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. Moreover, with the addition of t-butyl alcohol, the rate of the reaction was not lowered and hence eliminating the involvement of sulphate free radicals, since t-butyl alcohol is an effective scavenger of sulphate free radicals. Further EPR spectral measurement also confirmed the non-involvement of free radicals in this reaction.

Discussion

Lysine exists as a dipolar ion in aqueous solutions. The dissociation of lysine depends on the pH of the medium. The pK_a values of lysine [22] are 2.18, 8.95 and 10.53. Hence at pH 4.0 lysine exists both in the protonated form and as zwitterions as shown below.

$$\text{Protonated Lysine} \quad \underset{K_1}{\rightleftharpoons} \quad \text{Zwitter ion} \quad + \ H^+ \qquad (3)$$
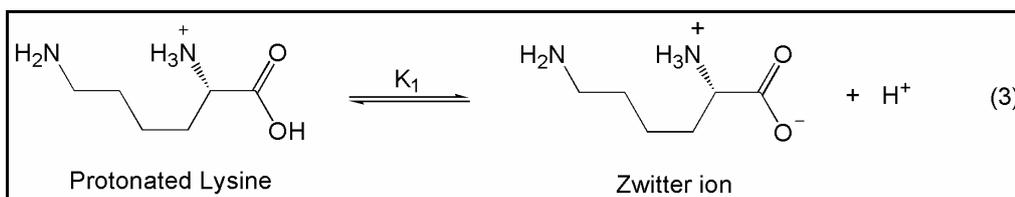
Peroxomonosulphate ion (HSO_5^-) is a weak acid with pk_a 9.4. The standard potential of HSO_5^-/ SO_4^{2-} and SO_5^{2-}/SO_4^{2-} couples is 1.75 V and 1.22 V, respectively. PMS exists as HSO_5^- in acidic condition i.e., pH 3-6 [23-24].
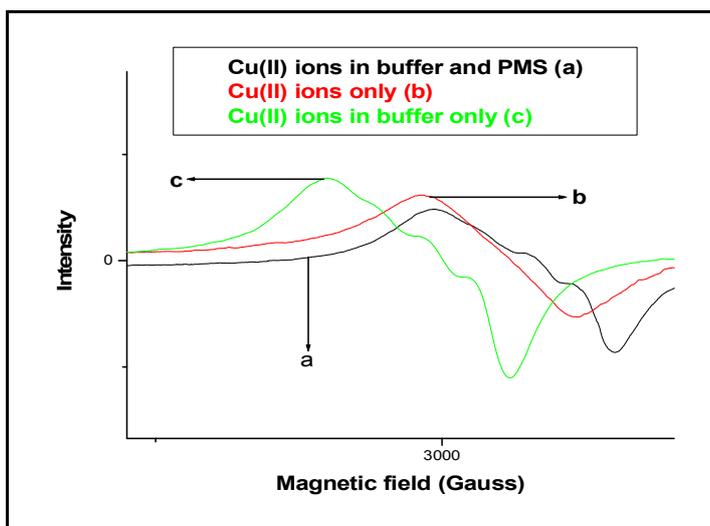

Figure 2. EPR spectra of copper(II) ions in different reagents.

(a) EPR plot of copper(II) ions (2.5×10^{-3} mol dm^{-3}) in water
(b) EPR plot of copper(II) ions in acetate buffered medium (pH = 4.0 ± 0.1) [sodium acetate] = 8.5×10^{-2} mol dm^{-3})
(c) EPR plot of copper(II) ions and PMS in acetate buffered medium ([PMS] = 3.86×10^{-3} mol dm^{-3})

