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## **Oxidation of Amino acids by Manganese (III) in aqueous Sulphuric acid**

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### **ABSTRACT**

*The Kinetics of Oxidation of amino acids glycine, alanine and valine by manganese (III) acetate in aqueous sulphuric acid has been studied. The reaction is found to proceed through the formation of intermediate complex. This shows an inverse dependence on  $[H_2SO_4]$ . The reaction has second order dependence with respect to Mn (III) and first order dependence with respect to substrate. The mechanism consistent with rate data has been proposed.*

**Key Words:** Amino acid, Oxidation, Kinetics, Mn(III), first order, Sulphuric acid.

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### **INTRODUCTION**

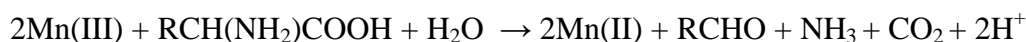
Manganese compounds have attracted much attention with regards to the oxidation of various biological substrates. In this respect Mn(III) oxidation of amino acids, their derivatives, protein-based polymers and peptides are gaining special importance owing to their biological relevance. Kinetics of oxidation of these compounds has been studied using Mn(III) as an oxidant in different media [1,2,3,4,5,6]. The kinetic studies on Mn(III) oxidation of organic or inorganic substrate in general and medicinal compounds in particular have been reported in perchlorate, sulphate, acetate and pyrophosphate medium [7, 8, 9, 10]. A medium can influence the reaction rate, due to its polarisability, hydrogen bond acceptor ability, electrophilicity, nucleophilicity and specific orientation including associative or dissociative nature. It is a specific character of manganese (III) that it can form different reactive species in presence of different acids. Generally the manganese (III) can be obtained by the processes of electrolysis [9] and it has a tendency to undergo hydrolysis. Manganese(III) sulphate has been scarcely used [11-14] in redox studies due to the difficulty in obtaining it in the pure and stable form. The manganese (III) acetate has been obtained in pure and stable form.

In the oxidation studies by manganese (III) species in sulphuric, perchloric, pyrophosphate and acetic acid media have different nature. To our knowledge there is no any report on the

manganese(III) acetate oxidation in sulphuric acid. Manganese(III) acetate forms  $\text{Mn}(\text{OAc})_3^-$  in acetic acid which form  $\text{Mn}(\text{OAc})_4^-$  by addition of acetate ion. In this study it is sort to understand how the manganese (III) acetate changes in the solution environment by taking sulphuric acid in place of acetic acid and how these species can bring about changes in the oxidation mechanism of amino acids namely Glycine, Alanine and Valine. Various studies have been reported on the oxidation of amino acids by various oxidants including manganese(III) [8,9,11,13,15,16,]. In sulphuric acid media the Mn(III) species are  $\text{Mn}(\text{III})_{\text{aq}}$ ,  $\text{MnOH}^{2+}_{\text{aq}}$  and  $\text{MnSO}_4^+$  and  $\text{MnOH}^{2+}_{\text{aq}}$  has been reported [9]. In oxidation the combine role of  $\text{Mn}(\text{III})_{\text{aq}}$  and  $\text{MnOH}^{2+}_{\text{aq}}$  has been observed as reactive species. In presence of acetic acid the reactive species of manganese (III) acetate is different from the sulphuric acid medium. In this media  $\text{Mn}(\text{OAc})_4^-$  has been reported [17]. We have used manganese(III) acetate in sulphuric acid to study the kinetics of oxidation of amino acids to investigate the mechanism of the reaction and reactive manganese(III) species. Secondly this study is essential in order to investigate the micellar effect on oxidation of amino acid under similar conditions.

