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KINETIC AND MECHANISTIC STUDY OF OXIDATION OF SERINE BY CERIUM (IV) IN PRESENCE OF MANGANESE (II) AS CATALYST IN AQUEOUS ACID MEDIUM

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Abstract

Kinetics of manganese(II) catalysed oxidation of serine by cerium(IV) has been studied in Sulphuric acid medium at 45 C. The reaction follows first order kinetics with respect to [Mn(II)] while negative effect was observed for the variation of [H⁺] on the rate of reaction. The reaction exhibits first order kinetics with respect to serine at its lower concentrations and tends towards zero order at its higher concentration. The reaction is first order with respect to Ce(IV). Under the experimental condition, the kinetically active species of cerium has been found to be Ce(SO₄)₂. The rate constants observed at three different temperatures were utilized to determine the activation parameters. A plausible mechanism has been proposed from the results of kinetics studies, reaction stoichiometry and product analysis.

Keywords: Serine, Cerium(IV), Manganese(II), Oxidation, Mechanism, Sulphuric Acid.

1. Introduction

Oxidation reactions are of fundamental importance in nature and are key transformations in organic synthesis. We know that amino acids are molecules containing an amine group, a carboxylic acid group and a side chain that varies between different amino acids. The key elements of an amino acid are carbon, hydrogen, oxygen and nitrogen. The kinetics and mechanism of oxidation of amino acids have been studied previously by some researchers¹⁻². However, the mechanism is different in the different reaction systems. These oxidation reactions display diverse reaction mechanisms, oxidative deamination and decarboxylation³⁻⁵.

The oxidation of serine has received much attention because of strengthening the immune system by providing antibodies and synthesizes fatty acid sheath around nerves fibres⁶. Oxidation of serine by some inorganic oxidants has been studied⁷⁻⁸ in both acidic and alkaline medium.

Ce(IV) solution in acidic media is stable for long time and is not influenced by light and increasing temperature for short time⁹. There are numerous mechanistic studies

of oxidation of organic compounds apart from useful synthetic studies¹⁰ in which cerium(IV) has been employed as an oxidant in acid sulphate medium. Transition metal ions have been extensively used¹¹ as catalyst for effecting a number of reactions. In recent times, the studies on the use of transition metal ions either alone or as binary mixtures as catalysts in many redox reactions have been gaining interest. Mn(II) has been used as a homogenous catalyst in various redox reactions¹² and its efficiency as a catalyst can be visualised from the oxidation studies of various organic substrates involving different oxidants¹³⁻¹⁶. The mechanism of catalysis is quite complicated due the formation of different intermediate complexes, free radicals and different oxidation states of manganese. Preliminary experimental results indicate that the reaction of serine with cerium(IV) in acid medium, without a catalyst was sluggish, but the reaction became facile in the presence of a small amount of Mn(II) catalyst. Therefore, in order to explore the mechanism of serine-cerium(IV) reactions and also to study the catalytic action of Mn(II), the manganous ion has been selected as a catalyst.

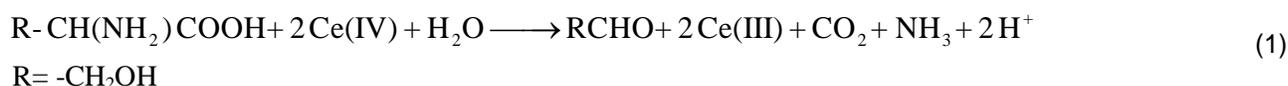
2. Experimental Work

2.1 Material and Method

Chemicals of pure quality were used without further purification. Stock solution of serine and manganese(II) were prepared in double distilled water. Ce(IV) stock solution were prepared by dissolving ceric ammonium sulphate in 1.0 M sulphuric acid and standardized with iron(II) ammonium sulphate solution using ferroin as an indicator. Other chemicals and reagents such as sodium sulphate, sulphuric acid, acrylonitrile were used of analytical grade with 99.9% purity. The stock solutions were diluted as required and standardized before use in kinetic reaction.

2.2 Kinetic measurements

Appropriate quantities of the solution were placed in separate glass vessels and kept for at least 15 minutes in a thermostated water bath at 45 C. The calculated amount of each reactant were then added together in a particular glass vessel followed by the requisite amount of double distilled water. The reaction



The oxidation products were identified as Ce(III), 2-hydroxyethanal, ammonia and carbon dioxide. 2-hydroxyethanal was detected by 2,4 DNP test. The yellow ppt of 2,4-dinitrophenyl hydrozone of aldehyde product was obtained. The other product ammonia was detected by Nessler's reagent test¹⁷ and CO₂ was qualitatively detected by passing the liberated gas through a tube containing lime water.

