

## MN (II) CATALYZED OXIDATION OF ALANINE BY CERIUM (IV) IN SULPHURIC ACID MEDIUM: A KINETIC AND MECHANISTIC STUDY

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### ABSTRACT

The kinetics of Mn (II) catalyzed oxidation of alanine with Cerium (IV) has been studied in Sulphuric acid medium at 40°C. The reaction is first order with respect to Ce (IV) and Mn (II) and positive fractional order with respect to alanine. The rate of reaction increases with increasing H<sup>+</sup> concentration and decreases with the increase of [HSO<sub>4</sub>]. From the dependence of k<sub>obs</sub> on the concentration of [HSO<sub>4</sub>], the kinetically active species has been found to be Ce(SO<sub>4</sub>)<sub>2</sub>. On the basis of experimental results, a mechanism has been proposed. The rate constants of the rate determining step and activation parameters have been evaluated.

**Key Words:** Kinetics, Oxidation, Alanine, Mn (II) catalyst, Cerium (IV), Sulphuric acid.

### INTRODUCTION

Several kinetic studies on the mechanism of oxidation of amino acids both in acid and alkaline medium and also in presence of metal and nonmetal ion catalysts have been reported<sup>1</sup>. There are studies where a group of workers indicate formation of the oxidation product was aldehyde through the hydrolysis of imine intermediate whereas the other group reports further oxidation of the imine to nitrile, while third group reported the formation of  $\alpha$ - keto acid. In view of these observations the controversy regarding the identification of oxidation products of amino acids still persists. Alanine is a neutral amino acid, in which hydrogen of one of the methyl group is replaced by amino group. Very few reports are available on the kinetics of oxidation of alanine by Ce (IV) in sulphuric acid medium. The paper deals with the kinetic and mechanistic study on the oxidation of alanine which has major biochemical and biotechnological significance. In aqueous H<sub>2</sub>SO<sub>4</sub> media, Ce(IV) is both thermodynamically and kinetically weaker as an oxidizing agent compared to Ce (IV) in aqueous HClO<sub>4</sub> media (E<sub>0</sub>=1.7V in 1.0 mol dm<sup>-3</sup> HClO<sub>4</sub>, E<sub>0</sub>=1.4V in 1.0 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>). However, Ce(IV) in aqueous H<sub>2</sub>SO<sub>4</sub> media is highly stable<sup>2</sup> and does not require any

special precautions to prevent its photochemical decomposition<sup>3</sup>, which occurs spontaneously in aqueous HClO<sub>4</sub> media. This is reason, Ce (IV) in aqueous H<sub>2</sub>SO<sub>4</sub> medium is often used in analytical chemistry<sup>4</sup>. On the other hand Ce (IV) oxidation reaction in aqueous H<sub>2</sub>SO<sub>4</sub> media is in many cases kinetically sluggish and needs metal ion catalysts<sup>5</sup>. Thus the use of suitable catalysts in Ce (IV) oxidation reaction in aqueous H<sub>2</sub>SO<sub>4</sub> media is of much importance in cerate oxidimetry<sup>4</sup> as well as in catalytic kinetic methods of analysis<sup>5</sup>. The mechanistic path of catalysis has been found to depend on the nature of substrate, metal ion acting as the catalyst and reaction medium. So, in order to have a further insight into the mechanism of oxidation of alanine, we have carried out kinetic investigations by Cerium (IV), a one electron oxidant in sulphuric acid medium.

### MATERIALS AND METHOD

The Kinetic study of oxidation of alanine by Cerium (IV) in sulphuric acid medium in the presence of Mn(II) as catalyst has been studied by monitoring Cerium (IV). The Cerium (IV) stock solution was prepared by dissolving Ceric Ammonium Sulphate (AR, E.Merck) in 1.0 mol dm<sup>-3</sup> sulphuric acid and standardized with iron (II) ammonium sulphate solution using ferroin as an indicator. All other reagents were Analytical Reagent grade and were used as supplied. Doubly distilled water was employed throughout the study.

