

OXIDATION OF α -ALANINE BY PEROXOMONOSULPHATE– AUTOCATALYTIC EFFECT OF COPPER PEROXIDE

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ABSTRACT

Kinetics and mechanism of oxidation of α -alanine (AA) by peroxomonosulphate (PMS) in the presence of Cu(II) ions at 35°C in perchloric acid medium was investigated. Autocatalysis was observed due to the formation copper peroxide intermediate. The rate constant for the catalyzed (k_2) and uncatalyzed (k_1) reaction were calculated. The kinetic data showed that both the reactions were first order with respect to [AA] and [Cu(II)]. Based on the experimental results a plausible mechanism was proposed. The influence of temperature on the rate of reaction was studied as well, the activation parameters and thermodynamic quantities were calculated with respect to slow step of the mechanism

Key words: Autocatalysis, oxidation, α -alanine, PMS

INTRODUCTION

The kinetic investigation of the oxidation of amino acids is important because of their biological significance and a precise understanding of the mechanism. The oxidation of amino acids by permanganate ion in various media were done by many workers, However no evidence for autocatalysis in the oxidation of amino acid by oxidants in strong acid media. The kinetics of oxidation of α -amino acids by PMS has been studied extensively in buffered medium (acetic acid/sodium acetate) and also in highly alkaline medium. In buffered medium, the observation was the exhibition of autocatalysis of the product aldehyde. Activation of PMS can be facilitated by the homogeneous catalysis of transition metal ions. Several transition metals were studied to assess their potential catalytic activity and the nature of the radical generated in the PMS decomposition. The oxidation of some amino acids in the presence Mn(II) and Ni(II) ions shows autocatalysis, in which the molecular intermediate produced from the amino acid significantly enhances the rate. This stimulated our interest in the oxidation of α -alanine by PMS in perchloric acid medium and also the catalytic effect of Cu(II) ions.

EXPERIMENTAL

Materials: Potassium peroxomonosulphate (PMS) was from Lancaster under the trade name “oxone”. Its purity was estimated by iodometry and found to be 98%. A fresh solution of PMS was prepared before starting the experiments. Other chemicals and reagents such as amino acids, coppersulphate, perchloric acid (70%, E.Merck) and all other chemicals were used of analytical grade and used as such.

Kinetic measurements

Kinetic studies were carried out at $35 \pm 0.1^\circ\text{C}$ in perchloric acid medium under pseudo first order conditions with a large excess of [AA] over [PMS]. The reaction rate was measured by monitoring the concentration of unreacted [PMS] at various time points by iodometry. The reaction mixture was thermostated in a 250 ml blackened iodine flask. Known volume of PMS was pipetted out in to the reaction mixture and simultaneously, a timer was started, the rate of oxidation of amino acids was followed by monitoring the concentration of unreacted [PMS] by iodometry. Autocatalysis was observed from the plot of $[\text{PMS}]_t$ vs. time (Figure.1). The rate constant for catalyzed and uncatalyzed reactions were calculated. 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%.

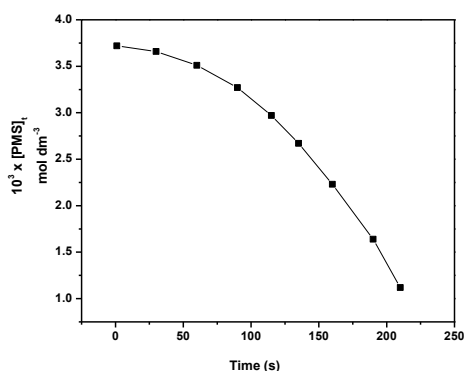


Figure.1. Plot of $[\text{PMS}]_t$ vs. time at 308 K, $[\text{AA}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Cu}^{2+}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$, $[\text{PMS}] = 3.6 \times 10^{-3} \text{ mol dm}^{-3}$

