Journal of Chemical Technology and Metallurgy, 60, 2, 2025, 199-205

KINETIC AND MECHANISTIC STUDIES ON THE RUTHENIUM (III) CATALYSED OXIDATION OF DL-ASPARTIC ACID WITH CERIUM (IV)

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Received 09 January 2024
Accepted 16 March 2024
DOI: 10.59957/jctm.v60.i2.2025.1

ABSTRACT

Kinetics of oxidation of DL-aspartic acid (Asp) was carried out at 30°C with cerium (IV) in sulphuric acid medium in presence of ruthenium (III) catalyst to elucidate its mechanism of oxidation. The reaction is first order with respect to [cerium (IV)] and [DL-aspartic acid], and the rate was determined to be independent of [H$^+$] and [bisulphate]. A suitable mechanism was proposed involving the protonated form of DL-aspartic acid and cerium (IV).

Keywords: DL-aspartic acid, cerium (IV), ruthenium catalysis, kinetics, oxidation.

INTRODUCTION

Aspartic acid is an amino acid useful in maintaining solubility and ionic character of proteins [1]. Aspartic acid facilitates normal cell function and increases endurance and resistance to fatigue by producing immune-globulins and antibodies, and reportedly removes highly toxic ammonia from central nervous system [1]. Aspartic acid has two enantiomers namely L-aspartic acid and D-aspartic acid. The L-aspartic acid is used in the synthesis of proteins, whereas the D-aspartic acid is used in the synthesis of hormones [2]. DL-aspartic acid is a racemic mixture of L-aspartic acid, and D-aspartic acid. DL-aspartic acid could serve as an indicator of age, based on the extent of racemization in the dentine [3]. DL-aspartic acid is mainly used as a flavouring agent in the wine and beverage industry. The extent of DL-aspartic acid and other amino acids in popular beer brands is reported [4]. DL-aspartic acid is also employed in dairy industry for producing lactic acid [5]. Oxidation of aspartic acid was reported with different oxidants like copper (II) [1], hexacyanoferrate [6], bismuth(V) [7], cerium (IV) [8], dihydroxydiperiodatoargentate (III) [9], manganese (III) [10], gold (III) [11], and peroxomonosulfate [12].

Tetravalent cerium in acid is a perfectly reversible one-electron oxidant, which can oxidize many inorganic and organic substances and is highly stable at room temperature. The oxidation potential of the cerium (IV) - cerium (III) system is 1.70 V in one mol dm^{-3} perchloric acid medium, 1.61 V in one mol dm^{-3} nitric acid medium and 1.44 V in one mol dm^{-3} sulphuric acid medium. Based on the above potentials, it is obvious that the nature and oxidizing capacity of cerium (IV) and cerium (III) species, differ from one acid medium to another.

The author has carried out the study of ruthenium (III) catalysed oxidation of DL-aspartic acid by cerium (IV), in sulphuric acid medium, and the kinetics of mechanism of its oxidation are reported in this research paper. During preliminary studies, the oxidation was found to occur at moderate speeds (about 1 h for 80 % of the reaction), hence spectrophotometric method was chosen as the most suitable method for conducting the study.

EXPERIMENTAL

Materials

All chemicals used are AR graded and 99.99 % pure (Merck). DL-Aspartic acid of 0.2 mol dm^{-3} strength in 0.2 mol dm^{-3} H_2SO_4 was prepared. An approximately 0.1 mol dm^{-3} solution of cerium (IV), was prepared from ceric sulphate, in 0.5 mol dm^{-3} H_2SO_4. The strength of the solution was determined, by titrating an aliquot of the solution with standard iron (II) solution, using ferroin as indicator. A 0.005 mol dm^{-3} solution of ruthenium (III) sulphate, was prepared from ruthenium trichloride (Johnson and Matthey, London), in 2.0 mol dm^{-3} H_2SO_4.

Kinetic measurement

The kinetic measurements were performed in one mol per dm^{-3} sulphuric acid medium under the experimental conditions [H^+] > [DL-aspartic acid] > [cerium (IV)] > [ruthenium (III)]. The absorbance of cerium (IV) at 400 nm, was monitored to study the progress of the reaction. At that wavelength no other species, except cerium (IV) has significant absorption. Absorption measurements were made with Sistronics visible spectrophotometer - 106 using 1 cm path length quartz cells. Temperature of the reaction mixture was kept constant using Siskin Julabo V thermostat.