### EXPERIMENTAL SECTION

The kinetics studies were carried out in Pyrex conical flask under pseudo first order reaction condition. The reaction where initiated by reaction of measured amount of substrate solution to the reaction mixture containing requisite quantities of other reactants. The progress of the reaction was monitored by the spectrophotometric estimation of Mn(III) at 340 nm. The second order rate constant were obtained from the slop of the plots between concentration of Mn(III) against time. The reproducibility of rate constant from replicate run was always higher than 98.5%. The amount of the manganese(III) used per mole of organic substrate was estimated by taking Mn(III) in large excess under experimental condition. The following stoichiometric reactions obtained from experimental results are given below-



Where  $R = H$  (glycine),  $\text{CH}_3$  (alanine),  $(\text{CH}_3)_2\text{CH}$  (Valine)

### RESULT AND DISCUSSION

Stoichiometric determination indicated the following overall reaction for the oxidation of amino acids.



Where  $R = H$  (glycine),  $\text{CH}_3$  (alanine),  $(\text{CH}_3)_2\text{CH}$  (Valine)

**Table 1: Variation of rate with initial [Mn (III)] at 301 K**

$[\text{Amino acid}] = 0.045 \text{ mol dm}^{-3}$ ,  $[\text{Mn (II) acetate}] = 0.10 \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{SO}_4] = 1.5 \text{ mol dm}^{-3}$

S.No.	[Mn (II)] mol dm <sup>-3</sup>	10 <sup>2</sup> k <sub>obs</sub> (mol <sup>-1</sup> dm <sup>3</sup> sec <sup>-1</sup> )		
		Glycine	Alanine	Valine
1	0.0015	1.29	1.21	0.77
2	0.0025	1.30	1.22	0.78
3	0.0030	1.31	1.24	0.79
4	0.0035	1.32	1.24	0.79
5	0.0040	1.33	1.25	0.80

**Effect of Oxidant:**

When amino acids were in excess, the rate at which Mn (III) disappears followed the pseudo second order rate law. The plot between time and concentration of manganese(III) was linear. The value of gradient of these plots gives the value of specific rate constant. The rate constants obtained with the variation of initial concentration of the Mn(III) in the range  $0.0015 \text{ mol dm}^{-3}$  to  $0.0040 \text{ mol dm}^{-3}$  are given in Table 1.

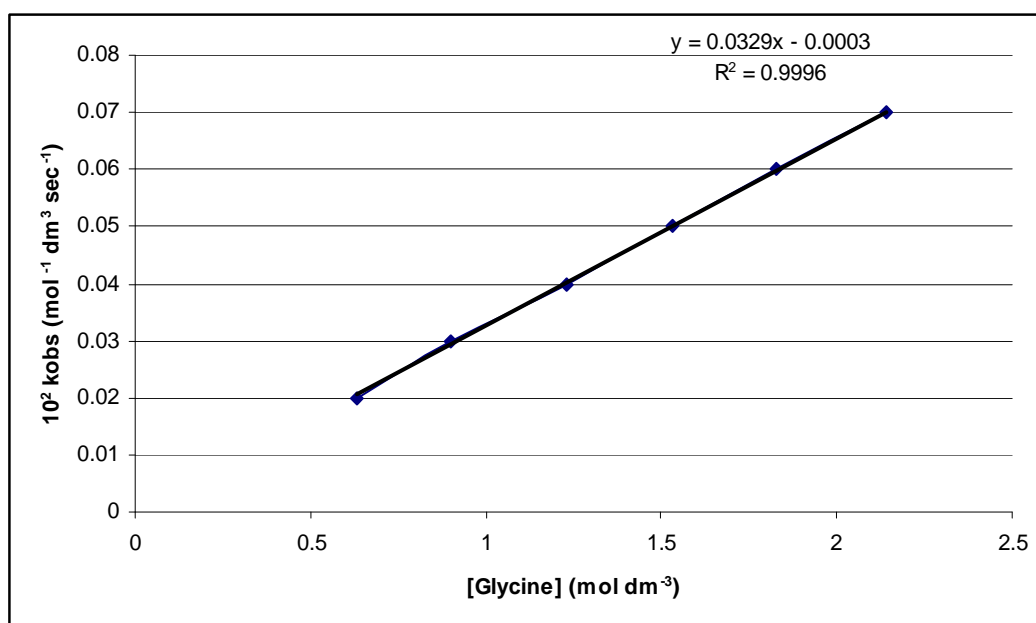
**Effect of substrate:** At constant Mn(III) concentration the reaction rate was observed with the variation of initial concentration of amino acids from  $0.02 \text{ mol dm}^{-3}$  to  $0.07 \text{ mol dm}^{-3}$ . The values of rate constant are given in Table 2.