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The reaction was initiated by mixing the pre-equilibrated reactant solutions taken at the desired conditions and progress of the reaction was followed by measuring the absorbance of Cerium(IV) at 360 nm, using UV-Visible spectrophotometer UV 3000<sup>+</sup>(LABINDIA) with 1 cm path length. The temperature was maintained by a peltier accessory (temperature-Controlled) attached to a UV-Visible spectrophotometer was used. The pseudo first order rate constant  $k_{obs}$  were calculated as usual from the measured rate of disappearance of Cerium (IV). The rate constants were found to be reproducible within  $\pm 5\%$ .

## RESULTS AND DISCUSSION

### Effect of Cerium (IV)

The concentration of Cerium (IV) was varied from  $5.0 \times 10^{-5}$  to  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup> at fixed concentration of [Ala] =  $5 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1.0 mol dm<sup>-3</sup>, I = 1.5 mol dm<sup>-3</sup> and [Mn(II)] =  $5 \times 10^{-5}$  mol dm<sup>-3</sup> at 40°C. The pseudo first order rate constant ( $k_{obs}$ ) are independent of the initial concentration

**Table 1. Effect of Cerium (IV), Alanine, [H<sup>+</sup>] and Mn(II) on oxidation of alanine by Cerium(IV) in sulphuric acid medium at 40°C.**

$10^4$ [Ce(IV)] mol dm <sup>-3</sup>	$10^3$ [Ala] mol dm <sup>-3</sup>	$10^5$ [Mn(II)] mol dm <sup>-3</sup>	[H <sup>+</sup> ] mol dm <sup>-3</sup>	$10^4 k_{obs}$ sec <sup>-1</sup>
0.5	5.0	5.0	1.0	8.31
0.7	5.0	5.0	1.0	8.32
1.0	5.0	5.0	1.0	8.34
2.0	5.0	5.0	1.0	8.30
3.0	5.0	5.0	1.0	8.32
4.0	5.0	5.0	1.0	8.33
5.0	5.0	5.0	1.0	8.31
5.0	2.0	5.0	1.0	4.16
5.0	3.0	5.0	1.0	5.49
5.0	4.0	5.0	1.0	7.07
5.0	5.0	5.0	1.0	8.31
5.0	7.5	5.0	1.0	12.0
5.0	10.0	5.0	1.0	13.8
5.0	20.0	5.0	1.0	23.9
5.0	5.0	2.0	1.0	3.22
5.0	5.0	5.0	1.0	8.31
5.0	5.0	7.0	1.0	11.1
5.0	5.0	10.0	1.0	16.6
5.0	5.0	15.0	1.0	25.0
5.0	5.0	20.0	1.0	33.3
5.0	5.0	5.0	0.2	3.5
5.0	5.0	5.0	0.4	5.5
5.0	5.0	5.0	0.6	6.9
5.0	5.0	5.0	0.8	7.9
5.0	5.0	5.0	1.0	8.31

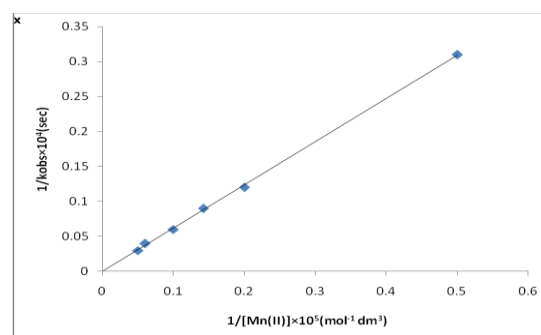
of Cerium(IV) (Table1).