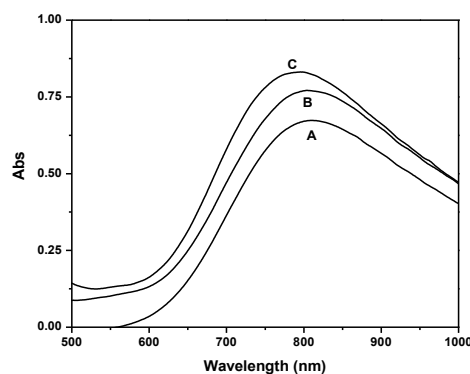


Figure.2. UV-Visible spectra for the reaction mixture in the presence of copper(II) ions at high concentration

Stoichiometry: The stoichiometry of the reaction was determined by allowing the reaction mixtures containing a large excess of [PMS] over [AA], that is, [PMS]/[AA]=2.5 with $[Cu^{2+}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ in perchloric acid was allowed to stand for 48 h. at room temperature and the excess [PMS] was then estimated iodometrically. The calculated stoichiometry of amino acids:PMS = 1:2.

Product analysis: The reaction mixture was allowed to stand for 48 h for the completion of the reaction, then the product was extracted with dichloromethane and the products obtained for the oxidation of α -alanine was identified as acetaldehyde by Gas Chromatography (GC). The chromatographic results showed that the purity of the products obtained were greater than 98% by compared the retention time with the authentic sample.

UV-Visible Spectral measurements: The electronic spectrum for Cu(II) ions catalyzed oxidation of α -alanine (AA) at low concentration showed an absorption (λ_{max}) at 282nm corresponds to $n \rightarrow \pi^*$ transitions due to intraligand charge transfer of α -alanine. The addition of Cu(II) ions to the reaction mixture shifted the band towards higher energies with λ_{max} at 275nm. This shift might be correlated with involvement of O atom of -COOH group and N atom of $-\text{NH}_2$ group of α -alanine coordination to Cu(II) ions, which caused a strengthening of the Cu-O and Cu-N bonds involved in the charge transfer processes for complex. The spectrum in the visible domain at higher concentrations of Cu(II) ions ($5 \times 10^{-2} \text{ mol dm}^{-3}$) with α -alanine consist of a broad weak band at 799 nm attributed to $^2E_g \rightarrow ^2T_{2g}$ and the formation of $[\text{Cu(II)-(AA)}_2]$ complex. The λ_{max} value shifted to 780 nm with PMS (Figure. 2). This blue shift in the λ_{max} confirmed the oxidation of amino acid in the complex with PMS.

(A). $[\text{Cu(II)}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$

(B). $[\text{Cu(II)}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$; $[\text{AA}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$

(C). $[\text{Cu(II)}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$; $[\text{AA}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$;
 $[\text{PMS}] = 3.6 \times 10^{-3} \text{ mol dm}^{-3}$

Cyclic Voltammetric studies: Cyclic voltammetric studies were used to investigate the interaction behavior of Cu(II) ions with α -alanine (AA). The voltammograms of Cu(II) ions showed the anodic peak at -0.47mV with AA this potential shifted to -0.52mV due to the formation of $[\text{Cu(II)-(AA)}_2]$ complex and the anodic peak potential further shifted to -0.49mV by the addition of PMS (Figure. 3). This suggested that the oxidation reaction was carried at lower energy state and the voltammogram for the metal ion showed single peak for both the cathodic and anodic modes [20] and every step was single electron process.