3.2 Reaction order

The reaction order were determined from the slop of log k_{obs} versus log concentrations plots by varying the concentration of cerium(IV), serine, sulphuric acid and manganese(II) catalyst in turn while keeping all other concentrations and conditions constant.

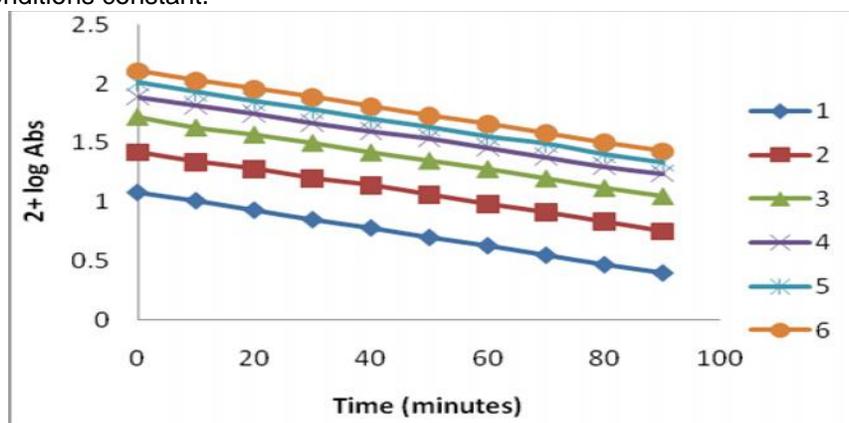


Fig. 1 Pseudo First Order Plots for The Variation Of Cerium(IV)

[Ser] = 5.0×10^{-3} mol dm⁻³, [Mn(II)] = 5.0×10^{-5} mol dm⁻³, [H⁺] = 1.0 mol dm⁻³, I = 1.50 mol dm⁻³, Temp.=45 C, [Ce(IV)] = (1) 0.50×10^{-4} mol dm⁻³, (2) 1.0×10^{-4} mol dm⁻³, (3) 2.0×10^{-4} mol dm⁻³, (4) 3.0×10^{-4} mol dm⁻³, (5) 4.0×10^{-4} mol dm⁻³, (6) 5.0×10^{-4} mol dm⁻³.

mixture was then placed in a thermostated water bath maintained at constant temperature of 45 C ($\pm 5\%$) and the reaction was initiated by adding the requisite amount of oxidant solution placed separately in the same water bath. The course of the reaction was followed by estimating the decrease in the absorbance of cerium(IV) from time to time at a wave length 360 nm by using a Systronics(166) UV-Visible spectrophotometer.

3. Results and Discussion

3.1 Stoichiometry and product analysis

A reaction mixture containing a known excess of [Ce(IV)] over [Serine] were kept in the presence of constant [H⁺], Mn(II) and ionic strength at 45 C for 48 hours. After completion of the reaction, the remaining Ce(IV) was estimated in different sets of the experiment. The results indicated that two moles of Ce(IV) were consumed by one mole of serine as given by equation (1)

3.3 Effect of Ce(IV)

At constant concentration of serine = 5.0×10^{-3} mol dm⁻³, Mn(II) = 5.0×10^{-5} mol dm⁻³, [H⁺] = 1.0 mol dm⁻³, and ionic strength I = 1.50 mol dm⁻³, the Ce(IV) concentration was varied from 5.0×10^{-5} to 5.0×10^{-4} mol dm⁻³ at 45 C. The order with respect to Ce(IV) concentration was found to be unity, since the rate constant k_{obs} was almost constant at different Ce(IV) concentration (Table-1). The pseudo-first order plots under these condition were almost parallel and linear over 80% completion of the reaction also indicates first order with respect to Ce(IV) (Fig-1).

3.4 Effect of Serine

The serine concentration was varied in the concentration range of 1.0×10^{-3} to 1.0×10^{-2} mol dm⁻³ at

40 C, 45 C, 50 C keeping all other conditions constant.

The rate constant, k_{obs} increases with increase in the concentration of serine (Table-1).