### Effect of Alanine

The concentration of alanine was varied from  $2.0 \times 10^{-3}$  to  $2 \times 10^{-2}$  mol dm<sup>-3</sup> at fixed concentration of Cerium (IV) =  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1.0 mol dm<sup>-3</sup>, I = 1.5 mol dm<sup>-3</sup>, and [Mn (II)] =  $5 \times 10^{-5}$  mol dm<sup>-3</sup> at three temperature viz 35°, 40°, 45°C respectively. Pseudo first order constant ( $k_{obs}$ ) increases with the increase of concentration of alanine (Table-1.) The reaction order of alanine is 0.75 obtained from the linear regression of log  $k_{obs}$  versus log [Ala], indicating fractional order with respect to alanine.

### Effect of Mn (II)

Manganese (II) concentration was varied from  $2.0 \times 10^{-5}$  to  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup> at constant concentration of Ce (IV) =  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [Ala] =  $5 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1.0 mol dm<sup>-3</sup>, I = 1.5 mol dm<sup>-3</sup>. A plot of  $1/k_{obs}$  versus  $1/[Mn(II)]$  yields a straight line passing through the origin indicating order with respect to Mn (II) to be one. (Fig-1)



**Figure 1: Linear plot of  $1/k_{obs}$  versus  $1/[Mn(II)]$  [Ce(IV)] =  $5 \times 10^{-4}$  mol dm<sup>-3</sup>, [Ala] =  $5 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1.0 mol dm<sup>-3</sup>, Temperature 40°C**

was varied in the range of 0.2 to 1.0 mol dm<sup>-3</sup> at fixed [H<sup>+</sup>] {[H<sup>+</sup>] = 0.2 mol dm<sup>-3</sup>} [Ce(IV)], [Ala], [Mn(II)], at 40°C. Here [HSO<sub>4</sub><sup>-</sup>] = [NaHSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub>] ignoring the dissociation of [HSO<sub>4</sub><sup>-</sup>] in strongly acidic medium. Linear plot of  $1/k_{obs}$  versus [HSO<sub>4</sub><sup>-</sup>] shows  $k_{obs}$  increases with the increase of [HSO<sub>4</sub><sup>-</sup>] (Fig-2) Therefore HSO<sub>4</sub><sup>-</sup> shows a rate retarding effect.

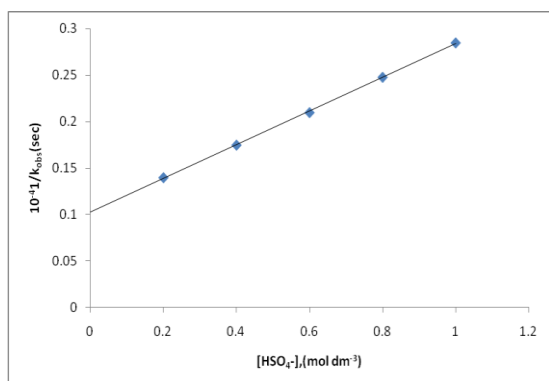
### Effect of ionic strength

At fixed [Ce (IV)], [Ala], [H<sub>2</sub>SO<sub>4</sub>], [Mn (II)] and temperature the ionic strength ( $\mu$ ) was varied 1.2- 2.0 mol dm<sup>-3</sup>, employing Sodium perchlorate for adjusting ionic strength. The rate of reaction increases slightly with increasing ionic strength.

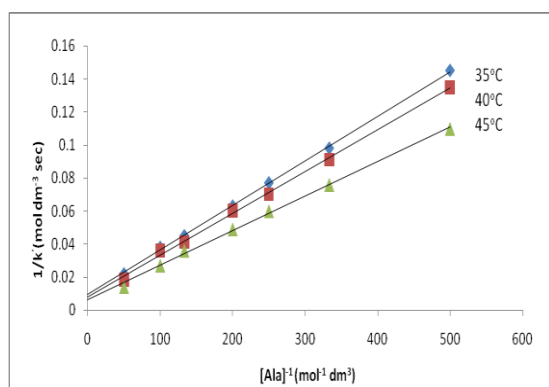
### Effect of added product

The effect of Cerium (III) on the rate was also

studied and was found to be independent of Cerium (III) concentration, ruling out any possibility of the rate limiting step preceded by the reversible equilibrium involving Cerium (III).



