

# Kinetics and Mechanism of Oxidation of Phenylalanine by Mn(III) in Sulfuric Acid Medium

A.K. KATARIA and B.L. HIRAN\*

*Department of Chemistry*

*Mohan Lal Sukhadia University, Udaipur-313 001, India*

Phenylalanine is oxidized by Mn(III) in sulfuric acid-water medium. Effect of rate by potassium permanganate,  $\text{MnSO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ , ionic strength, sodium pyrophosphate and temperature has been studied. Energy of activation is  $91.54 \text{ kJoule mole}^{-1}$ . Oxidation is affected by both Mn(III) and Mn(IV). Kinetically  $\text{Mn}(\text{OH})^{2+}$  and  $\text{HMnO}_4^{3-}$  are the active oxidising species. A free radical mechanism is suggested.

## INTRODUCTION

A considerable amount of pioneer work of oxidation of amino acids by Mn(III) has been initiated by Water<sup>1</sup>, Kamaluddin<sup>2</sup> and Varadrajana *et al.*<sup>3</sup> but they have ignored possible role of Mn(IV) in these oxidations. The present study suggests that the roles of Mn(III) and Mn(IV) are both responsible for oxidation of amino acid in sulphuric acid medium.

## EXPERIMENTAL

Solution of phenylalanine was prepared in 2% v/v sulphuric acid. Solution of Mn(III) sulphate was prepared by addition of excess (200%)  $\text{MnSO}_4$  in potassium permanganate in sulphuric acid medium. Predetermined volume of known concentration of Mn(II) sulphate, sulphuric acid, phenylalanine in water were mixed and allowed to reach thermostatic temperature solution. Aliquots were withdrawn at known intervals of time and concentration of Mn(III) was determined iodometrically, All chemicals were A.R. grade or purified and purity was checked by m.p. The products  $\text{CO}_2$ ,  $\text{NH}_3$  and benzaldehyde were confirmed by various tests.

The reaction induced polymerisation of acrylonitrile indicates free radicals presence. Order with respect to various reactants were determined by Ostwald method.

## RESULTS AND DISCUSSION

**Effect of [Mn(III)]:** The logarithm of concentration of Mn(III) decreased linearly with time indicates first order with respect to Mn(III).  $\log(a-x)$  vs time is a straight line. It is found that there is no change in first order rate constant with potassium permanganate.

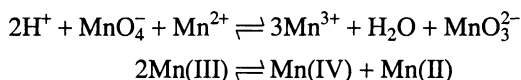
**Effect of phenylalanine concentration:** It has been found that the plot of inverts of the first order rate constant against inverts of amino acid concentration gives straight line passing through origin. This shows rate of oxidation is first order with respect to phenylalanine and no complex formation takes place in rate determining step.

TABLE-1

[H <sub>2</sub> SO <sub>4</sub> ] = 1.25 M; [KMnO <sub>4</sub> ] = 25 × 10 <sup>-4</sup> M;		[MnSO <sub>4</sub> ] = 5 × 10 <sup>-3</sup> M; Temp. 40°C				
[Phenylalanine] × 10 <sup>2</sup> M	4.00	5.00	7.50	0.00	15.00	20.00
k <sub>1</sub> × 10 <sup>5</sup> sec <sup>-1</sup>	25.03	30.70	47.98	68.80	104.68	127.98

**Effect of [Mn(II)]:** To study the effect of Mn(II) reactions were studied in absence and presence of Mn(II) (Table 2). It has been observed that addition of Mn(II) upto 1.5 × 10<sup>-3</sup> M increases the rate of reaction which was also observed by Shastry *et al.*<sup>4</sup> However, increasing the concentration of Mn(II) above 1.5 × 10<sup>-3</sup> M retards the rate of reactions.

Presence of excess of Mn(II) effectively suppresses the concentration of Mn(IV) as per the equilibria—



If only Mn(IV) is involved in the oxidation, the addition of Mn(II) will decrease the rate of reaction at all concentration. The present study therefore indicate that Mn(III) and Mn(IV) both are active in oxidation. A plot of log k<sub>1</sub> vs log [Mn(II)] gives straight line with slope 0.142. If only Mn(IV) was the reactive oxidant one would expect a linear graph of k<sub>1</sub> vs [Mn(II)] with slope equal to one. However, the observed slope is 0.2 indicating that Mn(II) is not only the reactive species. Mn(IV) is more reactive than Mn(III). Therefore addition of Mn(II) destroy the Mn(IV) reactive species and hence decrease in rate.