The log absorbance was plotted against time, which displayed linearity, even beyond the completion of 85 % of the reaction, indicating unit-order kinetic dependence of rate with [cerium (IV)], in the range varying from $5.0 - 10.0 \times 10^{-4}$ mol dm^{-3}. From the plots, the pseudo-first order rate constants k^1, were calculated, which on repeated trials, were found to be reproducible, within ± 4 % limits.

Product analysis

Diethyl ether was employed to extract the product of oxidation, from the reaction mixture containing DL-aspartic acid (4.0×10^{-2} mol dm^{-3}), sulphuric acid (1 mol dm^{-3}), Ru [III] (5.0×10^{-5} mol dm^{-3}) and Ce [IV] (5.0×10^{-4} mol dm^{-3}), after completion of the oxidation. LC MS was employed for product analysis, which identified the product of oxidation of DL-aspartic acid as 3-oxo propanoic acid. The mass spectrum peak at 89 m/z amu corresponds to the (M+1) peak of the product (Fig. 1).

The test for free radicals was carried out by adding a freshly prepared acrylamide solution to DL-aspartic acid, cerium (IV) and ruthenium (III) in one mol dm^{-3} H_2SO_4. The reaction mixture was kept aside for 24 h and no turbidity was observed indicating the absence of free radical formation.

RESULTS AND DISCUSSION

The stoichiometry of the reaction was determined by mixing known amounts of DL-aspartic acid, with a known excess of cerium (IV), in presence of ruthenium (III), as catalyst at 30°C, in one mol per dm^{-3}

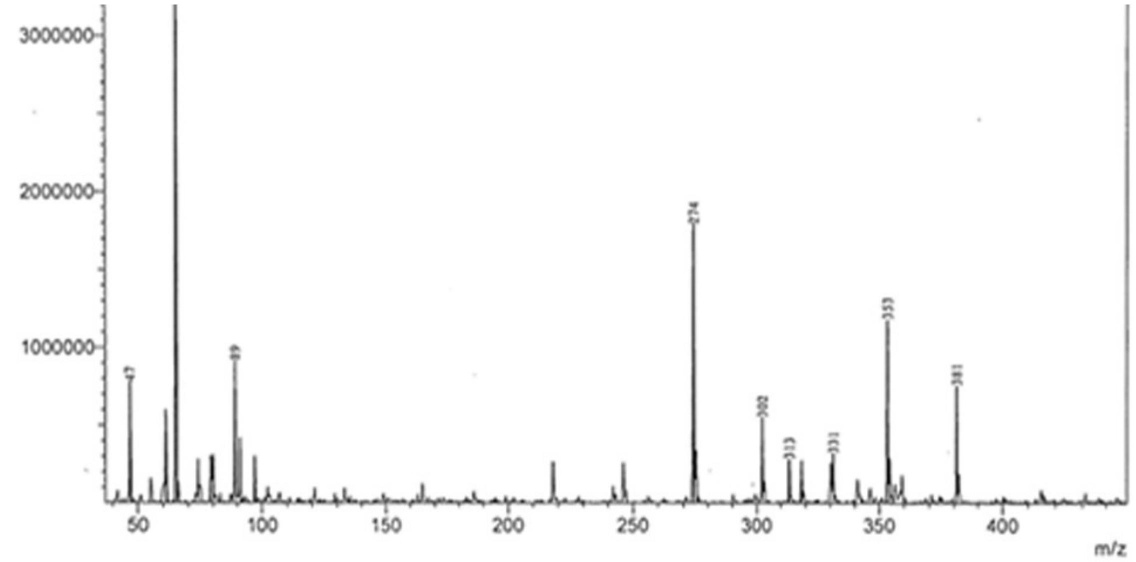

Fig. 1. Mass spectrum of the product.

sulphuric acid. After 24 h, the residual [cerium (IV)] was determined spectrophotometrically, at 400 nm. An analysis of the results showed that the stoichiometry of the reaction involved two moles of [cerium (IV)] for reaction, with one mole of DL-aspartic acid as shown below.

