

RESEARCH ARTICLE

Oxidative Degradation of Glycine by Peroxomonosulphate at Neutral Medium-Catalytic effect of Copper (II)

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ABSTRACT:

Kinetics and mechanism of copper (II) catalyzed and uncatalyzed oxidation of glycine (gly) by peroxomonosulphate (PMS) in neutral medium (phosphate buffer, pH 6-8) was studied at 278 K. The rate of the reaction increased with increase in pH values. The rate was first order in [Cu (II)] and [gly], and zero order in [PMS]. Variation of ionic strength did not have any effect on the rate of the reaction. The effect of dielectric constant on the rate constant was negligible ruling out the formation of polar intermediate. The reaction between PMS and glycine exhibited 1:1 stoichiometry. The product of the reaction was confirmed by IR and UV Visible spectral studies

KEYWORDS: Glycine; PMS; Copper (II); Homogeneous catalysis; Neutral medium.

1. INTRODUCTION:

Amino acids are one of the natural compounds, which contribute an important role both as building blocks of proteins and as intermediates in metabolism. They are useful for the human nervous system, hormone production, and muscular structure aside from playing an important role in protein and enzyme synthesis. Among the amino acids, glycine acts as a biosynthetic intermediate of all purines and porphyrins as well as a neurotransmission inhibitor of the central nervous system [1,2]. The wastewater containing amino acids and peptides may produce byproducts, which are potentially unsafe and may lead to serious health and environmental problems. Removal of these parent compounds by the use of the environmentally benign oxidant can be of much use to the human kind and the environment [3].

Peroxomonosulphate (PMS) is an inexpensive, eco-friendly oxidizing agent when compared with other oxidizing agents [4-8] due to its easy tendency to transfer oxygen.

It is used to oxidize both inorganic [9], organic [10-12] and waste water [13-17]. Transition metal ion catalyzed oxidation of amino acids have been carried either in acetic medium [18-20] or alkaline medium [21,22]. Copper complexes have occupied a major place in oxidation chemistry because of their abundance and relevance in biological chemistry [23,24]. However, glycine was the substrate of oxidation by several oxidizing agents but there are no reports on the oxidation of glycine by PMS in neutral medium. Hence, the present study focused the oxidation of glycine with PMS in neutral medium (phosphate buffer, pH 6-8) and also the effect of copper (II) ions at 273 K.

2. EXPERIMENTAL:

2.1. MATERIALS AND METHODS:

Peroxomonosulphate (PMS) was obtained from Aldrich, USA in the form of triple salt $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (oxone) and the purity of the sample was found to be 98% when tested by iodometric estimation [25]. A fresh solution of PMS was prepared every time before starting the experiments, doubly distilled water was used throughout this study. Glycine was obtained from Merck, India, and used as received. All other chemicals used in this study were of analar grade and used as received. Analar grade solvents like acetonitrile and 2-methyl-2-propanol were distilled and used in the

reactions.

2.2. Instrumentation:

For kinetic measurements, a Royal ultra cryostat (temperature control) was used. For product analysis, Jasco 6300 FT-IR spectrophotometer was used. The reaction mixture was scanned in the ultraviolet and visible regions on a Perkin Elmer LS 25 UV-visible spectrophotometer.

2.3. Measurement of Rate constant:

A known volume of PMS solution, thermostatted at the desired temperature (278K) was pipetted out into the reaction mixture of glycine in buffer and simultaneously a timer was started. Consumption of PMS in this reaction mixture was monitored by the iodometric method. The rate of the reaction followed first order kinetics as shown in fig.1 and the rate constant k_{obs} was calculated from the linear plot of $\log[PMS]$ vs time according to eq.1

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

Copper sulphate pentahydrate was used as a homogeneous catalyst. The effect of copper (II) was observed even at concentration of $5 \times 10^{-3} \text{ mol dm}^{-3}$ and hence concentration of Cu (II) in the reaction mixture was kept at $5 \times 10^{-3} \text{ mol dm}^{-3}$.

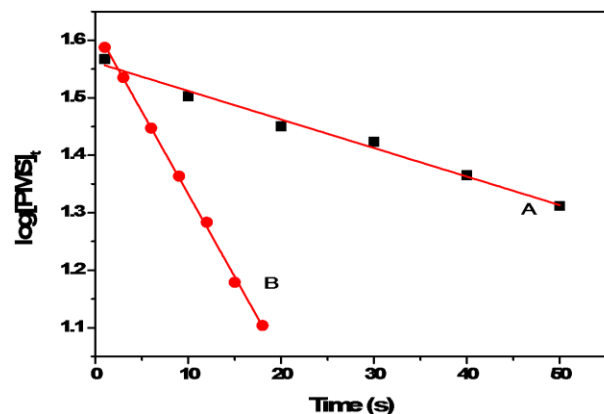


Fig. 1. Plot of $\log [PMS]_t$ vs Time in the absence (A) and presence of (B) copper (II) ions at 278K. $[\text{glycine}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Cu (II)}] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{pH} = 7.0 \pm 0.1$; $[\text{PMS}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$

The stoichiometries of the reactions were determined for both copper (II) catalyzed and uncatalyzed reactions for the reaction mixtures containing a large excess of [PMS] over [Glycine]. Then the reaction mixture was allowed to stand for 48 h and the unconsumed PMS was estimated iodometrically. The observed stoichiometry of the reaction in both copper(II) catalyzed and uncatalyzed reaction (Glycine:PMS=1:1)

Product analysis was done as given below. The reaction mixture containing a large excess of PMS over glycine 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 bisulfite, and then the mixture was extracted with diethylether. The organic layer was separated, dried and doing IR analysis. From the IR data, absorption at 1777 cm^{-1} is due to C=O of carbonyl group, absorption at 1590 cm^{-1} is due to acid carbonyl and the amine stretching frequency at 3400 cm^{-1} is disappeared Fig.2.