Interestingly no EPR signal was obtained for the reaction mixture in the absence of copper(II) ions however, EPR signal was obtained for the reaction mixture in the presence of copper(II) ions. The EPR spectra are shown in figure 2. EPR spectrum of copper(II) ions in water showed only one signal, however copper(II) ions in acetate buffer showed four signals revealing the formation of copper(II)-acetate complex. EPR spectrum of the mixture containing lysine in buffered medium in presence and absence of copper(II) ions were taken. No signal was obtained for lysine molecular species, but in the presence of copper(II) ions showed signal which corresponds to the formation of copper-lysine complex. EPR spectrum was taken for the reaction mixture at various time intervals however; the position of signal (g value) and nature of signal were not affected (Figure 3). 'g' and 'A' values were calculated for each case and are given in table 3.
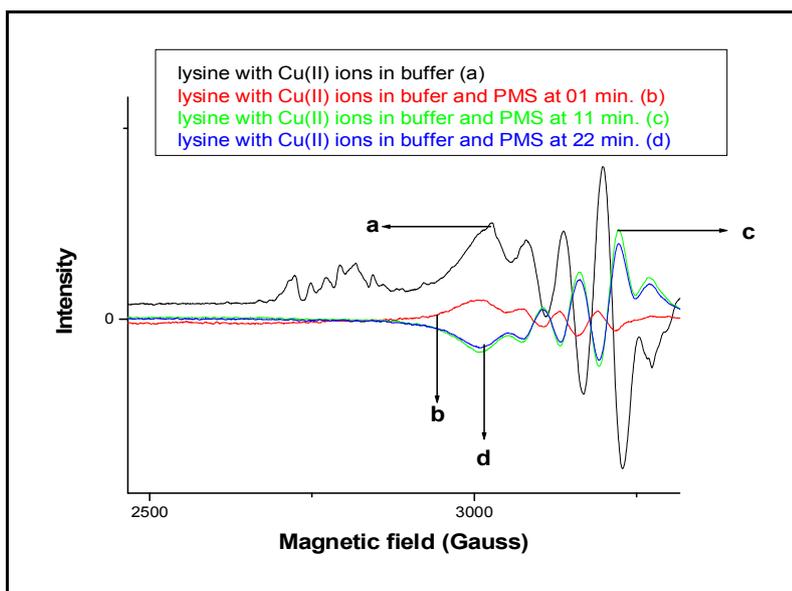
Figure 3. EPR spectra of the lysine reaction mixture in presence of copper(II) ions
[lysine] = 5 x 10^{-2} mol dm^{-3}; [Cu(II)] = 2.5 x10^{-3} mol dm^{-3} ; pH = 4.0 ± 0.1
[sodium acetate] = 8.5 x 10^{-2} mol dm^{-3} ; [PMS] = 3.90 x 10^{-3} mol dm^{-3}

Table 3. 'g' and 'A' values for the EPR spectrum of the reaction mixture

S.No.	Description	'g' Value	'A' Value (Gauss)
1	copper(II) ions in water	2.19	-
2	copper(II) ions in acetate buffer	2.17	40.28
3	copper(II) ions + acetate buffer + PMS	2.18	42.00
4	Lysine + copper(II) ions + acetate buffer	2.14, 2.10	57.84, 55.03
5	Lysine + Cu(II) + acetate +PMS at 01 Min.	2.14	57.46
6	Lysine + Cu(II) + acetate +PMS at 11 Min.	2.12, 2.05	57.65, 57.46
7	Lysine + Cu(II) + acetate +PMS at 22 Min.	2.12, 2.08	57.27, 57.08

EPR spectrum of the mixture containing lysine in buffered medium, in the presence of copper(II) ions, showed five signals which corresponded to the formation of (copper(II)-lysine) complex (spectrum 'a' of Figure 3). When lysine was added to copper(II) ions and acetate buffer mixture a dynamic equilibrium was established between copper(II)–lysine monomer and copper(II)-lysine dimer, which was reflected in the fifth signal (spectrum 'a' of Figure 3). However, When PMS was added to the (copper(II)-lysine monomer) complex and (copper(II)-lysine dimer) complex mixture the fifth signal disappear only four signals are appeared (spectrum 'b' of Figure 3). At the same time the spectrum 'c' and'd' of figure 3 show five signals. This is due to the interaction of PMS with both monomer and dimer complex. Positions of signals were not affected for the reaction mixture at different time intervals. This indicated that copper(II) ions were neither oxidised nor reduced but acted only as a catalyst.