$$\mathrm{HOOC{-}CH_2{-}CH(N^+H_3){-}COOH + 2\ Ce^{IV} + H_2O \rightarrow HOOC{-}CH_2{-}CHO + 2Ce^{III} + NH_3 + CO_2 + 3H^+}$$

The effect of [$\mathrm{Ce^{IV}}$] on the rate of oxidation of DL-aspartic acid was observed by varying the initial [$\mathrm{Ce^{IV}}$] from 5.0 to 10.0 x 10^{-4} mol $\mathrm{dm^{-3}}$ and maintaining all other experimental conditions constant. The results incorporated in Table 1 showed that an increase in cerium concentration caused a decrease in the rate constant (k^1). This decrease may be due to the dimerization of Ce (IV) with increasing concentration. Similar decrease was also reported in previous studies by Dindi and Sudarsan [13] and by Devra [14].

The dependence of [DL-aspartic acid] on the reaction rate was determined, by varying its concentration, from 1.0 - 6.0 x 10^{-2} mol $\mathrm{dm^{-3}}$. During the reaction, the concentrations of all other species were maintained constant, and the temperature was set at 30°C. From the results of the Table 2, it may be seen that the rate of reaction increases with increase in the concentration of DL-aspartic acid. Further, the plot (Fig. 2) of k^1 against [Asp], produced a straight line graph, which passed through the origin, indicating that the reaction is unit order with DL-aspartic acid.

Kinetic studies were carried out, to determine the dependence of reaction rate, on [ruthenium (III)], by varying the concentration of ruthenium (III), from 0.80 - 6.0 x 10^{-5} mol $\mathrm{dm^{-3}}$, while maintaining the concentrations of all other reactants constant. From the data presented in Table 3, it may be seen that the reaction rate increases

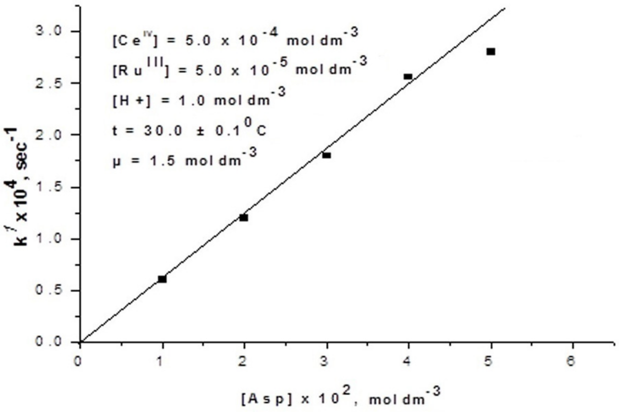

Fig. 2. Plot of k^1 versus [Asp].

Table 1. Influence of cerium (IV) on the pseudo first order rate constant, k' at 30°C.

[$\mathrm{Ce^{IV}}$]x10^4, mol $\mathrm{dm^{-3}}$	[Asp]x10^2, mol $\mathrm{dm^{-3}}$	[$\mathrm{Ru^{III}}$]x10^5, mol $\mathrm{dm^{-3}}$	[$\mathrm{H^+}$], mol $\mathrm{dm^{-3}}$	μ, mol $\mathrm{dm^{-3}}$	k' x10^4, $\mathrm{s^{-1}}$
5.0	4.0	5.0	1.0	1.5	2.56
6.0	4.0	5.0	1.0	1.5	1.40
7.0	4.0	5.0	1.0	1.5	0.80
8.0	4.0	5.0	1.0	1.5	0.80
9.0	4.0	5.0	1.0	1.5	0.60
10.0	4.0	5.0	1.0	1.5	0.40

Table 2. Influence of [DL-aspartic acid] on the pseudo first order rate constant, k' at 30°C.