**Figure 2:** Linear plot of  $1/k_{obs}$  versus  $[HSO_4^-][Ce(IV)] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[Ala] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[Mn(II)] = 5 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[H^+] = 0.2 \text{ mol dm}^{-3}$ ,  $Temp = 40^\circ C$



**Figure 3:** A plot of  $k^{-1}$  versus  $[Ala]^{-1}$  at three different temperatures.

### Test for free radicals

In the reaction mixture, acrylonitrile solution was added in an inert atmosphere for 4 hour. Then dilution with methanol, a white precipitate resulted suggesting the participation of free radicals in the reaction.

### Stoichiometry and Product Analysis

Under the kinetic conditions in presence of catalyst, excess of alanine over Cerium (IV) constant ionic strength and acidity in a thermostated water bath at  $40^\circ C$  for 24 hour. The products were extracted from the reaction mixture with ether. An addition of 2, 4-dinitrophenylhydrazine in the reaction mixture yield brown precipitate of hydrazone derivative of aldehyde<sup>6</sup>. The product aldehyde was confirmed by its I.R spectrum<sup>7</sup>, carbonyl stretching at 2930

$cm^{-1}$  due to the aldehyde stretching. From observations of different sets. The stoichiometry of the reaction can therefore be represented by equation (1).

The kinetic results,  $1/k_{obs}$  versus  $1/[Ala]$  fits well with the Michaelis Menen model, suggesting that 1:1 type complex of (Ala) and Mn(II) is formed in the first pre-equilibrium step. Alanine is protonized in acid media, indicating involvement of  $H^+$  is the reaction in the pre-equilibrium step. To explain the first order dependence on Ce(IV), it is assumed that the complex is oxidized by cerium(IV) is a slow step to produce Mn(II) substrate complex which collapses in a fast step to produce catalyst and free radical, which is responsible for polymerization of acrylonitrile<sup>8</sup>. The condition employed in the present investigation appears to be  $Ce(SO_4)_2$  as the reactive species of Cerium (IV). Thus a mechanism consistent with the above results is proposed. (Scheme-I)

Scheme-1

According to the mechanism, applying the steady state condition to the free radical<sup>9</sup>.

$$\frac{-d[Ce(IV)]}{dt} = \frac{2k K_1 K_2 [Mn(II)][Ce(IV)][Ala][H^+]}{K_1 K_2 [Ala][H^+] + 1} \quad (7)$$

$$\text{If } K = K_1 K_2$$

$$\frac{-d[Ce(IV)]/dt}{[Ce(IV)]} = k_{obs} = \frac{2kK[Mn(II)][Ala][H^+]}{K[Ala][H^+] + 1} \quad (8)$$

The rate of reaction is first order with respect to Mn (II), so equation (8) changes into equation (9)

$$k' = \frac{2kK[Ala][H^+]}{K[Ala][H^+] + 1} \quad k' = \text{second order rate constant} \quad (9)$$

Rearrangement of the equation (9)

$$\frac{1}{k'} = \frac{K[\text{Ala}][\text{H}^+] + 1}{2kK[\text{Ala}][\text{H}^+]} \quad (10)$$

$$= \frac{1}{2k} + \frac{1}{2kK[\text{Ala}][\text{H}^+]} \quad (11)$$

According to equation (11)  $1/k'$  versus  $1/[\text{Ala}]$  at constant  $[\text{H}^+]$  yielded straight line with non zero intercept. (Figure 3)

The ratio of intercept and slope of the line yielded the value of  $K$  36.9, 30.2, 28.3  $\text{dm}^3 \text{mol}^{-1}$  at 35°, 40°, 45°C respectively. The activation parameters of the rate determining step have been evaluated from the plot of  $\log k$  versus  $1/T$  and thermodynamic quantities were determined from the plot of  $\log K$  versus  $1/T$ . (Table-2)

