International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN: 2456-172X | Vol. 2, No. 3, September - November, 2017 | Pages 97-103

COMPARATIVE STUDIES OF INCLUSION COMPLEX OF AMINO ACIDS –KINETIC STUDIES

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ABSTRACT

The kinetics studies of effect of β– cyclodextrin on the oxidation of amino acids such as lysine, glutamine and histidine by PMS, in the presence of Cu (II) ions in acetic acid–sodium acetate buffered medium (pH 3.6-5.2) at 308 K was studied under pseudo first order conditions i.e., [amino acid] >> [PMS] at various time intervals.. The effect of various reacants on the rate was studied . The reaction was studied at five different temperatures and the thermodynamic parameters like free energy of activation ($\Delta G^{\ddagger}$) enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) were calculated

KEYWORDS: copper (II), histidine , Glutamine, peroxomonosulphate (PMS), β-cyclodextrin (β-CD) catalyst, inclusion complex, kinetics

1.0 Introduction

The high oxidation potential (~ –1.8 V) and propensity to react through oxygen transfer makes peroxomonosulphate (PMS), as one of the favorable oxidants [1-6]. Cyclodextrins are cyclic oligosaccharides containing 6, 7 or more units of glucose combined into a closed cycle. Due to the polar cavity these compounds it form inclusion complexes even with water-insoluble compounds. Cyclodextrins are toroidal-shaped molecules, composed of several glucose units, with a hydrophobic cavity [7]. Kinetic study of oxidation of β-cyclodextrin (β-CD) by permanganate in aqueous media was reported [8].The kinetics of electron-transfer reactions of the [Fe Cp (Cp CH_2N) $(CH_3)_3]^{+/2+}$ couple in the presence of cyclodextrins in aqueous media [9]was also studied. Kinetics and the mechanism of the decomposition of PMS in aqueous sodium hydroxide in the presence of β-CD were reported [10]. The kinetics of oxidation of α-amino acids (AAs) by Chloramines-T (CAT) using β-CD as catalyst was studied in aqueous sodium hydroxide medium at 313 K [11]. The literature survey revealed that no work has been published on the catalytic effect of β-CD in the oxidation of arginine by PMS. We report for the first time the effect of β-CD catalyst in the oxidation of arginine by PMS in acetic acid–sodium acetate buffered medium and also the effect of copper (II) ions and the results obtained are discussed here.

2.0 Experimental Methods:

2.1 Materials and Reagents

PMS was obtained from Aldrich, USA, and the purity of the sample was found to be 98% when tested by iodometric estimation and hence used without further purification. PMS solution was freshly prepared every day, stored in a blackened vessel to prevent photodecomposition, and standardized iodometrically.

Arginine was obtained from Merck, India, and used as received. β-CD was purchased from sd-fine, India. Acetic acid was distilled to remove impurities and used to make the buffer solution. Analar grade solvents such as acetonitrile and 2-methyl-2-propanol were distilled and used for the reactions.

2.2 Kinetic Measurements.

The kinetics of oxidation of arginine by PMS in the presence of β-CD, and also both in the presence and absence of copper (II) ions in acetic acid–sodium acetate buffered medium, was studied under pseudo-first-order conditions, i.e., [arginine] >> [PMS] .A known volume of PMS solution, thermostated at the desired temperature, was pipetted out into the reaction mixture and simultaneously a timer was started. Consumption of PMS in this reaction mixture was monitored by 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 $[PMS]_t$ vs. time according to the eq.1.

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

The method of least squares was used to calculate the slope and intercept. The relative standard errors of the above-mentioned rate constant for a single run and the relative standard errors of the mean were about 2%.