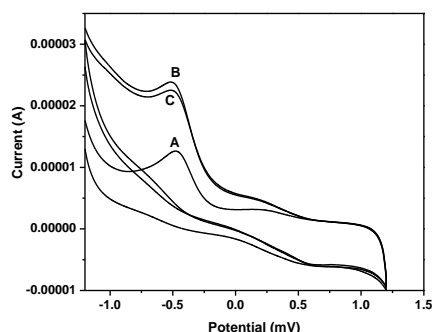


Figure-3: Comparison of the cyclic voltammogram of:

(A). $[\text{Cu}^{2+}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$

(B). $[\text{Cu}^{2+}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$; $[\text{AA}] = 0.05 \text{ mol dm}^{-3}$

(C). $[\text{Cu}^{2+}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$; $[\text{AA}] = 0.05 \text{ mol dm}^{-3}$;
 $[\text{PMS}] = 3.6 \times 10^{-3} \text{ mol dm}^{-3}$ in 0.1M KCl solution at a Pt button electrode

EPR Spectral Analysis: EPR spectrum was taken to ascertain the involvement of free radical intermediate and to describe the nature of the complex. The EPR spectrum of Cu(II) ions in perchloric acid shows a single peak with $A_{\text{iso}} = 135 \text{ G}$ and $g_{\text{iso}} = 2.2040$ due to formation of symmetric complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. Further, with α -alanine shows four well resolved unsymmetrical peaks with low intensities. This attributes to the formation of Cu(II)-amino acid complex (Figure.4). The observed hyperfine parameters for this complex $A_{\text{ans}} = 50 \text{ G}$ and $g_{\text{ans}} = 2.2179$ describes the axial symmetry with the unpaired electron residing in the $d_{x^2-y^2}$ orbital and coordinated to Cu^{2+} ions through the N and O atom of α -alanine. The PMS was added to reaction mixture these values remains the same, indicating that the orbital angular momentum of the uncoupled electron of Cu(II) ions has little influence on the hyperfine parameters and no superfine interaction due to the directly bonded atoms. From this it was confirmed that the Cu(II) ions was neither oxidized nor reduced but acted only as a catalyst by forming copper peroxide intermediate with PMS.

RESULTS

The rate of oxidation of α -alanine by PMS was very slow. However, the added Cu(II) ions even at a concentration of $5 \times 10^{-4} \text{ mol dm}^{-3}$ enhanced the reaction rate appreciably, hence the reaction has been studied only

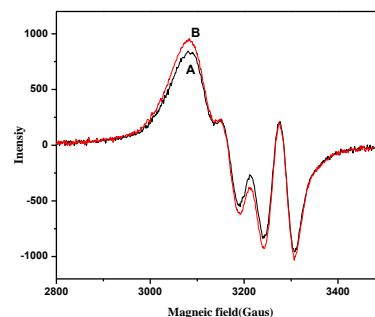


Figure-4: (A). EPR Spectrum for Copper-Alanine complex

(B). EPR Spectrum for copper- alanine complex with PMS

in the presence of Cu(II) ions at 35°C. The first order plot shows curvature toward the time axis (Figure. 1), which may be due to the intermediates product that catalyzes the reaction and the oxidation of α -alanine showed the autocatalysis.

Effect of [alanine] on k_{obs}

The reaction was carried out with various initial concentrations of α -alanine(AA), while keeping all other parameter constant. The pseudo first order rate constants k_1 and k_2 were increased with increase in [AA] (Table. 1). The plots of k_1 and k_2 vs.[AA] which gave a straight line with positive slope (Figure.5 and 6).These shows that the reaction obeyed first order with respect to [AA] for both the uncatalytic and catalytic pathways..

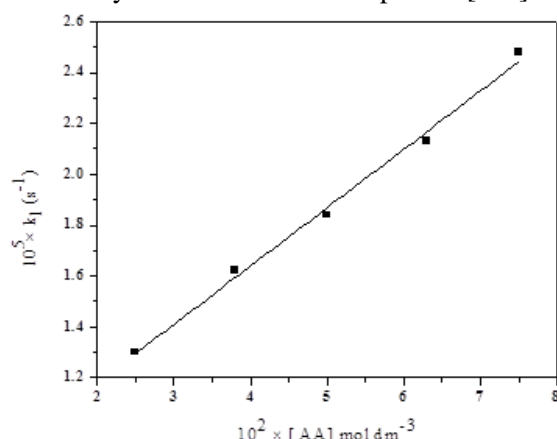


Figure.5.Plot of k_1 vs. [AA] at 308K,
[H⁺] = 0.10 mol dm⁻³; [Cu²⁺] = 5.0 × 10⁻⁴ mol dm⁻³;
[PMS] = 3.6 × 10⁻³ mol dm⁻³

