



Catalysed oxidation of aspartic acid by cerium (IV) in acidic medium: Kinetic study

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Abstract:

The oxidation of aspartic acid 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 rate of the reaction initially increases and tends towards a limiting value with further increasing concentration of aspartic acid. 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.

Key Words: Aspartic acid, Kinetics, Oxidation, Catalysis, Cerium.

Introduction:

The oxidation of aspartic acid has received much attention because of strengthening the immune system by providing antibodies and synthesizes fatty acid sheath around nerves fibres¹ Oxidation of aspartic acid by some inorganic oxidants has been studied^{2,3} in both acidic and alkaline medium. Preliminary experimental results indicate that the reaction of aspartic acid 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 aspartic acid - 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

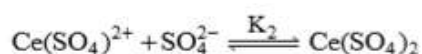
In the kinetic experiment, [Ce(IV)] was varied from 5×10^{-5} to 5×10^{-4} mol dm⁻³ at fixed concentration of [Asp] = 5×10^{-3} mol dm⁻³, and temperature = 45°C, the order was found to be unity. The plot of initial rate versus [Ce(IV)] was a straight line passing through the origin. The pseudo-first 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. Substrate Dependence:

At a fixed [Ce(IV)] = 2×10^{-4} mol dm⁻³, [Mn(II)] = 5×10^{-5} mol dm⁻³, [H₂SO₄] = 0.50 mol dm⁻³ and I = 1.0 mol dm⁻³, the effect of [Asp] on the rate of reaction was studied in the concentration range 1×10^{-3} to 7×10^{-3} mol dm⁻³ at three temperature viz. 40°C, 45°C and 50°C respectively. The rate of the reaction initially increases and tends towards a limiting value with further increasing concentration of aspartic acid.

3. Hydrogen Ion Dependence:

At fixed concentration of [Ce(IV)] and other species, the sulphuric acid concentration was varied at 40°C, 45°C and 50°C respectively in case of aspartic acid. The initial rate was found to decrease with increasing sulphuric acid concentration (Table-1). The [H⁺] ion concentration was calculated using known ionization constants of sulphate as in the earlier studies⁴⁻⁶. The order with respect to [H⁺] was negative. Results are shown in fig-1.



4. 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

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}/s 1/T (inverse of absolute temperature) is a straight line. This shows that Arrhinius equation is valid for this oxidation- Table-3

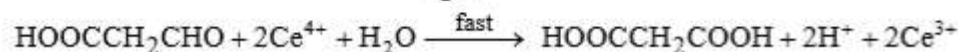
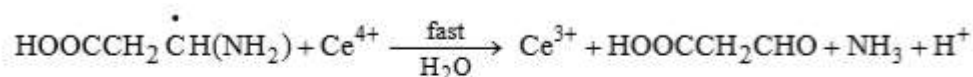
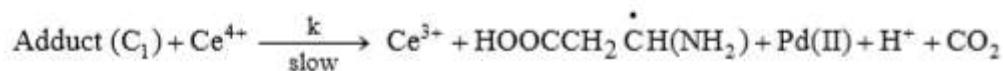
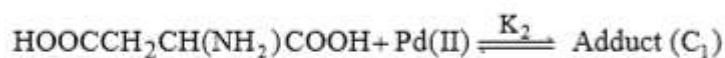
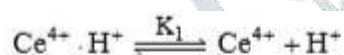
6. Test for Free Radical

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.

7. Discussion

The uncatalysed cerium(IV) oxidation of aspartic acid 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 amino acid 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 $\text{H}_2\text{Ce}(\text{SO}_4)_2^{2-}$. The order with H^+ ion concentration is less than unity and negative. Similar behaviour has been reported in the oxidation of antimony (III)⁷, mandelic acid⁸, malic acid⁹, fructose¹⁰ and L-glutamic acid¹¹ 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 aspartic acid 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 $1/\text{serine}$. Complex formation between amino acid and manganese(II) has also been reported in literature^{12,13}. The results suggests that aspartic acid combines with catalyst Mn(II) to form a adduct, 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), malonic acid, ammonia and carbon dioxide.



7. Conclusion

The oxidation of aspartic acid 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 $\text{Ce}(\text{SO}_4)_2$. 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 ACID CONCENTRATION

[Aspartic Acid]= 5×10^{-3} M [Cerium IV] = 2×10^{-4} M [MnII]= 4×10^{-5} M

[H ⁺] M	k _{obs} × 10 ⁷ sec ⁻¹		
	T = 313K	T = 318 K	T = 323 K
0.2	1.08	1.3	1.6
0.4	0.96	1.12	1.35
0.5	0.87	1.01	1.22
0.6	0.79	0.9	1.09
0.8	0.64	0.71	0.86
1	0.51	0.55	0.63

Table ---2

VARIATION OF RATE WITH Mn (II) CONCENTRATION

[Cerium IV] = 4×10^{-4} M [I] =1.5 M
[Aspartic Acid] = 4×10^{-3} M [H]⁺ =0.5 M

[MnII] × 10 ⁵	k _{obs} × 10 ⁵ sec ⁻¹
2	0.52
3	0.76
4	1.011
5	1.212
6	1.389
7	1.602
8	1.815
9	1.912

Table-3

VARIATION OF RATE WITH TEMPERATURE

Temp K	k _{obs} × 10 ⁷ sec ⁻¹
308	0.76
313	0.88
318	1.012
323	1.19
328	1.37

(c.f. Table -1)

VARIATION OF RATE WITH ACID CONCENTRATION

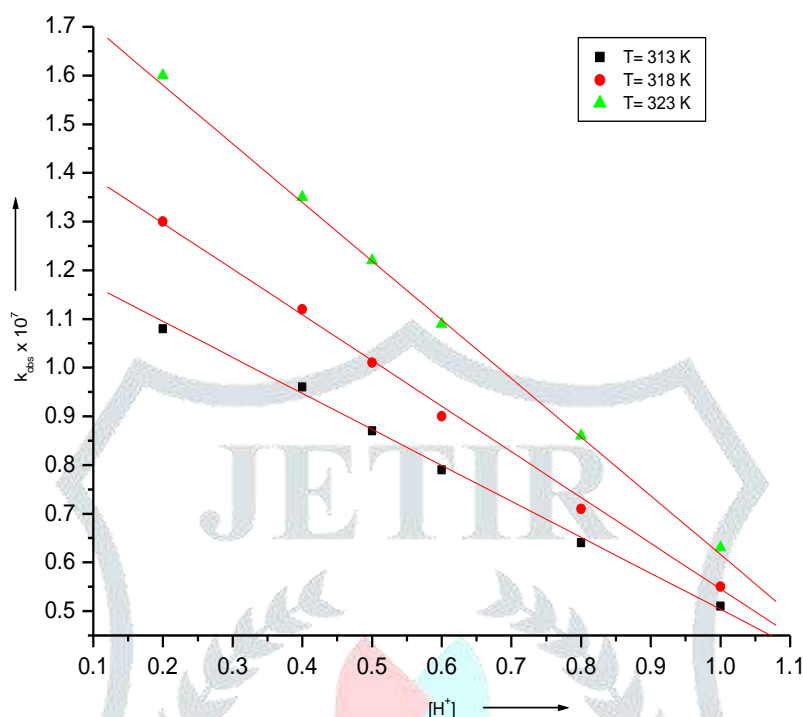
 k_{obs} v/s $[\text{H}^+]$ ASPARTIC ACID

Figure-1

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