2.3 EFFECT OF [AMINO ACIDS] ON k_{OBS}

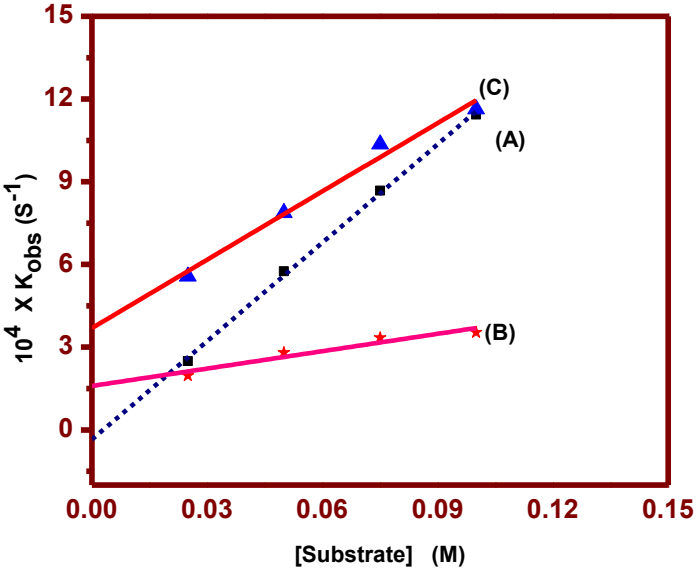
The values of k_{obs} were calculated for different concentrations of amino acids, by keeping the parameters at constant. Perusal of the kinetic results showed that the rate constant increased with an increase in [amino acid] (Table 4.3).

Table 2.3 Effect of [Amino acid] on k_{obs}

$[H^+]$ = 5 x 10^{-1} M; [sodium acetate] = 8.5 x 10^{-2} M ; [β-cyclodextrin] = 0.3 g; [copper (II)] = 2.5 x 10^{-3} M; [PMS] = 3.86 x 10^{-3} M ; Temperature=308 K.

[Aminoacid] (M)		10^4 x k_{obs} (s^{-1})	
	lysine	Glutamine	Histidine
0.025	**2.49**	**1.96**	**5.57**
0.050	**5.757**	2.80	**7.87**
0.075	**8.674**	**3.34**	10.36
0.100	**11.43**	**3.53**	**11.63**

Further, the plots of log [k_{obs}] vs. [amino acid] were linear. This result indicated first order dependence of rate on arginine. The positive intercept obtained in the above plots revealed that the reaction proceeded in two steps: one dependent on [amino acids] and the other independent of [amino acids]. The amino acids -independent step was due to the self-decomposition of PMS under the experimental conditions employed in this study. The linear plots of A, B &C represents as lysine, glutamine & histidine, while histidine and arginine are close together linearly if compared to faraway from glutamine linearly. This increasing in the order of effect of [amino acid] on k_{obs} in the presence of copper (II) sulphate catalyst is histidine > lysine > glutamine. Histidine & arginine is more effect of inclusion complex when compared to glutamine.



2.4 EFFECT OF [β-CYCLODEXTRIN] ON k_{obs}

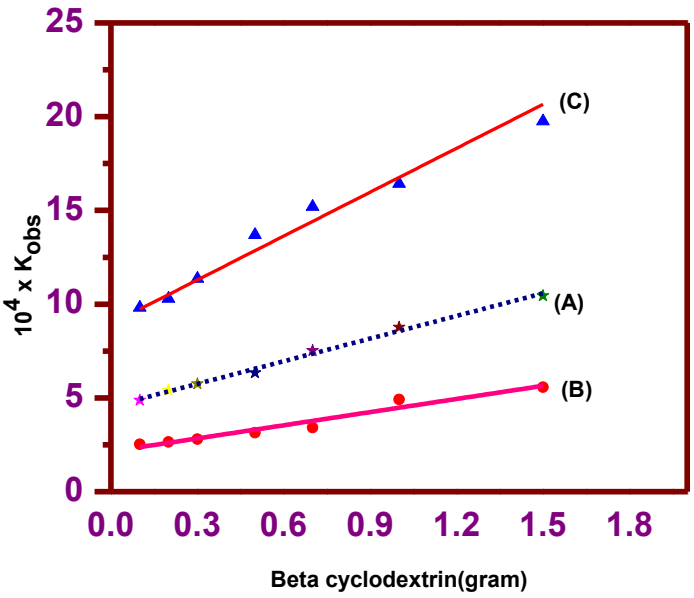
The values of k_{obs} were calculated for different quantities of β-cyclodextrin by keeping the parameters was kept constant at 308K. The rate of a reaction increased with increase in [β-cyclodextrin] (Table 4.4).

Table 4.4 Effect of [β-Cyclodextrin] on k_{obs}

[Amino acids]; $[H^+]$ = 5 x 10^{-1} M; [sodium acetate] = 8.5 x 10^{-2} M; [copper(II)] = 2.5 x 10^{-3} M; [PMS] = 3.86 x 10^{-3} M; Temperature=308 K.