**Table 2 : Variation of rate with initial [substrate] at 301 K**

$$[\text{Amino acid}] = 0.0040 \text{ mol dm}^{-3}, [\text{Mn (II) acetate}] = 0.10 \text{ mol dm}^{-3}, [\text{H}_2\text{SO}_4] = 1.5 \text{ mol dm}^{-3}$$

S.No.	[Substrate] $\text{mol dm}^{-3}$	$10^2 k_{\text{obs}} (\text{mol}^{-1} \text{ dm}^3 \text{ sec}^{-1})$		
		Glycine	Alanine	Valine
1	0.02	0.63	0.59	0.38
2	0.03	0.90	0.85	0.54
3	0.04	1.23	1.16	0.74
4	0.05	1.53	1.44	0.92
5	0.06	1.83	1.72	1.10
6	0.07	2.13	2.00	1.28

The rate increased with increase in initial concentration of the substrate. A plot of [Substrate] versus  $K_{\text{obs}}$  is linear as illustrated in Fig1.



**Fig 1: Plot of [Glycine] versus  $K_{\text{obs}}$  at 301K**

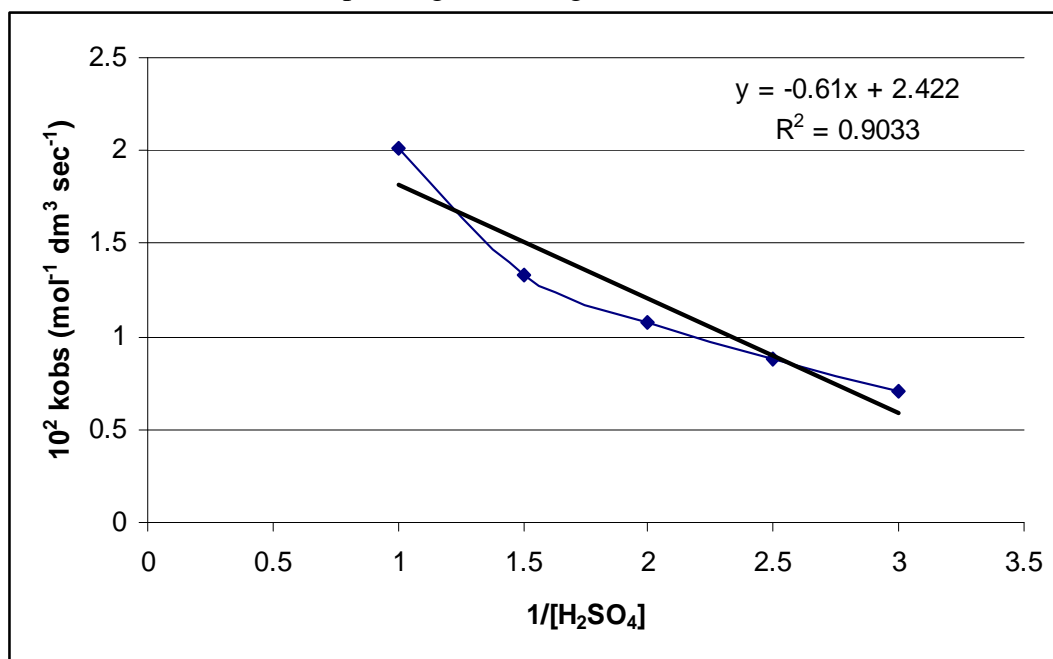
**Effect of  $\text{H}_2\text{SO}_4$ :** At constant concentration of amino acids and Mn(III) the rate constants were measured with the variation of initial concentration of sulphuric acid in the range from  $1.0 \text{ mol dm}^{-3}$  to  $3.0 \text{ mol dm}^{-3}$ . The rate constants obtained are listed in Table 3