In order to study whether copper(II) ions reacted directly with PMS, an EPR spectrum of copper(II) ions in acetate buffer with PMS was taken. It showed only four signals, ruling out the possibility of the formation of hydroxyl radical or any other radical (spectrum 'c' of Figure 2). Formation of a complex between lysine – copper(II) ions was confirmed by taking UV – visible spectra.

UV- visible spectrum of the mixture containing lysine, Cu(II) ions and PMS in acetic acid and sodium acetate buffered medium in the presence of copper(II) ions (2.5 x10^{-3} mol dm^{-3}) showed two absorption maxima

one at 237.34 nm (Figure 4) and an another domain containing, a wide band, centered at 707.33 nm (Figure 5). The maxima at 707.33 nm was due to the formation of lysine-copper(II) complex, Interestingly the peak was observed only at higher concentrations of copper(II) (1.5 x 10^{-2} mol dm^{-3}) and was attributed to the d-d

transition ($^2E_g \rightarrow \ ^2T_{2g}$), specific for Cu(II) complexes with tetragonally distorted octahedral complex due to Jahn-Teller effect.

　　　　Time history of the plot at various time intervals revealed that absorption at 237.34 nm increased whereas the absorption at 682 nm decreased (Figure 5). 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 lysine to the reaction mixture, λ_{max} was shifted to 678 nm revealing the formation copper acetate-lysine complex. When the reaction mixture reacted with PMS, λ_{max} was further shifted to 707 nm revealing the formation of copper acetate-lysine-PMS complex. A. All these observed shift (Figure 5) revealed the formation of different copper(II) complexes.
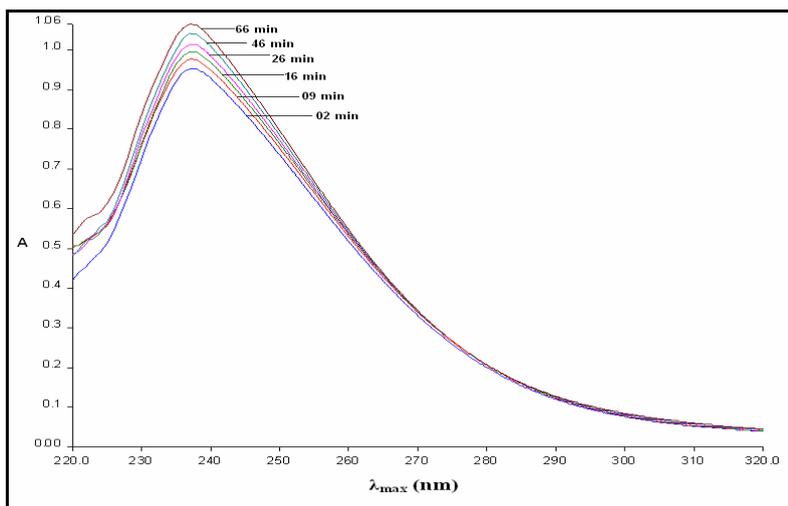

Figure 4. Absorption spectra of the lysine reaction mixture in presence of copper(II) ions at various time intervals
[lysine] = 5 x 10^{-2} mol dm^{-3}; pH = 4.0 ± 0.1; [sodium acetate] = 8.5 x 10^{-2} mol dm^{-3}
[Cu(II)] = 2.5 x10^{-5} mol dm^{-3}; [PMS] = 3.90 x 10^{-3} mol dm^{-3}
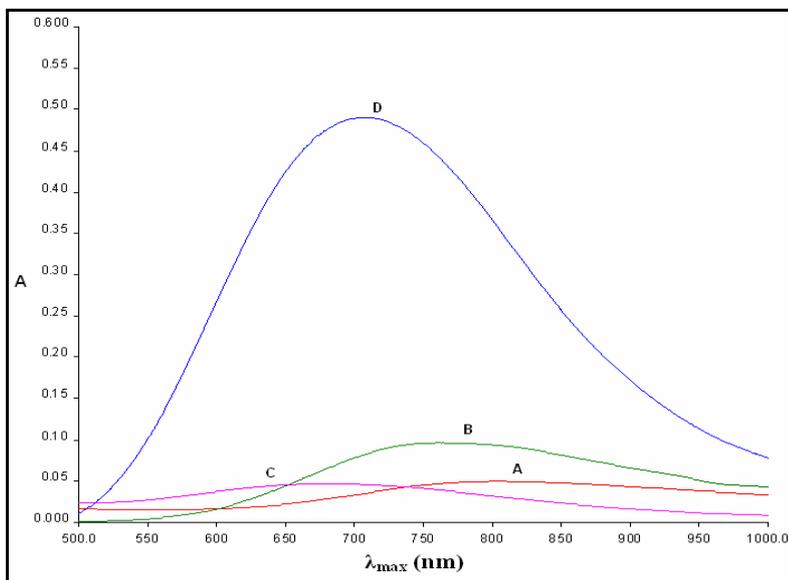