β-cyclodextrin	10^4 x k_{obs} (s^{-1}) *		
	Lysine	Glutamine	Histidine
0.1	4.87	2.53	8.82
0.2	5.41	2.65	9.97
0.3	5.75	2.80	10.36
0.5	6.33	3.14	14.70
0.7	7.52	3.42	16.19
1	8.77	4.91	16.42
1.5	10.44	5.57	**19.76**

Error bar for approximation was > 0.1 % < 0.6 %



The plot k_{obs} vs. [β-cyclodextrin] were linear with a positive intercept of amino acids. This linear plot clearly indicates that the formation of inclusion complex of various amino acids. The linear plots of A, B &C represents as arginine, glutamine & histidine linearly
in the presence of copper (II) sulphate catalyst. This increasing in the order of effect of [Amino acid] on k_{obs} is histidine.> lysine> glutamine.

EFFECT OF [COPPER(II)] ON k_{obs}

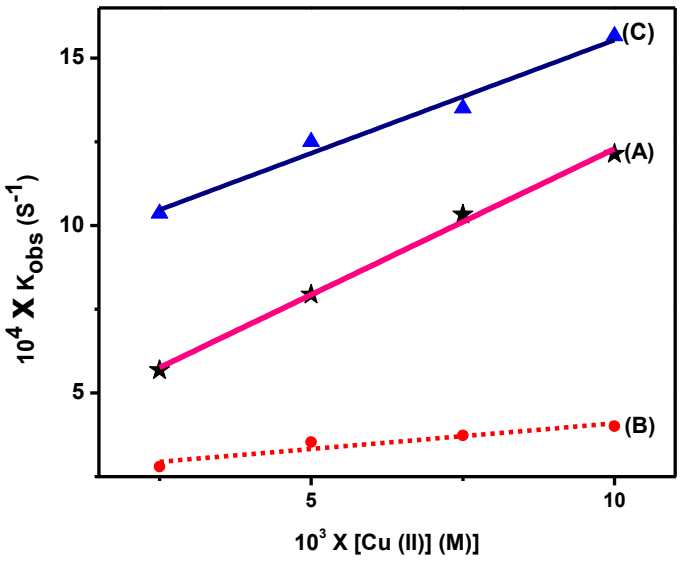
The effect of [copper(II)] on k_{obs} was calaculated by determining the values of k_{obs} at different concentrations of [copper(II)], by keeping the parameters as [amino acid]; [H^+]; [sodium acetate]; [β-cyclodextrin]; [PMS] was kept constant at 308K.. The kinetic results showed that the rate of a reaction increased with increase in [β-Cycclodextrin] in the presence of Cu (II) catalyst (Table 4.7).

Table 2.5 Effect of [copper(II)] on k_{obs}

[Amino acids] = 5 x 10^{-2} M; [H^+] = 5 x 10^{-1} M; [sodium acetate] = 8.5 x 10^{-2} M: [β-cyclodextrin] = 0.3g; [PMS] = 3.80 x 10^{-3} M; Temperature=308 K.

10^3 x [Cu(II)] (M)	**10^4 x k_{obs} (s^{-1})**		
	lysine	**Glutamine**	**Histidine**
2.5	5.68	2.80	10.36
5.0	7.94	3.53	12.5
7.5	10.33	3.73	13.5
10.0	12.14	4.01	15.66

Error bar for approximation was > 0.1 % < 0.6 %



The plot of k_{obs} vs [copper(II)] was linear with a positive intercept. This linear plot clearly indicates that the formation of inclusion complex of various amino acids. The linear plots of A, B &C represents as arginine, glutamine & histidine linearly in the presence of various concentration of copper (II) sulphate catalyst. This increasing in the order of effect of [copper(II)] on k_{obs} is histidine.> lysine> glutamine.

2.6 EFFECT OF TEMPERATURE ON k_{obs}

The thermodynamics parameter such as the free energy of activation ($\Delta G^{\#}$), enthalpy of activation ($\Delta H^{\#}$) ,and entropy of activation ($\Delta S^{\#}$) was studied by keeping all the parameters as [amino acid]; [H^+]; [sodium acetate] ; [β-cyclodextrin]; [copper(II)] sulphate catalyst ; [PMS] was kept constant at four different temperatures, viz., 303, 308, 313 and 318 K. The k_{obs} increased with the increase in temperature (Table 4.8).