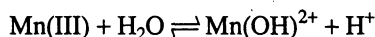
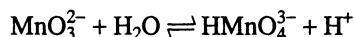
TABLE-2

[H <sub>2</sub> SO <sub>4</sub> ] = 1.25 M; [KMnO <sub>4</sub> ] = 2.5 × 10 <sup>-4</sup> M; [Phenylalanine] = 5.0 × 10 <sup>-2</sup> M; Temp. 40°C										
[Mn(II)] × 10 <sup>3</sup> mole dm <sup>-1</sup>	0.0	1.0	1.5	2.5	4.0	5.0	1.0	4.0	62.5	
k <sub>1</sub> × 10 <sup>5</sup> sec <sup>-1</sup>	15.78	33.21	35.38	32.67	31.12	30.71	27.00	23.50	21.73	

**Effect of potassium permanganate:** By increasing concentration of potassium permanganate there is no effect on first order rate constant. This shows rate is first order with respect to Mn(III).

**Effect of H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub>:** Increase in the concentration of H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> decreases the rate of oxidation. This is contrary to the observation made by Shastry *et al.*<sup>4</sup> in the oxidation of amino acid by KMnO<sub>4</sub> in moderately strong acid. From the results of the effect of Mn(II) on the rate of reaction, it is evident

that Mn(IV) is also involved in the reaction. It is therefore that the reaction species in the oxidation are  $\text{HMnO}_4^{3-}$  and  $\text{Mn}(\text{OH})^{2+}$



soluble species of Mn(IV) can exist as  $\text{MnO}_3^{2-}$ . The increase of hydrogen ion concentration will decrease the concentration of Mn(IV) and Mn(III) reactive species and hence decrease in rate of oxidation.

There is another possible explanation for the observed effect of  $[\text{H}^+]$  ions on the reaction rate. In acidic medium amino acid is protonated  $\text{RCH}_2\text{—NH}_3^+\text{COOH}$  which is less reactive than unprotonated and hence rate decreases.

TABLE-3

$[\text{H}_2\text{SO}_4] = 1.25 \text{ M}$ ;  $[\text{MnSO}_4] = 5 \times 10^{-3} \text{ M}$ ; Temp.  $40^\circ\text{C}$ ;  $[\text{Phenylalanine}] = 5 \times 10^{-2} \text{ M}$ ;  
 $[\text{KMnO}_4] = 2.5 \times 10^{-4} \text{ M}$

$[\text{HClO}_4] \text{M}$	0.0	0.2	0.4	0.6	1.0	1.2	1.5
$k_1 \times 10^5 \text{ sec}^{-1}$	30.71	23.52	18.20	15.35	9.48	8.00	1.52
$[\text{H}_2\text{SO}_4] \text{M}$	1.00	1.10	1.25	1.50	2.00	2.50	
$k_1 \times 10^5 \text{ sec}^{-1}$	36.55	34.12	30.69	23.62	16.51	13.59	

$$\text{Total } [\text{H}^+] = [\text{H}^+]\text{H}_2\text{SO}_4 + [\text{H}^+]\text{HClO}_4$$

$$[\text{H}^+]\text{H}_2\text{SO}_4 = [\text{H}_2\text{SO}_4] + K_2/[\text{H}_2\text{SO}_4]$$

where  $K_2 = 1.2 \times 10^{-2}$  is second dissociated constant of  $\text{H}_2\text{SO}_4$ .