Figure 5. Absorption spectra of copper(II) ions in different reagents
A - Copper(II) ions in water
B - Copper(II) ions in acetate buffered medium
C - Copper(II) ions with lysine in acetate buffered medium
D - Copper(II) ions with lysine and PMS in acetate buffered medium
[lysine]= 5 x 10^{-2} mol dm^{-3}; pH = 4.0 ± 0.1; [sodium acetate] = 8.5 x 10^{-2} mol dm^{-3}
[Cu(II)]= 1.5 x 10^{-2} mol dm^{-3}; [PMS] = 3.86 x 10^{-3} mol dm^{-3}

The cyclic voltammogram of Cu(II) ions and acetate buffer system was recorded. Peak potentials of various cyclic voltammogram are tabulated in table 4. The peak potential corresponding to reduction of Cu(II) ions was -0.71 V. The cyclic voltammogram of lysine in buffered medium showed the peak potential at -0.34 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 lysine showed three different reduction peak potentials: -0.21, -0.42 and -0.74 V (Figure 6). Comparing these peak potentials with those of free copper(II) ions in buffer, lysine in buffer and PMS in buffer, it was observed that a new peak -0.21 V has appeared. This could be assigned to reduction of 1:1 Cu(II)-lysine complex. Since, the value was lower than that of free lysine (-0.34 V), it is confirmed that lysine in the Cu(II) complex has more tendency to undergo reduction than the free lysine. The cyclic voltammogram of Cu(II)- lysine - PMS system showed two peaks at -0.38 V and -0.65 V (Figure 7). The peak potential of Cu(II) ions in Cu(II) – lysine complex was shifted to a low value (-0.38 V and -0.65 V) compared to those of Cu(II)-lysine complex (-0.42 V and -0.74 V). So, from the study of cyclic voltammetry it was established that Cu(II) form complex with lysine and PMS form complex with Cu(II) – lysine complex.

Table 4. Reduction potential values of different reaction mixtures

S. No.	Description	'E' (Potential in Volts)		
		Peak I	Peak II	Peak III
1	copper(II) + buffer	- 0.71	-	-
2	Lysine + acetate buffer	- 0.34	-	-
3	PMS + acetate buffer	- 0.80	-	-
4	Lysine + copper(II) + buffer	- 0.21	- 0.42	- 0.74
5	Lysine + copper(II) +buffer + PMS	-	- 0.38	- 0.65