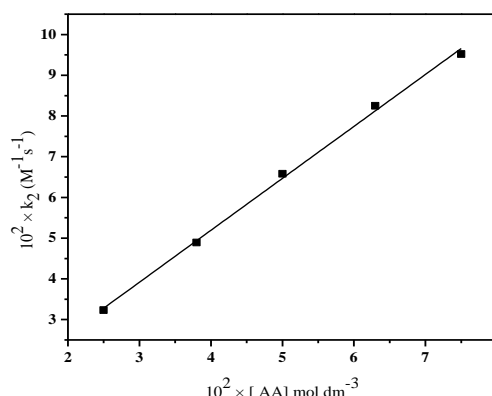


Figure.6.Plot of k_2 vs. [AA] at 308K,
[H⁺] = 0.10 mol dm⁻³; [Cu²⁺] = 5.0 × 10⁻⁴ mol dm⁻³;
[PMS] = 3.6 × 10⁻³ mol dm⁻³

Effect of varying [H⁺] on k_{obs}

The effect of [H⁺] has been investigated by varying [H⁺] (5.6×10⁻² -14.6×10⁻² mol dm⁻³) and keeping all other parameters at predetermined values. The rate constants k_1 and k_2 were decreased with the increase of [H⁺] (Table. 1). The retardation of reaction rate by increase in high [H⁺] may be attributed to the conversion of the more reactive neutral species of AA to the less reactive protonated form. Further, the plot of k_1 and k_2 against 1/[H⁺] were linear with a positive slope indicating that this reaction was inverse first order with respected to [H⁺].

Effect of varying [Cu (II)] on k_{obs}

The effect of Cu(II) on the rate constant values was studied by keeping other parameters at constant values. The observed rate constant k_1 and k_2 were found to increase linearly with the increase in the [Cu(II)] and the plots of k_1 and k_2 vs. [Cu(II)] gave straight lines with good correlation coefficients($r = 0.99$) (Table. 1).

Effect of [PMS] on k_{obs}

The reaction was studied at various concentrations of PMS (1.80 × 10⁻³ to 8.90 × 10⁻³ mol dm⁻³). It has been observed that the increase in [PMS] does not alter the reaction rate and found to be fairly constant. It showed that rate of oxidation was independent of [PMS] and order of reaction with respect to [PMS] was one (Table.1).

Effect of Ionic strength. The reaction was studied with various [NaClO₄] (5.0×10⁻² - 20.0×10⁻² mol dm⁻³) by keeping the other parameters at constant values. No significant effect of ionic strength (μ) on the reaction rate was observed which ruled out the interaction between COO⁻ of AA with HSO₅⁻ of PMS.

Effect of dielectric constant: The effect of dielectric constant on the reaction rate was studied by varying the t-butyl alcohol-water (v/v) and acetonitrile content in the reaction mixture with all other parameters constant. It was found that dielectric constant of the medium has no significant effect on the rate of both catalyzed and uncatalyzed reactions which ruled out the formation of a more polar intermediate.

Test for free radicals: The reaction failed to initiate polymerization of added acrylonitrile in to the reaction mixture, which ruled out the involvement of free radical intermediates. Moreover the addition of t-butyl alcohol, a scavenger for sulphate free radicals to the reaction mixture did not change the rate revealing the non-involvement of sulphate free radical intermediates. The EPR spectral analysis also confirmed the noninvolvement of free radical intermediate.