Table 1. Effect of cerium(IV), serine and [H⁺] on oxidation of serine by cerium(IV) in presence of manganese(II) as catalyst

Mn(II) = 5.0×10^{-5} mol dm⁻³, I = 1.50 mol dm⁻³, Temp. = 45 C

10^4 [Ce(IV)] mol dm ⁻³	10^3 [Ser] mol dm ⁻³	[H ⁺] mol dm ⁻³	$10^4 k_{\text{obs}}$, (sec ⁻¹)
0.50	1.0	1.0	2.89
1.0	1.0	1.0	2.84
2.0	1.0	1.0	2.86
3.0	1.0	1.0	2.84
4.0	1.0	1.0	2.82
5.0	1.0	1.0	2.89
5.0	1.0	1.0	0.91
5.0	2.0	1.0	1.51
5.0	3.0	1.0	2.11
5.0	4.0	1.0	2.62
5.0	5.0	1.0	2.89
5.0	6.0	1.0	3.21
5.0	7.0	1.0	3.51
5.0	8.0	1.0	3.51
5.0	9.0	1.0	3.51
5.0	10.0	1.0	3.52
5.0	5.0	0.20	7.31
5.0	5.0	0.40	5.52
5.0	5.0	0.60	4.31
5.0	5.0	0.80	3.46
5.0	5.0	1.0	2.89

From the slope of the plot of log k_{obs} versus log [serine], the order with respect to serine concentration was found to be less than unity.

3.5 Effect of [H⁺]

The effect of H⁺ concentration on the reaction rate was studied in the range 0.20 M to 1.0 M at constant concentration of serine, Ce(IV), Mn(II) and ionic strength of 1.50 mol dm⁻³ at 45 C. The results are represented in (Table-1). According to results it was found that the rate of reaction decreases with increase of sulphuric acid concentration in Mn(II) catalysed

oxidation. The order with respect to [H⁺] was negative as found from a plot of $1/k_{\text{obs}}$ versus [H⁺].

3.6 Effect of Mn(II)

The effect of catalyst concentration on the reaction was studied between the concentration range of 1.0×10^{-5} to 1.0×10^{-4} mol dm⁻³ at constant concentration of other reactants. The order for [Mn(II)] was found to be unity (Table-2) as determined from the slope of log k_{obs} versus log [Mn(II)] plots.

Table 2. Pseudo-first order and second order rate constant for the reaction of serine and cerium(IV) in H₂SO₄ medium at different manganese(II) concentration

[Ce(IV)] = 5.0×10^{-4} mol dm⁻³, [serine] = 5.0×10^{-3} mol dm⁻³, [H⁺] = 1.0 mol dm⁻³, I = 1.50 mol dm⁻³, Temp = 45 C

10^5 [Mn(II)] mol dm ⁻³	$10^4 k_{\text{obs}}$, sec ⁻¹	k' dm ³ mol ⁻¹ sec ⁻¹
1.0	0.58	5.80
2.0	1.17	5.85
3.0	1.82	5.86
4.0	2.38	5.87
5.0	2.89	5.78
6.0	3.54	5.83
7.0	4.12	5.88
8.0	4.65	5.81
9.0	5.12	5.83
10.0	5.84	5.84

3.7 Effect of $[\text{HSO}_4^-]$

The reactions were studied at different concentration of $[\text{HSO}_4^-]$, while keeping all reactants constant. The

graphical plot of $1/k_{\text{obs}}$ versus $[\text{HSO}_4^-]$ is found to be linear with positive intercept and slope (fig.-2), which indicates that the rate of the reaction is inversely proportional to the HSO_4^- ion concentration.