The PMS complexation was observed to lower reduction potential of Cu(II) - lysine complex. Though PMS can donate electrons to form complex with Cu(II) ions, electron might be donated back predominantly, in order to decrease the reduction potential of Cu(II) ions. Hence PMS might also be interacting with free lysine forms lysine – PMS complex, thus establishing existence of Cu(II) – lysine – PMS complex and lysine – PMS complex. ESR spectral data also confirmed distorted octahedron complex.
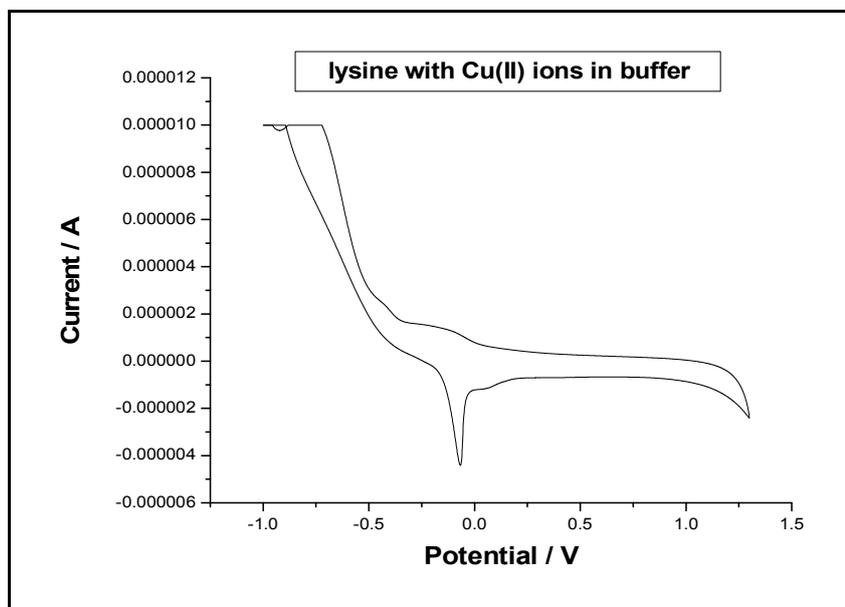

Figure 6. Cyclic voltammogram of lysine with Cu(II) ions in acetate buffered medium
[lysine] = 2.5 x 10^{-2} mol dm^{-3}; pH =4.0 ± 0.1
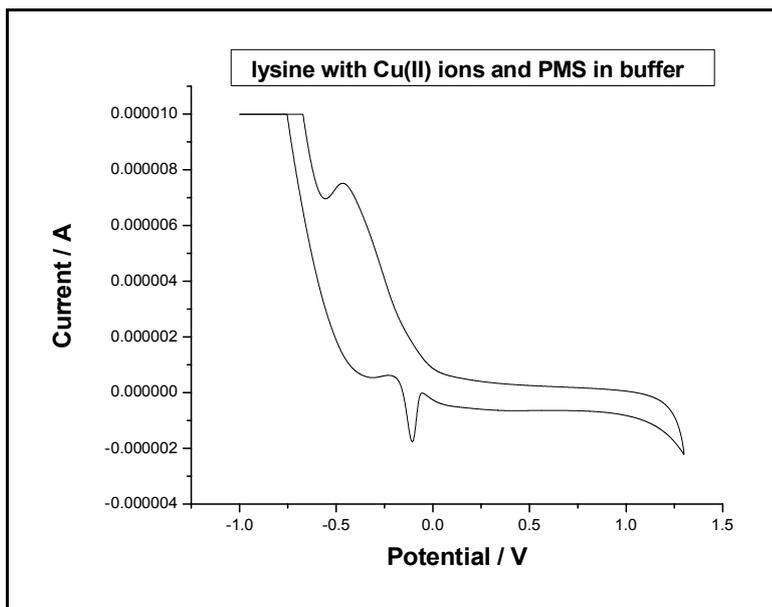[sodium acetate] = 8.5 x 10^{-2} mol dm^{-3}; [Cu(II)] = 5 x 10^{-5} mol dm^{-3}

Figure 7. Cyclic voltammogram of the lysine reaction mixture with Cu(II) ions and PMS in acetate buffered medium
[lysine] = 2.5 x 10^{-2} mol dm^{-3}; pH = 4.0 ± 0.1; [sodium acetate] = 8.5 x 10^{-2} mol dm^{-3}
[Cu(II)] = 5 x 10^{-5} mol dm^{-3}; [PMS] = 8.0 x 10^{-4} mol dm^{-3}

