

The Kinetics And Mechanism Study Of The Oxidation Of A Amino Carboxylic Acids By Mn(III)

Jyoti Chaudhary* and Paridhi Kataria

*Department of Polymer Science
M. L. S. University, Udaipur (Raj.) India. 313001
jyotichaudhary13@gmail. Com*

ABSTRACT

The present paper deals with kinetic study of the oxidation of α -amino carboxylic acid by Mn(III). The oxidation has been carried out in sulphuric acid and water mixture. The rate of reaction was found to be first order with respect to Mn (III) in both amino acids i.e. Glycine and Alanine. For glycine the rate of reaction is first order with respect to [substrate] concentration. In case of alanine Michaelis Menton type kinetics is observed. The rate of reaction decreases with increasing H^+ ions concentration in both cases. No effect was observed with Ag (I) on rate of reaction. The reaction rate has been determined at different temperature and activation parameters calculated for oxidation reaction. A suitable mechanism has been proposed.

Keywords: - α amino carboxylic acid, kinetics, oxidation, mechanism, Mn (III), sulphuric acid

INTRODUCTION

Kinetics of oxidation of Mn (III) are more interesting due to its several oxidation states to which it can be reduced. (1) For chemical transformations, electrochemically or chemically generated Mn(III) is used as a mild Oxidizing agent and has special importance due to its biological relevance. (2-3)

In the present paper Mn(III) is used to oxidize amino acids i.e. glycine and alanine. Amino acids are important molecules for generation of aldehydes. Glycine occurs in every third amino acid in collagen. (4) Many kinetic studies have been carried out on the oxidation of Glycine (5-9)

Alanine is present in prostate fluid and it may play a role in supporting prostate health. It is also a source of energy for muscular tissues, the brain and the central nervous system. So the kinetics of oxidation studies of this two amino acid also

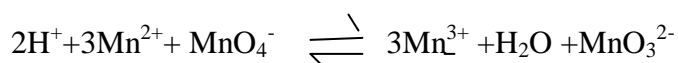
attract attention of Scientist. (10-12)

In the present study we report the mechanism of oxidation of these two amino acids by using Mn(III) in sulfuric acid water medium

EXPERIMENTAL

Materials

All the chemical used in this study were of analytical grade. Mn(III) solution were prepared by addition of manganese sulphate with potassium permanganate in sulphuric acid .The ratio of Mn(II):MnO₄⁻ was 20:1 .



Kinetic measurements

Reaction were carried out in stoppered flask at constant temperature. Kinetic runs were performed under pseudo first order conditions with a large excess of substrate over oxidant. Manganese sulphate , sulphuric acid , amino acids and water were mixed in a reaction vessel(A) and allowed to reach thermostate temperature.

A solution of potassium permanganate was separately allowed to reach thestomate temperature. Reaction was started by rapidly mixing potassium permanganate solution in reaction vessel (A). The course of the reaction were followed by monitoring the decrease in (Mn(III)) for at least half hour.

Product Study

The quantitative product study was made under kinetic conditions .The oxidized reaction mixture was completely neutralised by aqueous sodium bicarbonate and then extracted with ether. The ether layer extracted was treated with 2,4 dinitrophenyl hydrazine solution. Ether was evaporated then filtered the ppt. Glycine and alanine give formaldehyde and acetaldehyde respectively .The product obtained by their melting point (Table-1).

Table-1 : Product Study

Substrate	Product identified	Melting point of product formed	
		Reported (°C)	Observed (°C)
Glycine	Formaldehyde	166	163
Alanine	Acetaldehyde	168	167

RESULTS AD DISUCISON

Variation of rate with Mn(III)

In the oxidation of glycine and alanine by Mn(III),the logrithm of concentration of [Mn(III)] decreased linearly with time , thereby showing that the rate law of the reaction is first order with Mn(III) concentration.