Table.1. Rate Constants for the Autocatalytic Reaction Pathway in the oxidation of α -alanine by PMS in the presence of Cu(II) ion in perchloric acid medium at 308K

$10^2 \times$ [AA] mol dm ⁻³	$10^4 \times$ [Cu ²⁺] mol dm ⁻³	[H ⁺] mol dm ⁻³	$10^3 \times$ [PMS] mol dm ⁻³	$10^2 \times$ [NaClO ₄] mol dm ⁻³	Alanine			
					$10^5 \times k_1$ (s ⁻¹)	$10^2 \times k_2$ (M ⁻¹ s ⁻¹)		
2.5	5.0	0.1	3.6	-	1.30	3.23		
3.8	5.0	0.1	3.6	-	1.62	4.89		
5.0	5.0	0.1	3.6	-	1.84	6.58		
6.3	5.0	0.1	3.6	-	2.13	8.25		
7.5	5.0	0.1	3.6	-	2.48	9.52		
5.0	2.5	0.1	3.6	-	1.28	4.05		
5.0	3.8	0.1	3.6	-	1.58	5.86		
5.0	5.0	0.1	3.6	-	1.89	8.02		
5.0	6.3	0.1	3.6	-	2.25	9.25		
5.0	7.5	0.1	3.6	-	2.63	11.85		
5.0	5.0	0.06	3.6	-	2.53	10.53		
5.0	5.0	0.08	3.6	-	2.06	8.15		
5.0	5.0	0.1	3.6	-	1.62	6.25		
5.0	5.0	0.13	3.6	-	1.36	5.02		
5.0	5.0	0.15	3.6	-	1.13	3.86		
5.0	5.0	0.1	1.8	-	1.21	4.35		
5.0	5.0	0.1	3.6	-	1.30	4.89		
5.0	5.0	0.1	5.3	-	1.43	5.03		
5.0	5.0	0.1	7.1	-	1.52	5.14		
5.0	5.0	0.1	8.9	-	1.63	5.27		
5.0	5.0	0.1	3.6	0.05	1.65	3.94		
5.0	5.0	0.1	3.6	0.10	1.62	4.05		
5.0	5.0	0.1	3.6	0.15	1.84	4.10		
5.0	5.0	0.1	3.6	0.20	1.75	4.12		
5.0	5.0	0.1	3.6	0.25	1.68	4.25		

Effect of Temperature: The reaction rate was measured at different temperatures (303K to 323K). It was observed that the rate constant for both uncatalyzed and catalyzed reactions were increased with increase in temperature and the plot of $\log k_1$ vs. $1/T$ and $\log k_2$ vs. $1/T$ gave a straight line. The activation energy E_a was calculated from the slope of the above Arrhenius plot. From the Eyring plot of $\log (k_1/T)$ vs. $1/T$ and $\log (k_2/T)$ vs. $1/T$, thermodynamic parameters like ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger were calculated (Table. 2). The high positive values of free energy of activation (ΔG^\ddagger) in this study indicated that the transition state was highly solvated. The negative value of entropy of activation (ΔS^\ddagger) suggested the formation of more ordered transition state than the reactants with the reduction of degree of freedom of molecules.

Table.2. Temperature Variation, Thermodynamic and Kinetic Parameters for the Cu(II) ion Catalyzed Oxidation of α -alanine by PMS

Parameters Temperature (K)	Alanine	
	$10^5 \times k_1$ (s ⁻¹)	$10^2 \times k_2$ (M ⁻¹ s ⁻¹)
303	1.62	6.91
308	1.89	8.79
313	2.28	10.45
318	2.64	12.35
E_a (KJ mol ⁻¹)	10.93	12.76
ΔH^\ddagger (KJ mol ⁻¹)	9.85	11.67
ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	-169.61	-189.22
ΔG^\ddagger (KJ mol ⁻¹)	62.09	69.95

DISCUSSION

The [PMS]_t-time profiles showed the oxidation of α -alanine by PMS in the presence of copper(II) ions, the rate was slow at initial period after which the reaction proceeds at a faster rate and the plot shows a simple curves. This is characteristic of autocatalysis and the rate equation can be expressed as,

$$-\frac{d[PMS]}{dt} = k_1 \times [PMS]_t + k_2 \times [PMS]_t \times ([PMS]_0 - [PMS]_t) \quad (4)$$