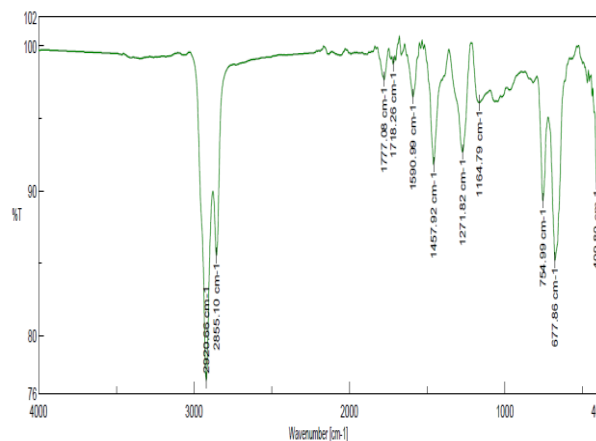


Fig. 2. FT-IR spectrum of 3-oxoproponic acid

3. RESULTS AND DISCUSSION:

Kinetics and mechanism of copper(II) catalyzed and uncatalyzed oxidation of glycine by PMS in neutral medium was studied at 278 K. The rate of the reaction was monitored by measuring the concentration of unreacted PMS as a function of time.

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 unaffected with increase in [PMS] in the absence of copper (II) whereas the rate increased with increase in [PMS] in the presence of copper(II). The k_{obs} vs [PMS] is presented in Table 1.

3.2. Effect of [Glycine] on k_{obs} :

The values of k_{obs} were calculated for the reactions conducted both in the presence and absence of copper(II) catalyst for different concentrations of glycine, by keeping other parameters at constant values. The kinetic results showed that the rate constant increased with increase in [glycine] as presented in Table 1.

3.3. Effect of pH on k_{obs} :

In order to ascertain the effect of pH on the rate of the reaction, reactions in the presence and absence of copper(II) ions at different pH values were carried out. The rate constant (k_{obs}) values increased with an increase in pH values in both cases. The rate constant values are presented in Table 1

3.4. Effect of [Copper(II)] on k_{obs} :

The effect of [copper(II)] on the rate was studied by determining the values of k_{obs} at different [copper(II)], by keeping other parameters at predetermined values. The kinetic results showed that the rate increased with an increase in [copper(II)] (Table 1), and the plot of k_{obs} vs [copper(II)] was linear with a positive intercept confirming the oxidation of glycine proceeded in the absence of copper ions as well.

3.5. Effect of Temperature on k_{obs} :

The reaction was studied at five different temperatures, viz., 278, 283, 288 and 293 K, by keeping all other parameters constant. The k_{obs} increased with the increase in temperature, and the plot of $\log k_{obs}$ vs $1/T$ was a straight line (Arrhenius plot) Fig.3.

3.6. Effect of Dielectric Constant on k_{obs} :

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

3.7. 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 from 0.05 to 0.2 mol dm⁻³, maintaining the other parameters at constant values. The increase in the ionic strength had no effect on the k_{obs} value. This ruled out the interaction between SO₅²⁻ of PMS and carboxylate group of glycine. The negligible effect of ionic strength on the rate of the reaction revealed that glycine is the active form and not the zwitter ionic form of glycine.

Table 1. Effect of Varying concentration on the reaction rate at 278K

10 ⁻³ [PMS] (mol dm ⁻³)	10 ⁻² [glycine] (mol dm ⁻³)	pH±0.1	10 ⁴ k_{obs}^a (s ⁻¹)	10 ⁻³ [Cu(II)] (mol dm ⁻³)	10 ⁴ k_{obs}^b (s ⁻¹)	temp (K)
2	5	7	0.65	5	0.21	278
4	5	7	0.65	5	7.29	278
6	5	7	0.65	5	5.72	278
8	5	7	0.65	5	4.85	278
4	2.5	7	0.38	5	2.22	278
4	5	7	0.76	5	5.64	278
4	7.5	7	0.97	5	10.93	278
4	10	7	1.49	5	18.50	278
4	5	6	0.11	5	0.53	278
4	5	6.5	0.19	5	1.99	278
4	5	7	0.23	5	8.48	278
4	5	7.5	1.34	5	44.18	278
4	5	8	3.87	5	60.10	278
4	5	7	0.76	2.5	0.10	278
4	5	7	0.76	5	2.87	278
4	5	7	0.76	7.5	4.33	278
4	5	7	0.76	10	6.25	278
4	5	7	1.11	5	4.06	278
4	5	7	1.30	5	13.20	283
4	5	7	2.18	5	49.32	293
4	5	7	7.02	5	79.24	293

^aWithout Cu(II). ^bWith Cu(II).