The first order rate constant is independent of the initial concentration of potassium permagnate and of Mn(III). There is no change in first order rate constant with potassium permanganate concentration. This shows rate is first order with respect to Mn(III) in two amino acids .

$$-d/dt[\text{Mn(III)}] = K_1[\text{Mn(III)}]$$

Table-2: Variation of rate with Mn(III)

[Oxidant] $\times 10^4 \text{ mol dm}^{-3}$	$K_1 \times 10^5 \text{ sec}^{-1}$	
	Glycine	Alanine
1.25	19.51	1.08
2.50	19.48	1.09
5.00	19.55	1.06
7.50	19.53	1.08
10.00	19.49	1.10

Variation of rate with substrate

The rate of oxidation is first order with respect to glycine and alanine. In Glycine there is no kinetic evidence for the formation of a complex between substrate and Mn(III). In case of alanine michaelmenten type kinetics is observed.

Table-3: Variation of rate with [Amino acids]

[Substrate] $\times 10^2 \text{ mol dm}^{-3}$	$K_1 \times 10^5 \text{ sec}^{-1}$	
	Glycine	Alanine
4.00	16.90	0.91
5.00	19.50	1.09
8.00	31.20	1.63
10.00	39.20	1.81
20.00	76.90	2.74

Variation of rate with sulphuric acid and perchloric acid concentration.

Increase in concentration of $[\text{H}^+]$ decreases the rate of reaction. The results on the effect of sulphuric acid and perchloric acid concentration are summarized in the Tables -4.

An attempt to correlate rate oxidation rate with acid concentration, various hypotheses for the mechanism of acid catalysis have been tested. For the oxidation of these amino acids by Mn(III), both the Zucker-Hammett and bunnett's hypothesis was tested. The two Bunnett plots i.e. $\log K_1 + \text{H}_0$ against $\log a_{\text{H}_2\text{O}}$ and $\log K_1 - \log [\text{acid}]$ against $\log a_{\text{H}_2\text{O}}$ are given in Table -5. Zucker-Hammett plots are nearly linear show that the reaction is acid catalysed.

According to Bunnett's empirical observation the values in both sulphuric acid

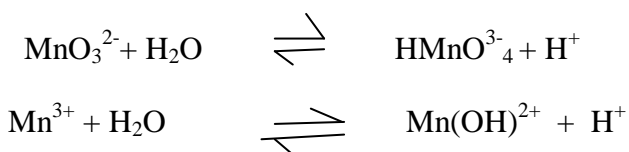
and perchloric acid indicate that the water molecule should act as a proton abstracting agent in the rate determining step.

$[H^+]$ in H_2SO_4 was calculated by the formula -

$$[H^+] = [H_2SO_4] + k_2 / H_2SO_4$$

Where $k_2 = 1.2 \times 10^{-2}$ is second dissociation constant of H_2SO_4 . In $H_2SO_4 + HClO_4$ medium total $[H^+] = [H^+]_{H_2SO_4} + [H^+]_{HClO_4}$.

The results of the effect of H^+ concentration can be explained in terms of the following equilibria.



[Mn(IV) may exist as MnO_3^{2-}].

The effect of $[H^+]$ shows that the reactive species Mn^{3+} and Mn^{4+} are $Mn(OH)^{2+}$ and $HMnO_4^{3-}$ respectively.

Increase of $[H^+]$ will decrease the concentration of reactive species thus causing the decrease in the reactive rate. From the equilibrium one would expect that the rate constant will vary as $[H^+]$.

The effect of H^+ ion can also be explained in terms of protonation of the acids with increasing acidity of the amino acids RCH_2NH_2COOH will exist in protonated form i.e. $R.CH_2NH_3^+COOH$

But it assumed that protonated form is not reactive and that the reaction take place with unreacted protonated amino-acids. The rate expected to decrease with the increase in H^+ ion concentration observed.