Equation (16) may be written as

$$k_{\text{obs}} = \frac{A}{1 + Q_3[\text{HSO}_4^-]} \quad (17)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{A} + \frac{Q_3[\text{HSO}_4^-]}{A} \quad (18)$$

Equation (18) suggests that  $1/k_{\text{obs}}$  versus  $[\text{HSO}_4^-]$  should be linear and agrees with observed experiment data. From the slope  $Q_3/A$  and intercept  $1/A$  obtained by the linear plot of  $1/k_{\text{obs}}$  versus  $[\text{HSO}_4^-]$  (Figure 2), the ratio of slope to intercept was calculated to be 1.66 i. e.  $Q_3$  which is good agreement with the previously reported value<sup>11</sup>. All the above results show that  $\text{Ce}(\text{SO}_4)_2$  is

**Table: 2 Activation parameter and thermodynamics quantities evaluated from the rate constants.**

Temperature (K)	$k(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$	Activation parameters	$K(\text{dm}^3 \text{mol}^{-1})$	Thermodynamic quantities
308	52.0	$\Delta H^\ddagger(\text{KJ mol}^{-1}) = 37.59$ $E_a(\text{KJmol}^{-1}) = 40.19$	36.9	$\Delta H(\text{KJ mol}^{-1}) = -20.6$
313	67.5	$\Delta S^\ddagger(\text{JK}^{-1} \text{mol}^{-1}) = -82.02$	30.2	$\Delta S(\text{J K}^{-1} \text{mol}^{-1}) = -282.8$
318	83.3	$\Delta G^\ddagger(\text{KJ mol}^{-1}) = 80.57$	28.3	$\Delta G(\text{KJ mol}^{-1}) = 67.9$

### Active Cerium Species

Under the experimental conditions in aqueous sulphuric acid medium, the important Ce(IV) sulphato complexes are  $\text{Ce}(\text{SO}_4)_2^{2+}$ ,  $\text{Ce}(\text{SO}_4)_2$  and  $\text{HCe}(\text{SO}_4)_3^-$  and relevant equilibria are:-

The value of equilibrium constants<sup>10</sup> at 25°C are  $Q_1 = 3.5 \times 10^3$ ,  $Q_2 = 2 \times 10^2$  and  $Q_3 = 3.4$ . Insignificant amount of unhydrolyzed species of cerium (IV) would also exist along with these sulphato complexes. In the light of the equilibrium (equation 12-14), inverse bisulphate dependence (Fig.-2) can be explained by assuming  $\text{Ce}(\text{SO}_4)_2$  as the reactive species. The concentration of this active species is given by equation (15)

$$\text{Ce}(\text{SO}_4)_2 = \frac{[\text{Ce}(\text{IV})]}{1 + Q_3[\text{HSO}_4^-]} \quad (15)$$

$$= f[\text{Ce}(\text{IV})]_{\text{T}}$$

Thus equation (8) can be written as

$$k_{\text{obs}} = \frac{2kK[\text{Mn}(\text{II})][\text{Ala}][\text{H}^+]}{K[\text{Ala}][\text{H}^+] + 1 + Q_3[\text{HSO}_4^-]} \quad (16)$$

$$A = \frac{2kK[\text{Mn}(\text{II})][\text{Ala}][\text{H}^+]}{K[\text{Ala}][\text{H}^+] + 1}$$

the kinetically active species. Furthermore the rate of reaction slightly affected by ionic strength, indicate that there must be a neutral molecule in the rate determining step, which confirm  $\text{Ce}(\text{SO}_4)_2$  as the kinetically active species in present study.

### CONCLUSION

The reaction between Cerium(IV) and alanine in presence of Mn(II) as a catalyst occurs with measureable velocity in sulphuric acid media. The rate of hydrogen ion is crucial to the reaction. Among various species of Cerium(IV) in acid medium,  $\text{Ce}(\text{SO}_4)_2$  is considered as active species for the title reaction. Rate constant with respect to slow step and equilibrium constant involved in the mechanism are evaluated. The activation parameters with respect to the slow step and thermodynamics quantities are also calculated.

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