[$\mathrm{Ce^{IV}}$]x10^4, mol $\mathrm{dm^{-3}}$	[Asp]x10^2, mol $\mathrm{dm^{-3}}$	[$\mathrm{Ru^{III}}$]x10^5, mol $\mathrm{dm^{-3}}$	[$\mathrm{H^+}$], mol $\mathrm{dm^{-3}}$	μ, mol $\mathrm{dm^{-3}}$	k' x10^4, $\mathrm{s^{-1}}$
5.0	1.0	5.0	1.0	1.5	0.60
5.0	2.0	5.0	1.0	1.5	1.02
5.0	3.0	5.0	1.0	1.5	1.80
5.0	4.0	5.0	1.0	1.5	2.56
5.0	5.0	5.0	1.0	1.5	2.80
5.0	6.0	5.0	1.0	1.5	3.00

Table 3. Influence of [Ru^{III}] on the pseudo first order rate constant, k' at 30°C.

[Ce^{IV}] x10^4, mol dm^{-3}	[Asp]x10^2, mol dm^{-3}	[Ru^{III}]x10^5, mol dm^{-3}	[H$^+$], mol dm^{-3}	μ, mol dm^{-3}	k' x10^4, s^{-1}
5.0	4.0	0.8	1.0	1.5	0.20
5.0	4.0	1.0	1.0	1.5	0.40
5.0	4.0	2.0	1.0	1.5	0.76
5.0	4.0	4.0	1.0	1.5	1.28
5.0	4.0	5.0	1.0	1.5	2.56
5.0	4.0	6.0	1.0	1.5	2.80

Table 4. Influence of ionic strength μ, on the pseudo first order rate constant, k' at 30°C.

[Ce^{IV}] x10^4, mol dm^{-3}	[Asp]x10^2, mol dm^{-3}	[Ru^{III}]x10^5, mol dm^{-3}	[H$^+$], mol dm^{-3}	μ, mol dm^{-3}	k' x10^4, s^{-1}
5.0	4.0	5.0	1.0	1.5	2.56
5.0	4.0	5.0	1.0	2.0	1.53
5.0	4.0	5.0	1.0	2.5	1.28
5.0	4.0	5.0	1.0	3.0	1.02
5.0	4.0	5.0	1.0	3.5	0.76
5.0	4.0	5.0	1.0	4.0	0.51

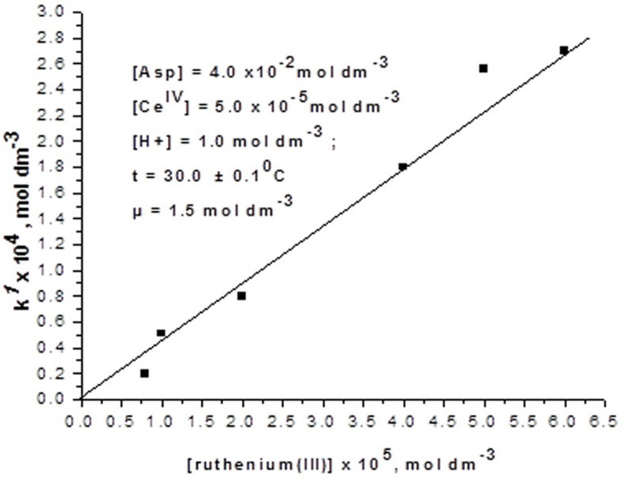

Fig. 3. Plot of k^1 versus [ruthenium(III)].

with increase in [ruthenium (III)]. Further, the plot (Fig. 3) of k^1 Vs [ruthenium (III)] produced a straight line graph, which passed through origin, indicating that the reaction exhibited unit order kinetics with [ruthenium (III)].

The influence of ionic strength, on the pseudo - first order rate constant, was determined, by varying the ionic strength, from 1.5 - 4.5 mol dm^{-3}, using sodium perchlorate solution. During this reaction, the concentrations of all other reactants were maintained constant. It may be seen from Table 4, that the pseudo-first order rate constant, k^1, decreases as the ionic strength increases.

A kinetic study was conducted to determine the effect of [cerium (III)], and from the data obtained (Table 5), it was found that it has practically no effect on the reaction rate. The influence of the hydrogen ion concentration [H$^+$], on the reaction rate was studied, and from the data obtained (Table 6), it was found that [H$^+$] has no appreciable effect on the reaction rate. The influence of [HSO$_4^-$] was studied, and from the data obtained (Table 7), it was found that [HSO$_4^-$] has negligible effect on the reaction rate.