Table-4: Variation of rate with $[H^+]$

$[H_2SO_4]$ mol dm ⁻³	$[H^+]$ mol dm ⁻³	$K_1 \times 10^5$ sec ⁻¹	
		Glycine	Alanine
1.00	1.01	30.9	2.09
1.25	1.26	19.5	1.08
1.50	1.51	13.2	0.68
2.00	2.01	8.9	0.33
2.50	2.51	5.7	0.20

Table-5: Correlation of rate with acid concentration

Correlation	Slope	
	Glycine	Alanine
$\log k_1$ v/s $\log [H^+]$	1.70	1.28
$\log k_1$ v/s H_0 Zucker-Hammet plot	0.64	0.58
$\log k_1 + H_0$ v/s $\log a_{H_2O}$ Bunnett plot slope (ω)	3.26	2.93

Effect of rate with Mn(II) ions

The effect of Mn(II) on oxidation reaction were studied in absence and Presence of Mn(II) anions. (Table-6)

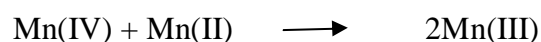
Addition of Mn(II) anions upto $1.5 \times 10^{-3} M$ increases the rate of reaction, beyond $1.5 \times 10^{-3} M$ it is observed that addition of Mn(II) retard the rate of reaction .

Small addition of Mn(II) will accelerate the production of Mn(III) and Mn(IV) in solution and if these are the reactive species addition of small amount of Mn(II) should accelerate the rate as observed. However, at large concentration of Mn(II) the retardation observed may be due to the reaction of Mn(II) and active reactive intermediate may be Mn(IV).

Even in Mn(III) pyrophosphate solution , Mn(IV) can exist in considerable proportion.

It is thus quite possible that Mn(IV) is also produced as a reaction intermediate in the reaction of $KMnO_4$ and Mn(II). Mn(IV) is more reactive than Mn(III). Therefore addition of Mn(II) destroy the Mn(IV) reactive species, thus it bring reduction in the rate of reaction .

The reaction-

**Table-6: Variation of rate with [Mn(II)]**

Mn(II) mol dm ⁻³	$K_1 \times 10^5 \text{ sec}^{-1}$	
	Glycine	Alanine
10.0	17.30	8.71
5.0	19.51	10.89
2.5	22.28	12.70
1.5	25.00	16.61
1.0	21.85	14.13
0.0	8.12	10.73

Effect of sodium pyrophosphate (SPP)

The reactions were studied in absence or presence of pyrophosphate. (Table-7)

It has been observed that addition of pyrophosphate, decreases the rate of reaction. The retardation effect with increase in pyrophosphate may be due to the total $[P_2O_7^{4-}]$ present in the reaction mixture, which inhibits the formation of intermediary cyclic complex.

Table-7: Variation of rate with [SPP]

SPP mol dm ⁻³	K ₁ × 10 ⁵ sec ⁻¹	
	Glycine	Alanine
0.0	19.50	10.89
2.5	13.80	7.94
5.0	12.59	5.75
10.0	7.67	4.21
20.0	5.25	2.88

Effect of temperature

Rate of reaction increases with temperature Table-8. A plot of $\log K_2$ ($K_2 = K_1/\text{substrate}$) vs. $1/T$ (inverse of absolute temperature) is a straight line. This shows that Arrhenius equation is valid.

The Energy of activation favors C-H bond, fission in this oxidation the negative value of entropy pointed that reaction is slow. The entropy of activation ranges between -11.0 to +0.6 Table-9. The substrate form a cyclic complex with Mn(III) or Mn(IV) and this proportionate via one electron change. It will lead to c-c fission. Further since a cyclic intermediate is formed from a non-cyclic reactants the energy of activation will be negative. Because internal rotation in the reactant become vibration in activated complex with the loss of energy.

Thus the effect of temperature are consistence with the mechanism.

Table-8: Variation of rate with Temperature

Temperature °K	K ₁ × 10 ⁵ sec ⁻¹	
	Glycine	Alanine
313	19.5	1.1
318	33.8	1.8
323	60.0	2.9
328	98.0	4.8

Table.9: Thermodynamic Parameters for Amino Acids

THERMODYNAMIC PARAMETERS	Values	
	Glycine	Alanine
Energy of activation ΔE_a kJ mol ⁻¹	21.7	21.0
Entropy of Activation ΔS JK ⁻¹ -	-3.85	-8.37

Mechanism

On the basis of above observation the probable mechanism of the oxidation is given in Figure-1.