Table 2.6 Effect of temperature on k_{obs}

[Amino acids] = 5 x 10^{-2} M; [H^+] = 5 x 10^{-1} M; [sodium acetate] = 8.5 x 10^{-2} M; [β-cyclodextrin] = 0.3g; [copper(II)] = 2.5 x 10^{-3} M; [PMS] = 3.86 x 10^{-3} M

* Error bar for approximation was > 0.1 % < 0.6

Temperature (K)	10^4 x k_{obs} (s^{-1})		
	Lysine	Glutamine	Histidine
303	3.18	0.7676	7.216
308	5.75	2.80	10.36
314	9.86	3.201	13.63
318	12.2	3.917	16.50

Figure 5.8 Plot of log k_{obs} vs 1/T (Arrhenius plot)

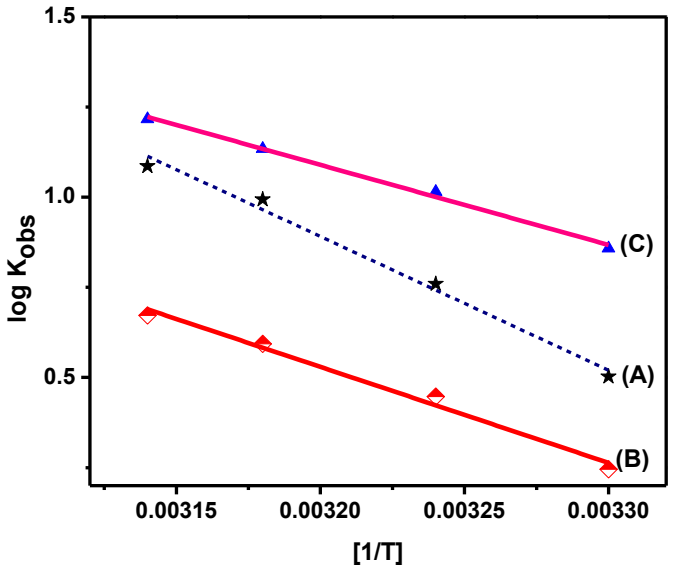
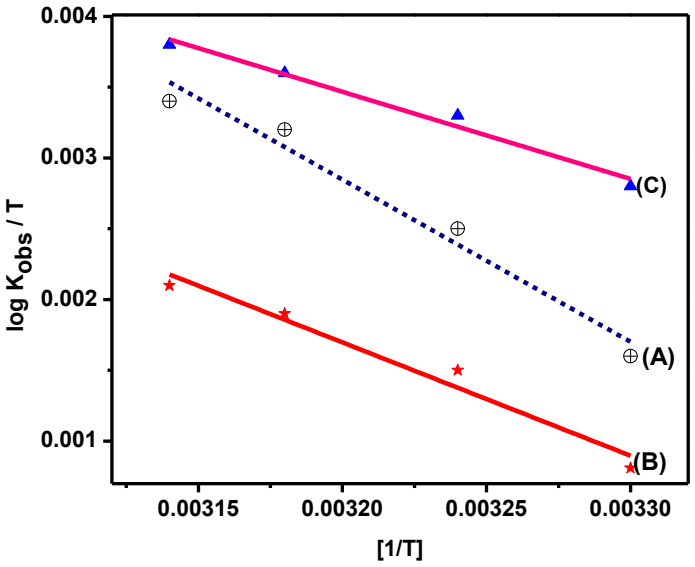


Figure 5.9 Plot of log (k_{obs}/T) vs 1/T (Eyring's plot)



The plot of log k_{obs} vs. 1/T was a straight line (Arrhenius plot) and a plot of log k_{obs}/T vs. 1/T was also linear (Eyring's plot). From the slope and intercept of the straight line, the thermodynamic parameters were calculated (Table 4.9). The positive values of free energy of activation (ΔG) and enthalpy of activation (ΔH) obtained in this study indicated that transition state was highly solvated, while the negative values of entropy of activation (ΔS) suggested the formation of a rigid transition state than the reactants with reduction of degree of freedom of molecules.

Table 2.7Thermodynamic parameters for the oxidation of aminoacids at 308 K

Amino acids	E_a kJ mol^{-1}	$\Delta H^{\#}$ KJ mol^{-1}	$\Delta S^{\#}$ J K^{-1}mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}
Lysine	30.84	95.28	-197.79	61.02
GLUTAMINE	22.12	66.54	-197.80	60.98
HISTIDINE	18.45	51.18	-197.73	60.95

Conclusion

Kinetic results for the variation of lysine, glutamine, histidine and β-cyclodextrin showed that the k_{obs} increased with increase in [histidine] and β- Cyclodextrin. Hydrophobic interaction essentially involves favorable positive entropy together with a slightly positive enthalpy change.

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