To estimate the activation parameters, the rate of reaction was studied at three different temperatures. The energy of activation, E$_a$ was found to be 38.46 ± 1.56 kJ mol^{-1}, and the entropy of activation, ΔS$^\#$, was found to be -195.34 ± 5.15 J K^{-1} mol^{-1}.

In the current kinetic study, when the experimental conditions were set as, [H$^+$] = 1.0 mol dm^{-3}, DL-aspartic acid predominantly (99 %) exists as protonated aspartic acid (HAsp) and only 1 % as Zwitterion (Asp$_z$), as may be seen from the equilibrium (Fig. 4). Therefore, the

Table 5. Influence of Cerium III, on the pseudo first order rate constant, k' at 30^{o}C.

[Ce^{IV}] x10^{4}, mol dm^{-3}	[Asp]x10^{2}, mol dm^{-3}	[Ru^{III}]x10^{5}, mol dm^{-3}	[H^{+}], mol dm^{-3}	μ, mol dm^{-3}	[Ce^{III}] x 10^{4}, mol per dm^{-3}	k^{1} x 10^{4}, s^{-1}
5.0	4.0	5.0	1.0	1.5	5.0	2.56
5.0	4.0	5.0	1.0	1.5	6.0	2.53
5.0	4.0	5.0	1.0	1.5	7.0	2.50
5.0	4.0	5.0	1.0	1.5	8.0	2.50
5.0	4.0	5.0	1.0	1.5	9.0	2.56
5.0	4.0	5.0	1.0	1.5	10.0	2.51

Table 6. Influence of [H^{+}], on the pseudo first order rate constant, k' at 30^{o}C.

[Ce^{IV}] x10^{4}, mol dm^{-3}	[Asp]x10^{2}, mol dm^{-3}	[Ru^{III}]x10^{5}, mol dm^{-3}	μ, mol dm^{-3}	[H^{+}], mol per dm^{-3}	k^{l} x 10^{4}, s^{-1}
5.0	4.0	5.0	3.5	0.50	0.62
5.0	4.0	5.0	3.5	0.75	0.60
5.0	4.0	5.0	3.5	1.00	0.64
5.0	4.0	5.0	3.5	1.25	0.62
5.0	4.0	5.0	3.5	1.50	0.65
5.0	4.0	5.0	3.5	1.75	0.60

Table 7. Influence of [HSO$_{4}^{-}$], on the pseudo first order rate constant, k' at 30^{o}C.

[Ce^{IV}] x10^{4}, mol dm^{-3}	[Asp]x10^{2}, mol dm^{-3}	[Ru^{III}]x10^{5}, mol dm^{-3}	[H^{+}], mol dm^{-3}	μ, mol dm^{-3}	[HSO$_{4}^{-}$], mol per dm^{-3}	k^{l} x 10^{4}, s^{-1}
5.0	4.0	5.0	1.0	1.5	1.25	0.82
5.0	4.0	5.0	1.0	1.5	1.50	0.85
5.0	4.0	5.0	1.0	1.5	1.75	0.84
5.0	4.0	5.0	1.0	1.5	2.00	0.86
5.0	4.0	5.0	1.0	1.5	2.25	0.82
5.0	4.0	5.0	1.0	1.5	2.50	0.80