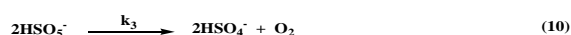
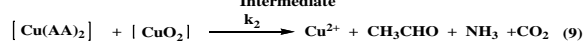
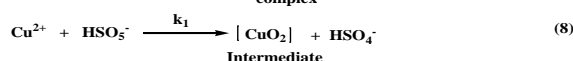
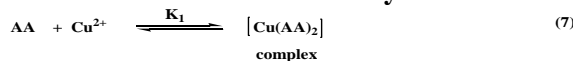
$$\frac{\text{rate}}{[PMS]_t} = k_1 + k_2 \times [PMS]_0 - k_2 \times [PMS]_t \quad (5)$$

A plot of (rate/[PMS]_t) vs. [PMS]_t, according to Eq. (5), should be a straight line with a negative slope. From the slope and intercept of this plots we can calculate k_1 and k_2 using the known value of [PMS]₀. The k_1 and k_2 values also be calculated more easily and accurately by nonlinear regression analysis of the [PMS]_t-time profile using Eq. (6), the integrated form of Eq. (5);

$$[PMS]_t = \frac{k_1 + k_2 \times [PMS]_0}{k_2 + (k_1/[PMS]_0) \times \exp(t \times (k_1 + k_2 \times [PMS]_0))} \quad (6)$$

In the present system, the oxidation of α -alanine by PMS in perchloric acid medium in the presence of Cu(II) ions forms the very reactive intermediate of copper peroxide which may be responsible for the autocatalysis. PMS will exist as HSO₅⁻ under these experimental conditions and this may be the active form of the oxidant. The linear decrease in the rate with an increase in the [H⁺] suggest that the amino acid is being removed progressively as a kinetically inactive form. The kinetics and spectral results suggest the possibility of formation of the chelate complex by the interaction of non-bonded electrons in the carboxylate oxygen and amine nitrogen of amino acid with Cu(II) ions. It reacts with HSO₅⁻ which gives copper peroxide active intermediate which is responsible for the autocatalysis process and the peroxide oxygen atom transfer leads the oxidative decarboxylation of amino acids to form end products of aldehyde. The formation of moderately stable intermediate is supported by the observed thermodynamic parameters. The complex formation is favored by the enthalpy term but negative entropy indicates a rigid structure and the transition state become highly solvated. Based on the observed results, we can propose a detailed kinetic scheme for the oxidation of amino acids as follows.

Scheme-1. Mechanism for the metal ions catalyzed oxidation of AA by PMS



$$-\frac{d[HSO_5^{2-}]}{dt} = k_1 [Cu^{2+}] [HSO_5^-] - k_2 [Cu(AA)_2] [CuO_2] + k_3 [HSO_5^-]$$

$$= \frac{k_1 K_1 [Cu^{2+}]}{[H^+]} + k_3$$

$$k_{\text{obs uncatalyzed}} = \frac{k_1 K_1 [Cu^{2+}]}{[H^+]} + k_3 \quad (11)$$

$$k_{\text{obs catalyzed}} = \frac{k_2 K_1 [AA] [Cu^{2+}]}{[H^+]} + k_3 \quad (12)$$

CONCLUSIONS

The biomimetic oxidative decarboxylation of α -alanine by PMS with Cu(II) ions proceeds through autocatalysis due to the formation of copper peroxide which is the active intermediate and the reaction involves a molecular mechanism, probably peroxide oxygen atom transfer to amino acid leads to the oxidation reaction. No free radical intermediates was involved. The activation parameters for both uncatalyzed and catalyzed reactions were calculated and the easily accessible tools of FT-IR, UV-Vis spectroscopy, CV and EPR methods were used for characterizations and investigate the coordination property of amino acid to copper metal ion.

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