**Effect of Sodium pyrophosphate:** Addition of sodium pyrophosphate retard the rate of reaction, this is because of Mn(III) and Mn(II) form stable complex with pyrophosphate which is less reactive compared to Mn(III) and Mn(IV) aq.<sup>5</sup>

**Effect of ionic strength:** Addition of  $\text{KNO}_3$  has no effect on rate of reaction, this suggests non involvement of ion pair in rate determining step.<sup>6</sup>

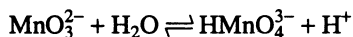
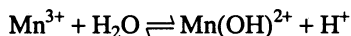
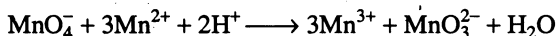
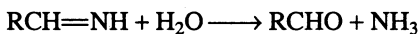
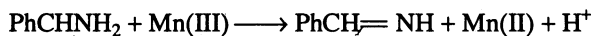
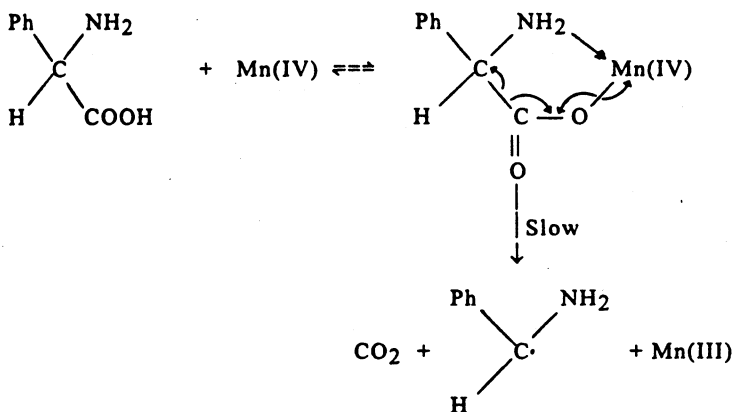
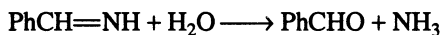
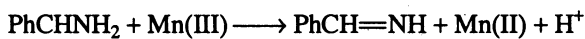
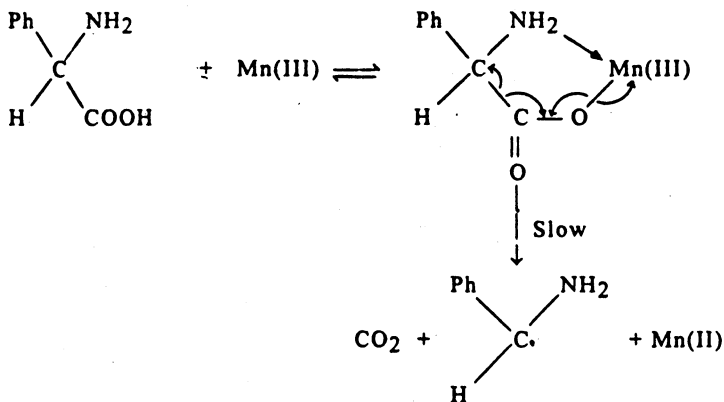
**Effect of temperature:** Rate of reaction increases with increase in temperature.  $\log k_1$  v/s  $1/T$  gives a straight line and temp. coefficient = 3. Energy of activation for the reaction in  $51.54 \text{ kJ mole}^{-1}$ . This is in range observed for C—C fission in the decomposition of organic substrate by Mn(III). The entropy of activation is  $+2.34 \text{ kJ/mole}$ , a very small +ve value. The entropy of activation is also in the range of unimolecular decomposition of a complex.<sup>7</sup> The substrate form a cyclic complex with Mn(III) or Mn(IV) and this disproportionate via one electron change. It will lead to C—C fission.

TABLE-4

$[\text{H}_2\text{SO}_4] = 1.25 \text{ M}$ ;	$[\text{Phenylalanine}] = 5 \times 10^{-2} \text{ M}$ ;					
$[\text{MnSO}_4] = 5 \times 10^{-3} \text{ M}$ ;	$[\text{KMnO}_4] = 2.5 \times 10^{-4} \text{ M}$					
Temp. (K)	313	318	323	328	331	333
$k_1 \times 10^5 \text{ sec}^{-1}$	30.71	54.83	95.96	157.37	188.04	267.40

$$\Delta E_a^\ddagger = 91.54 \text{ kJ mole}^{-1}$$

Considering all the above observations, the following mechanism may be suggested as:



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*For more information, contact:*

IUPAC Secretariat

Tel: +1 919 485 8700

Fax: +1 919 485 8706

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