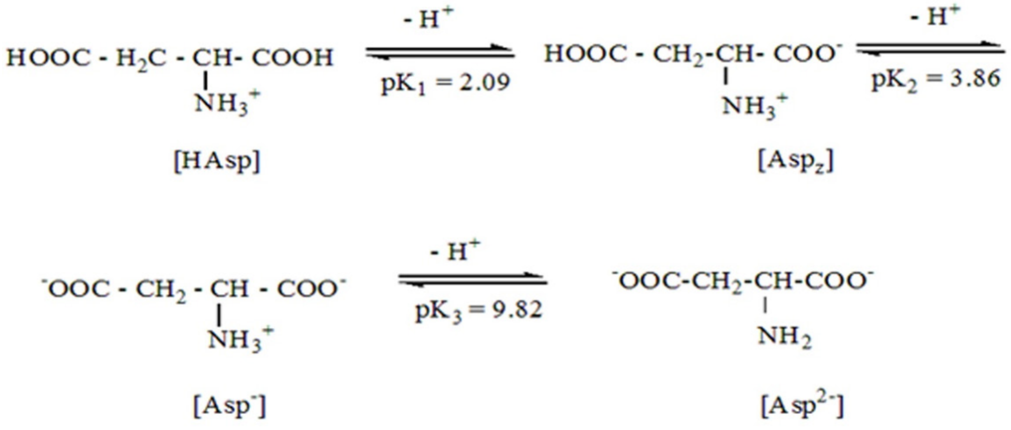

Fig. 4. Protonic equilibria of DL-aspartic acid.

active species, in acid medium is presumed to be the protonated form of the DL-aspartic acid.

Surasiti and Sandell, while studying the oxidation of arsenic (III) by cerium (IV) sulphate, catalysed by ruthenium, pointed out that ruthenium present in lower oxidation state, will be converted to ruthenium (VIII), within ten seconds [15]. They also observed that ruthenium (III) and ruthenium (VIII), have same catalytical activity.

In view of the observed reaction parameters, the reaction mechanism may be represented as follows:

$$Ru^{III} + Ce^{IV} \overset{fast}{\rightleftharpoons} Ru^{VIII} + Ce^{III} \quad (1)$$

$$Ru^{VIII} + HAsp \overset{K}{\rightleftharpoons} \text{Intermediate (I)} \quad (2)$$

$$I + Ce^{IV} \xrightarrow[slow]{k} \text{Aspartic aldehyde} + Ru^{VII} + Ce^{III} + NH_3 + + CO_2 \quad (3)$$

$$Ru^{VII} + Ce^{IV} \xrightarrow{fast} Ru^{VIII} + Ce^{III} \quad (4)$$

where $HAsp \equiv HOOC - CH_2 - CH(NH_3^+) - COOH$

$$rate = - d/dt\,[Ce^{IV}] = k\,[I]\,[Ce^{IV}] \quad (5)$$

where, $[I] = K\,[HAsp]\,[Ru^{VIII}]$; substituting for [I] in rate equation (5),

$$rate = k\,K\,[HAsp]\,[Ce^{IV}]\,[Ru^{VIII}] \quad (6)$$

but $[HAsp] = [Asp]_t$ and $[Ru^{VIII}] = [Ru^{III}]_t$

$$rate = k\,K\,[Asp]_t\,[Ru^{III}]_t\,[Ce^{IV}] \quad (7)$$

The expression for the pseudo first order rate constant k^1 may be written as follows,

$$k^1 = rate / [Ce^{IV}] = k\,K\,[Asp]_t\,[Ru^{III}]_t \quad (8)$$

The above rate equation clearly explains unit order in [Asp], $[Ce^{IV}]$ and $[Ru^{III}]$.

CONCLUSIONS

The experimental results obtained indicate that the stoichiomerty of the DL-aspartic acid and cerium (IV), to be 1: 2. The reaction exhibited first order kinetics with [DL-aspartic acid], and with $[Ce^{IV}]$. An Increase in ionic strength caused an inhibition in the reaction rate. $[H^+]$ did not exhibit any significant effect on the reaction rate. $[HSO_4^-]$ did not exhibit any significant effect on the reaction rate. Cerium (III) $[Ce^{III}]$ has negligible effect on the reaction rate. The activation parameters of the reaction were computed from the experimental data, and the entropy of activation, $\Delta S^{\#}$, was found to be -195.34 ± 5.15 J K^{-1} mol^{-1} and the energy of activation, E_a, was found to be 38.46 ± 1.56 kJ mol^{-1}.

Acknowledgements

The main author R. R. Makena thanks UGC SERO, India for minor research project (Ref No: F MRP-4551/14 (SERO/UGC), dated 17 March 2014), and Andhra University, Visakhapatnam, India for providing the research facilities.

Authors' contributions: *The main authorR.R. Makenaunder took this study, as part of Phd in Chemistry, at JNTU-Kakinada, India. Prof. V.Parvataneni supervised the benchwork, and provided expertise, in formulating the reaction mechanisms. Prof. R. Rallabandi supervised the progress, and in the literature survey.*

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