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STUDY OF CATALYTIC OXIDATION OF SERINE BY CERIUM (IV) IN PARTIAL-AQUEOUS ACIDIC MEDIUM.

Chemistry

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ABSTRACT

The oxidation of serine catalysed by cerium(IV) has been studied in sulphuric acid medium at 318 K. 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 to zero order kinetics with respect to serine at its lower to higher concentrations. Under the experimental condition, the kinetically active species of cerium(IV) has been found to be Ce(SO4)2. Activation parameters has been calculated. The mechanism has been proposed from the results of kinetic studies, reaction stoichiometry and product analysis.

KEYWORDS

Serine, Kinetics, Oxidation, Catalysis, Cerium.

INTRODUCTION:

The oxidation of serine has received much attention because of strengthening the immune system by providing antibodies and synthesizes fatty acid sheath around nerves fibres[1] Oxidation of serine by some inorganic oxidants has been studied[2,3] in both acidic and alkaline medium. Preliminary experimental results indicate that the reaction of serine with cerium (IV) in acid medium, without a catalyst was sluggish, but the reaction became fast 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.

Experimental

All reagents were either of Anala R or G.R. grade and used as supplied without any further treatment. Doubly distilled water was employed throughout the study. Appropriate quantities of the solution were placed in separate glass vessels and kept for at least 15 minutes in a thermostatted water bath at 45°C. The reaction was followed by measuring the absorption of cerium(IV) at 380 nm with time in a 1 cm cell placed in the Systronics(167) Visi-scan spectrophotometer.

RESULTS :

1. Cerium(IV) Dependence

The concentration of cerium(IV) was varied from 4.0×10^{-5} to 4.0×10^{-4} mol dm^{-3} at fixed concentration of $[H^+]$ = 1.5 mol dm^{-3}, [Mn(II)] = 4.0×10^{-5} mol dm^{-3} and I =1.50 mol dm^{-3} at three different concentration of serine viz. 4.0×10^{-3}, 6.0×10^{-3} and 8.0×10^{-3} mol dm^{-3} at 45°C. The order with respect to cerium(IV) was found to be unity, since the rate constant (k_{obs}) was almost constant at different Ce(IV) concentration. Results are given in Table-1.The pseudo-first order plots under these conditions were almost parallel and linear over 80% completion of the reaction also indicates first order with respect to Ce(IV).

2. Serine Dependence

The serine concentration was varied in the concentration range of 1.0×10^{-3} to 8.0×10^{-3} mol dm^{-3} at fixed concentration of [Ce(IV)], [Mn(II)], and $[H^+]$, at 40°C, 45°C and 50°C temperature respectively. Observed reaction order of serine is (0.68) obtained from the linear regression of log k_{obs} versus log concentration of serine, indicating fractional order with respect to serine. The reaction exhibits first order kinetics with respect to serine at its lower concentration that tends towards zero order at its higher concentration. Results are given in Table-1

3.Manganese(II) Dependence

The effect of catalyst concentration on the reaction was studied between the concentration range of 1.0×10^{-5} to 8.0×10^{-5} mol dm^{-3} at constant concentration of other species at 45°C. The reaction is of first order with respect to Mn(II). Table-2

4. Hydrogen Ion Dependence

The effect of H^+ concentration on the reaction rate was studied in the range 0.30 mol dm^{-3} to 1.5 mol dm^{-3} at constant concentration of [Ser] , [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 acid concentration in Mn(II) catalysed oxidation. The order with respect to $[H^+]$ was negative.

5. Effect of Temperature:

Rate of oxidation increases with increases in temperature. Rate of reactions were determined at different temperature (308 to 323 K). In all the cases, a plot of log k_{obs} v/s 1/T (inverse of absolute temperature) is a straight line. This shows that Arrhinius equation is valid for this oxidation- Table-3

6.Test for Free Radical

To test for the presence of free radicals in the reaction, acetonitrile solution was added to reaction mixtures containing the substrate and the cerium(IV) solution. When the reaction mixture was diluted with the methanol a precipitate was formed in the reaction mixture. This confirms the formation of free radicals in the redox reactions under investigation.

6. DISCUSSION

The uncatalysed cerium(IV) oxidation of serine is very slow in sulphuric acid under the present experimental conditions. However, the reaction is appreciably fast in the presence of a minute quantity of manganese(II). The reaction is first order with respect to cerium(IV) and manganese(II) concentrations, and the order with respect to serine varies from first to zero order. In effect of hydrogen ions, it was found that as the concentration increases, the rate of reaction decreased. This is due to formation of an active inhibitor $H_2Ce(SO_4)_2^{2-}$. The order with H^+ ion concentration is less than unity and negative. Similar behaviour has been reported in the oxidation of antimony(III)[4], mandelic acid[5], malic acid[6], fructose[7] and L-glutamic acid[8] by cerium(IV).

The amino acid dependence from first to zero order can be ascribed to complexation with cerium (IV) or manganese (II). 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/ serine. Complex formation between amino acid and manganese(II) has also been reported in literature[9,10]. The results suggests that serine combines with catalyst Mn(II) to form a adduct, which then reacts in a slow step with one mole of $Ce(SO4)_2$ to give the product cerium(III), complex-serine and SO_4^{2-} The $[Adduct]^+$ is converted in a free radical derived from serine and Mn(II) catalyst is regenerated. The free radical then reacts with another mole of $Ce(SO_4)_2$ in a further fast step to give cerium(III), 2-hydroxyethanal, ammonia and carbon dioxide.

7. CONCLUSION

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.

Table -1 Variation Of Rate With Serine Concentration [cerium Iv] =4x10^{-4} M [mnii]= 4x10^{-5} M [h+] 1.5 M I]=1.5 M [solvent] =[50 %acn+50 %water]

[Serine] x 10^{3} M	k_{obs}x10^{5} sec^{-1}		
	T = 313K	T = 318 K	T = 323 K
1	0.94	1.16	1.51
2	1.28	1.58	2.03
3	1.54	1.94	2.33
4	1.76	2.16	2.63
5	2.02	2.41	2.81
6	2.22	2.61	3.01
7	2.41	2.83	3.26
8	2.63	3.07	3.54

Table-2 Variation Of Rate With Mn(ii) Concentration

[MnII] x10^{-5} M	k_{obs}x10^{5} sec^{-1}
1	0.87
2	1.36
3	1.785
4	2.167
5	2.65
6	3.09
7	3.48
8	3.84

Table-3 Variation Of Rate With Temprature

Temp K	k_{obs}x10^{5} sec^{-1}
308	1.44
313	1.76
318	2.16
323	2.63
328	3.12

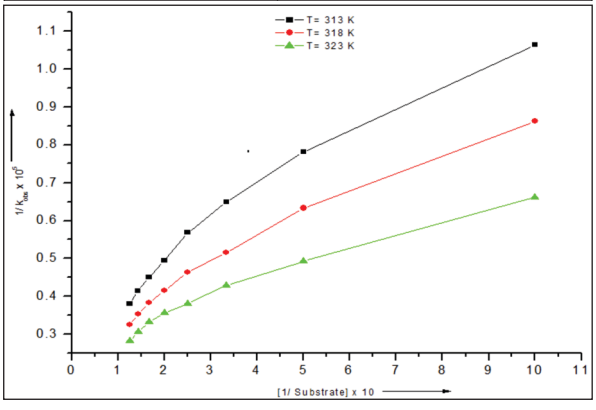

Fig-1 Variation Of Rate With Substrate Concentration 1/ k_{obs} v/s 1/substrate

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