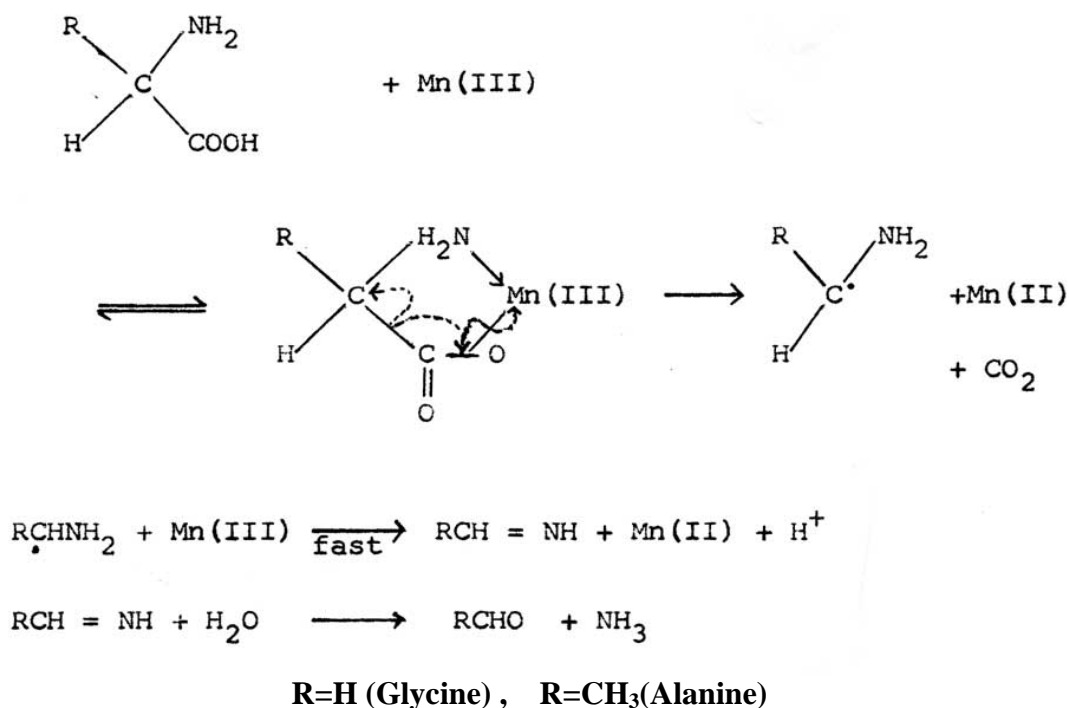


Figure: 1

CONCLUSION

The order of reaction with respect to $[\text{Mn(III)}]$ [substrate] is one. In case of alanine the reaction follows Michaelis-Menten kinetics and give the evidence of reactions proceeding through a complex between Alanin and Mn(III). However, it does not necessarily mean that such a complex is not formed. If the formation constant of the complex is low its existance can not be detected by kinetic method. Further addition of Mn(II) upto a concentration $1.5 \cdot 10^{-3} \text{M}$ accelerate the rate of reaction. This is due to the rapid disproportion of KMnO_4 into Mn(IV) and Mn(III) in presence of Mn(II). If Mn(IV) is involved in the oxidation, addition of Mn(II) will decrease the rate of reaction indicate the Mn(III) and Mn(IV) both are active in the oxidation. Increase in the concentration of $[\text{H}^+]$ decrease the rate of oxidation. Amino acids gives protonated species is expected to be less reactive then unprotonated species. Thus increase in $[\text{H}^+]$ decrease the concentration of unprotonated amino acids. The value of energy of activation is approximately same as indicates C-C fission in one electron transfer reaction through a complex between substrate and oxidant.

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