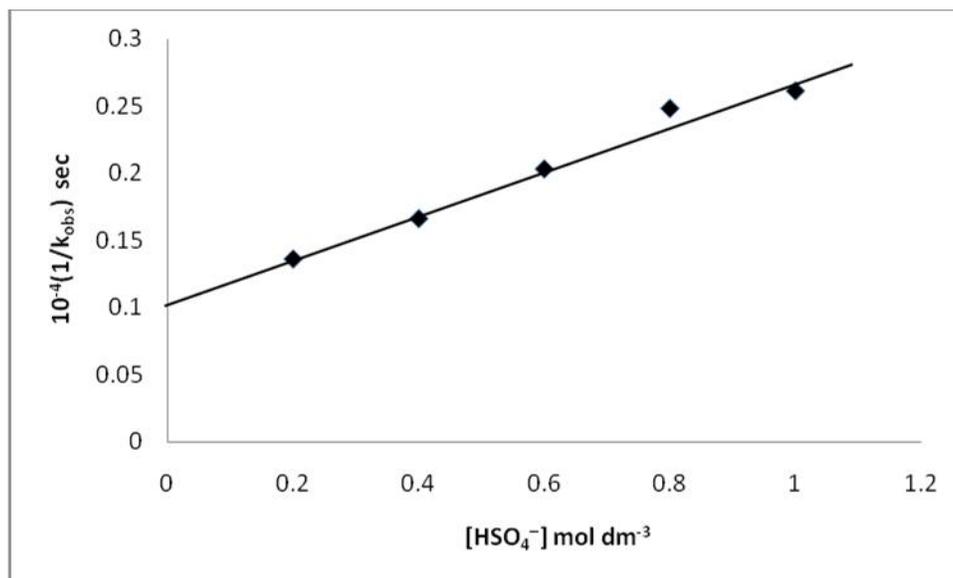


Fig. 2 A Plot of $1/k_{\text{obs}}$ versus $[\text{HSO}_4^-]$

$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Ser}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Mn(II)}] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 1.50 \text{ mol dm}^{-3}$, Temp. = 45 C.

3.8 Effect of ionic strength

The effect of ionic strength on the reaction rate was studied using Na_2SO_4 , with other experimental conditions held constant. The rate of reaction slightly increases with increasing ionic strength.

3.9 Effect of added products

The effect of initially added product of cerium(III) do not have any significant effect on the rate of reaction.

3.10 Test for free radical

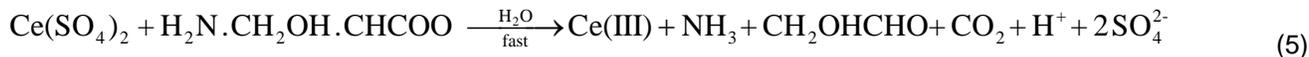
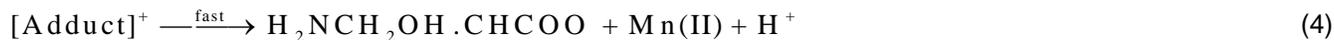
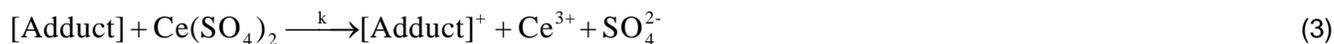
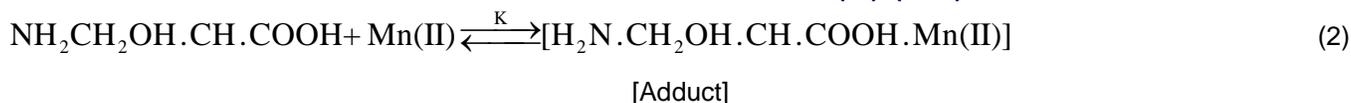
To test for the presence of free radicals in the reaction, 20% acrylonitrile solution was added to reaction mixtures containing the substrate and the cerium(IV) solution and was placed in an inert atmosphere for 24 hours. When the reaction mixture was diluted with methanol a precipitate was formed in the reaction mixture. This confirms the formation of free radicals in the redox reactions under investigation.

3.11 Mechanism

A few experiments were carried out with initially added Mn(II), and it was observed that the reaction rate increases with increase in Mn(II) concentration. Catalysis by Mn(II) ions in the case of oxidation by cerium(IV) is well known¹⁸. The uncatalyzed cerium

(IV) oxidation of serine is slow in aqueous sulphuric acid media under the present experimental conditions. However, the rate of reaction is appreciably faster in the presence of manganese(II) in sulphuric acid. The order with respect to serine changes from unity to zero. Such an amino acid dependence can be ascribed to complexation with cerium (IV) or manganese (II). The adduct formation between Ce^{+4} and serine was ruled out on the premise that the absorbance of Ce^{+4} did not change at the addition of excess serine. Therefore it appears that an adduct between manganese(II) and serine is initially formed that on further interaction with cerium(IV) yields another adduct of higher valent manganese.

The formation of the complex was implicated by non zero intercept of the plot of $1/k'$ versus $1/\text{serine}$ (Fig. 3). Complex formation between amino acid and manganese(II) has also been reported in literature¹⁹⁻²⁰. The results suggest that serine combines with catalyst Mn(II) to form a complex, which then reacts in a slow step with one mole of $\text{Ce}(\text{SO}_4)_2$ to give the product cerium(III), complex-serine and SO_4^{2-} . The $[\text{Adduct}]^+$ is converted in a free radical derived from serine, and Mn(II) catalyst is regenerated. The free radical then reacts with another mole of $\text{Ce}(\text{SO}_4)_2$ in a further fast step to give cerium(III), 2-hydroxyethanal, ammonia and carbon dioxide. The results are accommodated in scheme-1.