**Table 3 : Variation of rate with initial [H<sub>2</sub>SO<sub>4</sub>] at 301 K**

[Amino acid] = 0.045 mol dm<sup>-3</sup>, [Mn (III) acetate] = 0.0040 mol dm<sup>-3</sup>, [Mn (II) acetate] = 0.10 mol dm<sup>-3</sup>

S.No.	[H <sub>2</sub> SO <sub>4</sub> ] mol dm <sup>-3</sup>	10 <sup>2</sup> k <sub>obs</sub> (mol <sup>-1</sup> dm <sup>3</sup> sec <sup>-1</sup> )		
		Glycine	Alanine	Valine
1	1.0	2.01	1.89	1.21
2	1.5	1.33	1.25	0.80
3	2.0	1.08	1.01	0.64
4	2.5	0.88	0.82	0.52
5	3.0	0.71	0.67	0.42

Increase in [H<sub>2</sub>SO<sub>4</sub>], decreased the rate and the plots of 1/[H<sub>2</sub>SO<sub>4</sub>] versus K<sub>obs</sub> were linear for each amino acids. An illustrative plot is given in Fig. 2.

**Fig 2: Plot of 1/[H<sub>2</sub>SO<sub>4</sub>] versus k<sub>obs</sub> for glycine at 301K**

**Effect on initial [Mn (II)]:** We have always used [Mn(II)] = 0.10 mol dm<sup>-3</sup>. At lower concentration the variation of initial concentration of Mn(II) 0.04 mol dm<sup>-3</sup> to 0.10 mol dm<sup>-3</sup>. The experimental results are given in Table 4

**Table 4 : Variation of rate with initial [Mn (II)] at 301 K**

[Amino acid] = 0.045 mol dm<sup>-3</sup>, [Mn (III) acetate] = 0.004 mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] = 1.5 mol dm<sup>-3</sup>

S.No.	[Mn (II)] mol dm <sup>-3</sup>	10 <sup>2</sup> k <sub>obs</sub> (mol <sup>-1</sup> dm <sup>3</sup> sec <sup>-1</sup> )		
		Glycine	Alanine	Valine
1	0.04	1.37	1.29	0.82
2	0.05	1.35	1.26	0.80
3	0.06	1.32	1.23	0.82
4	0.08	1.31	1.23	0.79
5	0.10	1.33	1.25	0.80

The experimental data of Table 4 indicates that the addition of Mn(II) has no effect on reaction rate. It is used to stabilize the Mn(III) in aqueous sulphuric acid. In the lower concentration range up to 0.1 dm<sup>-3</sup> it has no inhibitory effect on reaction rate as reported in literature [16].

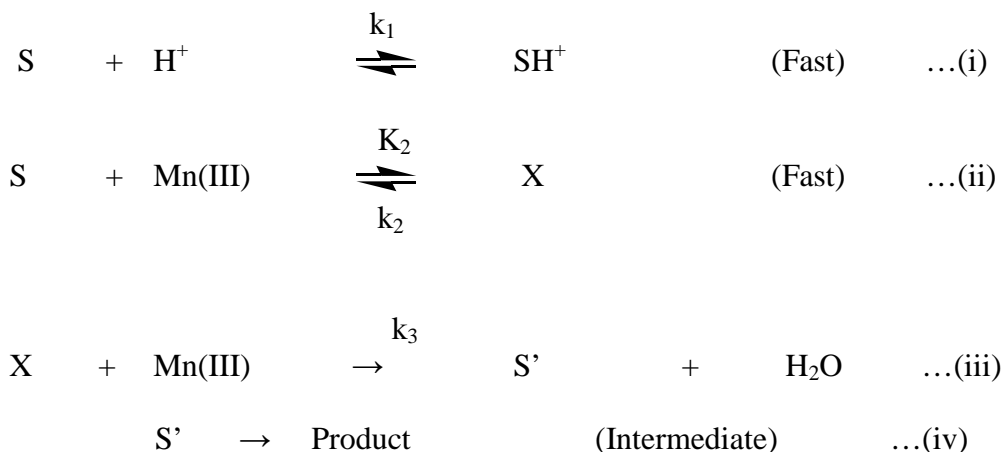
The results of the study of oxidation of amino acids by manganese (III) acetate in sulphuric acid could be summarized as below.