Based on the above discussion, the detailed mechanism for the copper(II) catalyzed reaction pathway is given in Scheme 1.
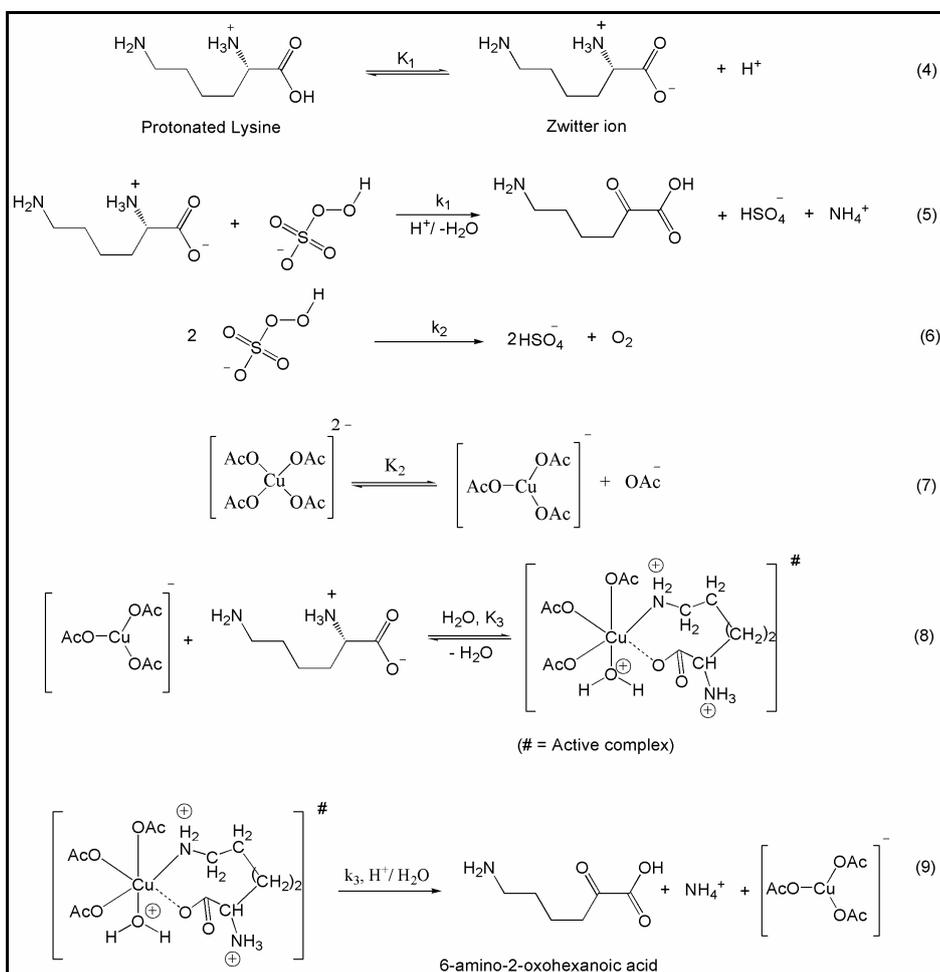
Scheme 1. Mechanism for the oxidation of lysine in the presence of copper(II) ions by peroxomonosulphate.

k_{obs} was derived as

$$k_{obs} = \frac{k_1 K_1 [Lysine]}{[H^+]} + k_2 + \frac{k_3 K_1 K_2 K_3 [Lysine] [Cu^{2+}]}{[OAc^-] [H^+]} \quad (10)$$

From equation (10) values of $k_1 K_1$, $k_3 K_1 K_2 K_3$ & k_2 were calculated from different plots and average values have been given in the table 2.

4. Conclusion

Kinetics of the oxidation of lysine by peroxomonosulphate in acetic acid-sodium acetate buffered medium (pH 3.6-5.2) in the presence of copper(II) ions was studied at 308 K. Variation of ionic strength did not show any effect on the rate of the reaction and it revealed that PMS attack the amino group of lysine rather than the carboxylate group of lysine. Effect of polarity was studied with two different solvents viz, acetonitrile, and 2-ethyl-2-propanol and in both the cases, the rate constant remained the same even while changing the solvent composition. A suitable reaction mechanism was proposed to explain the experimental observation. EPR spectra taken for the reaction mixture at various time intervals, confirmed the reaction proceeding through molecular intermediate. Cyclic voltammetric studies and absorption studies confirmed the formation of copper(II) – lysine – PMS complex. The optimum pH was 5.0 for the maximum removal of lysine from the waste water at 308 K.

Acknowledgements

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