Scheme -1.

The proposed mechanism leads to the rate law(6)

$$\frac{-d[\text{Ce(IV)}]}{dt} = \frac{kK[\text{Ce(IV)}][\text{Ser}][\text{Mn(II)}]}{1 + K[\text{H}^+][\text{Ser}]} \quad (6)$$

$$\frac{-d[\text{Ce(IV)}]/dt}{[\text{Ce(IV)}]} = k_{\text{obs}} = \frac{kK[\text{Ser}][\text{Mn(II)}]}{1 + K[\text{H}^+][\text{Ser}]} \quad (7)$$

Where k_{obs} is pseudo first order rate constant. Since the order with respect to manganese(II) is one (Table-2), the rate law further change to (8)

$$k' = \frac{kK[\text{Ser}]}{1 + K[\text{H}^+][\text{Ser}]} \quad (8)$$

Where k' = second order rate constant
After rearranging eqⁿ (8)

$$\frac{1}{k'} = \frac{1}{kK[\text{Ser}]} + \frac{[\text{H}^+]}{k} \quad (9)$$

A plot of $1/k'$ versus $1/[\text{Ser}]$ was made from equation (9) at constant hydrogen ion concentration that yielded straight line with nonzero intercept (Fig.-3). The value of rate constant (k) of the slow step of scheme-1 was obtained from the intercept. The ratio of intercept and slope of the line yielded the value of formation

constant (K) to be $219 \text{ dm}^3 \text{ mol}^{-1}$. The value of K obtained in the title reaction in comparison to $K = 215 \text{ dm}^3 \text{ mol}^{-1}$ for cerium(IV) leucine in 1.0 M H_2SO_4 at 45 C, indicates strong complexation in H_2SO_4 medium²¹.

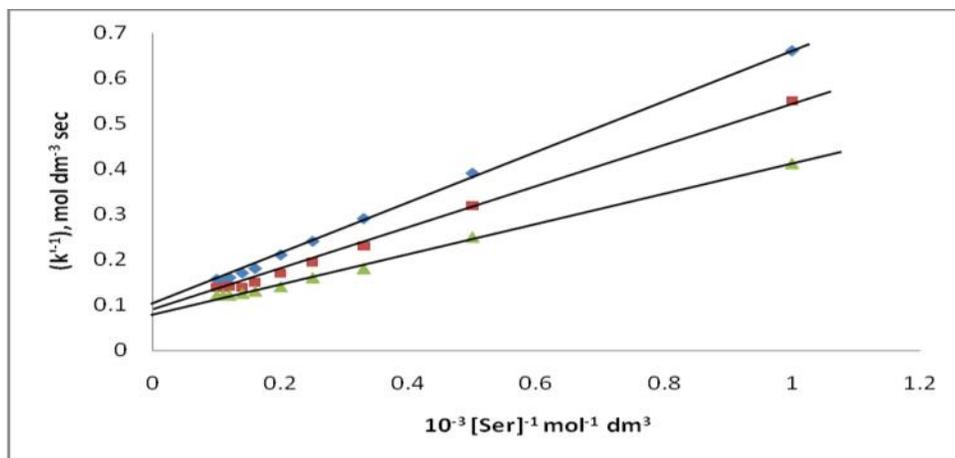
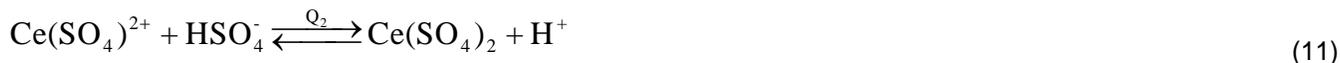


Fig. 3 A Plot of $(k)^{-1}$ versus $[\text{Ser}]^{-1}$

$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Mn(II)}] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$, $I = 1.50 \text{ mol dm}^{-3}$, Temp. = () 40 C, () 45 C, () 50 C

Cerium(IV) forms a number of complexes in sulphuric acid solution. Hardwick and Robertson²² have reported



The value of equilibrium constants Q_1 , Q_2 and Q_3 for step (10) to (12) are reported to be 3500, 200 and 20 at 25 C respectively spectrophotometrically. Considering the range of concentration of acid in which the present study was performed and the steep fall in rate of the reaction with the increasing concentration of sulphuric acid indicates that the other species would be present in insignificantly small concentration and may be considered negligible²³.

the following equilibrium between various complexes in sulphuric acid solution of 2M ionic strength at 25 C.