- i. The reactions have second order dependence with respect to manganese (III) because the time versus [manganese (III)] plots is linear in nature. The value of linearity always found greater than 0.95.
- ii. The order with respect to the substrate concentration is always first as confirmed by a linear plot between [substrate] versus  $k_{obs}$  values, which passed through origin.
- iii. The reaction rate is retarded by  $H_2SO_4$ . The reaction shows an inverse dependence on  $[H_2SO_4]$  and the plot of  $1/[H_2SO_4]$  versus  $k_{obs}$  is linear which didn't pass through the origin. This highlights the point that it is the unprotonated species, which takes part into the reaction.
- iv. The concentration of Mn (II) in the reaction mixture is  $0.1 \text{ mol dm}^{-3}$ . Below this concentration the variation of Mn (III) has no effect on reaction rate. In the study the Mn (II) promotes the stability of Mn(III) in the solution through the established equilibrium.



- v. The absence of polymerization in the reaction mixture in presence of acrylonitrile indicates the absence of free radical formation in the oxidation process. It reveals that the reaction takes place through the formation of intermediate complex.

The mechanism for the oxidation of amino acids in sulphuric acid medium has been proposed by considering that the manganese (III) and substrate molecule interacts with each other to yield the product as given in scheme 1.



**Scheme 1**

Where, S = Substrate or Amino acid

S' = Intermediate

SH<sup>+</sup> = Protonated substrate or protonated amino acid

Amino acid in the solution in presence of acid can have protonated and unprotonated form. The total concentration of the amino acid can be given as

$$[S]_T = [S] + [SH^+] \quad \dots(3)$$

According to proposed scheme 1 the concentration of unprotonated amino acid can be calculated as

$$K_1 = \frac{[SH^+]}{[S][H^+]}$$

$$\text{and } [S] = \frac{[S]_t}{\{1 + K_1[H]\}} \quad \dots(4)$$

According to the proposed scheme 1 the rate of oxidation may be represented as

$$-\frac{d[Mn(III)]}{dt} = \frac{K_2 k_3 [S]_t [Mn(III)]^2}{\{1 + K_1[H]\}} \quad \dots(5)$$

$$k_{obs} = \frac{K_2 k_3 [S]_t [Mn(III)]^2}{\{1 + K_1[H]\}} \quad \dots(6)$$

The rate law equation 6 is consistent with the experimental data, first order in substrate, second order in Mn(III) and inverse first order in H<sub>2</sub>SO<sub>4</sub>. The second order in Mn(III) is in agreement with the observed kinetics and earlier reported results [15, 18]. The addition of Mn(II) has no effect on the rate which is in agreement with the previous report on oxidation of amino acids by manganese(III) acetate in sulphuric acid [19]. In sulphuric acid, it was shown that the manganese(III) solution in aqueous sulphuric acid contains Mn(III)<sub>aqua</sub> and MnOH<sup>2+</sup><sub>aqua</sub> as reactive species. Both the species remains in equilibrium [18].

## CONCLUSION

In our study we have taken Mn(III) as reactive species which is consistent with the report in which Mn(III) has been considered more reactive [20]. The decrease in reaction rate with increase in sulphuric acid concentration may attribute to the formation of protonated species of the substrate which is non reactive in oxidation process. In case of amino acids the decrease was found in the reaction rate with increase of [H<sup>+</sup>/H<sub>2</sub>SO<sub>4</sub>] has been reported which also supports our observations [21]. Finally, the observed kinetic data and others results discussed earlier are supportive of the derived rate law equation 6, the proposed mechanism in scheme 1 and kinetically considered active species Mn(III) involve in the oxidation.

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