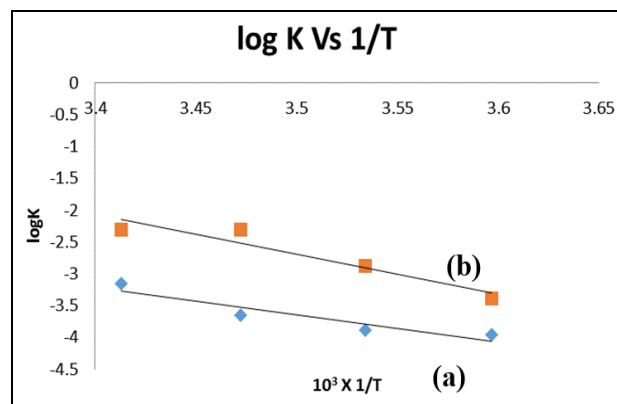


Fig. 3. Plot of log k vs 1/T in the absence (a) and presence of (b) copper (II) ions at different K. [glycine]=5.0 x 10⁻² mol dm⁻³; [Cu (II)]=2.5 x 10⁻³ mol dm⁻³; pH=7.0±0.1; [PMS]=4 x 10⁻³ mol dm⁻³

3.8. Test for Free Radical Intermediates:

In this kinetic study, the reaction failed to initiate the polymerisation of added acrylonitrile, which ruled out the involvement of free radical intermediate. Further ESR study also confirmed the noninvolvement of free radical intermediate in this reaction.

The UV-visible spectrum of the mixture containing glycine and PMS in phosphate buffered medium showed λ_{max} at 215 nm. Scanning at different time intervals showed an increase in absorbance, as shown in Fig 4a. However, in the presence of copper (II), two absorption maxima were obtained, one at 235 nm and another domain containing a wide band centered at 690 nm. λ_{max} at 630 nm was due to the formation of glycine-copper (II) complex; interestingly the peak was observed only

at higher concentrations of $[Cu] > 5 \times 10^{-2}$ M 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 the Jahn-Teller effect. Further, copper(II) in water has λ_{max} at 805 nm, whereas copper(II) in buffer has λ_{max} at 692 nm, copper (II) in buffer with glycine has λ_{max} at 635 nm, and copper (II) with glycine and peroxomonosulfate in buffer has λ_{max} at 632 nm, which indicates a hypsochromic shift revealing the formation of copper(II)-phosphate complex initially (Fig 4b), followed by formation of complexes with glycine and PMS, viz., copper phosphate-glycine complex and copper phosphate-glycine-PMS complex.

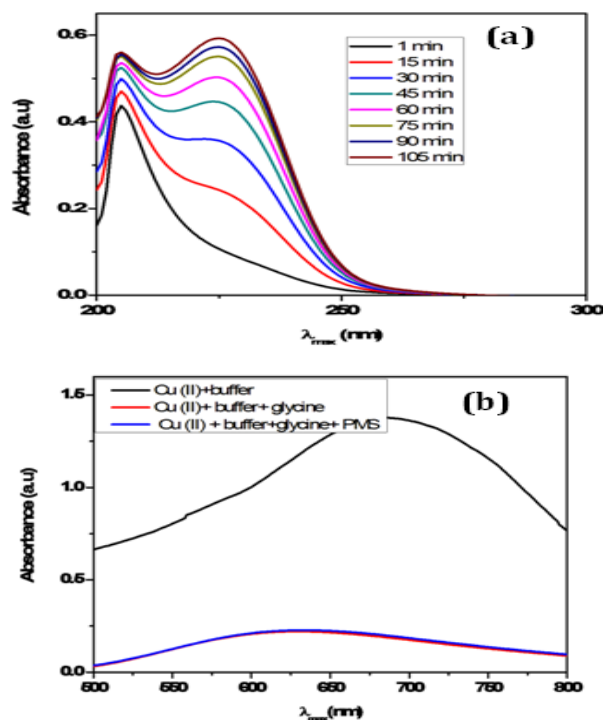


Fig. 4a. The absorption spectra of the reaction mixture in the absence of copper (II) ions in different time interval: $[glycine]=5.0 \times 10^{-2}$ mol dm^{-3} ; $[Cu(II)]=1.5 \times 10^{-5}$ mol dm^{-3} ; $pH=7.0 \pm 0.1$; $[PMS]=4.0 \times 10^{-3}$ mol dm^{-3} , 4b. Copper peak at high concentration.

4. CONCLUSION:

The kinetics of the oxidation of glycine by peroxomonosulfate in phosphate buffered medium (pH 6–8) in the presence and absence of copper (II) catalyst was studied at 278 K. The rate of the catalyzed reaction is faster than that of the uncatalyzed reaction. Variation of ionic strength did not show any effect on the rate of reaction. The product of the reaction was confirmed by IR and UV Visible spectral studies.

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