Thus, $\text{Ce}(\text{SO}_4)_2$ has been taken as the reactive species of cerium(IV) in aqueous sulphuric acid medium. In light of equilibrium step (10-12) inverse bisulphate dependence (Fig-2) can be explained by assuming $\text{Ce}(\text{SO}_4)_2$ as the reactive species. In the oxidation of L-glutamic acid²⁴ and L-leucine²⁵ by cerium(IV) in sulphuric acid-sulphate media, $\text{Ce}(\text{SO}_4)_2$ had been identified as the active species, which support the present work.

The concentration of this active species is given by equation (13)

$$\text{Ce}(\text{SO}_4)_2 = \frac{[\text{Ce(IV)}]_{\text{T}}}{1 + Q_3[\text{HSO}_4^-]} = f [\text{Ce(IV)}]_{\text{T}} \quad (13)$$

Thus equation (7) can be written as

$$k_{\text{obs}} = \frac{kK[\text{Ser}][\text{Mn(II)}]}{1 + K[\text{H}^+][\text{Ser}][1 + Q_3[\text{HSO}_4^-]} \quad (14)$$

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

So eqⁿ (14) becomes $k_{\text{obs}} = \frac{A}{1 + Q_3[\text{HSO}_4^-]} \quad (15)$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{A} + \frac{Q_3[\text{HSO}_4^-]}{A} \quad (16)$$

Equation(16) suggest 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 $1/A$, the ratio of slope to intercept was calculated to be 1.62 i. e. Q_3 , which is good agreement with the previously reported value²⁶.

formation²⁷ of an active inhibitor $\text{H}_2 \text{Ce}(\text{SO}_4)_2^{2-}$. All the above results show that $\text{Ce}(\text{SO}_4)_2$ as the kinetically active species. A small influence of ionic strength on the value of experimental rate constant is in agreement with the idea that a non charged particle $\text{Ce}(\text{SO}_4)_2$ enters in to reaction in the rate determining step, which further confirms $\text{Ce}(\text{SO}_4)_2$ as the kinetically active species in the present study.

The order with respect to H^+ concentration was less than unity and negative. As the sulphuric acid concentration increases, the H^+ concentration increases, but there is also a corresponding increase in HSO_4^- ion concentration. Since the rate is inversely dependent on the HSO_4^- concentration, the overall effect of adding sulphuric acid would be lower the rate. Increasing sulphuric acid concentration results in a decrease in rate constants, this may be due to the

The activation parameters of the rate determining step have been evaluated from the linear plot of $\log k$ versus $1/T$. The results of Table-3 shows the K increase with increase of temperature, indicating the reaction is endothermic, which is consistent with $H^\ddagger > 0$. The moderate value of H^\ddagger and S^\ddagger were favourable for electron transfer processes.

The value of S^\ddagger within range of radical reaction has been ascribed²⁸ to the nature of electron pairing and electron unpairing processes and to the loss of degrees of freedom formerly available to the reactants

upon the formation of rigid transition state. A negative value of S^\ddagger suggests that the complex is more ordered than reactants²⁹

Table 3. Effect of temperature on the reaction between cerium(IV) and serine catalysed by manganese(II) in presence of sulphuric acid medium

Temp (K)	k (dm ³ mol ⁻¹ s ⁻¹)	Activation parameters	K (dm ³ mol ⁻¹)	Thermodynamic quantities
313	9.09	E_a (kJ mol ⁻¹) = 25.84	198	H^\ddagger (kJ mol ⁻¹) = 21.06
318	10.0	S^\ddagger (JK mol ⁻¹) = -145.00	219	S^\ddagger (J K mol ⁻¹) = -134.87
323	12.50	G^\ddagger (kJ mol ⁻¹) = 67.17	257	G^\ddagger (kJ mol ⁻¹) = 63.94

4. Conclusions

The oxidation of serine by cerium(IV) experienced a slow reaction rate in sulphuric acidic media, but increased in rate in the presence of the Mn(II) catalyst. The reactive species for the oxidation of cerium(IV) in a sulphuric acidic medium was Ce(SO₄)₂. The rate constant of a slow step and other equilibrium constants involved in the mechanism were evaluated and activation parameters with respect to the slow step of the reaction were estimated. The observed results were explained by plausible mechanisms and the related rate laws were deduced. It can be stated that Mn(II) acts as an efficient catalyst for the oxidation of serine by cerium(IV) in sulphuric acid medium.

Acknowledgments

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