



KINETICS AND MECHANISM OF OXIDATION OF L-ASPARTIC ACID BY POTASSIUM PERMANGANATE IN AQUEOUS ACID MEDIUM

J. S. DIGGIKAR

Department of Industrial Chemistry
Shri Chhatrapati Shivaji College, Omerga, (M.S) India

ABSTRACT

The oxidation of L-aspartic acid by potassium permanganate in aqueous perchloric acid medium has been studied. The reaction is first order dependence on potassium permanganate concentration and order in L-aspartic acid is fractional which suggests intermediate complex formation between L-aspartic acid and potassium permanganate. The thermodynamic parameters are reported. The rate was found to increase with increasing concentration of perchloric acid. Suitable mechanism is proposed and rate laws derived explain the results obtained.

INTRODUCTION

Extensive studies have been made on permanganate oxidations of organic and inorganic substrates in both acid and alkaline media¹⁻⁹. Amino acids play an important role in metabolism and in protein synthesis. Enzymatic dehydrogenation of α -amino acid by flavoenzymes has attracted considerable attentions in recent years. Infact a precise understanding of the mechanism of such biological redox reactions¹⁰⁻¹² is important as it helps in the synthesis of specific reaction products. Many attempts were made to mimic flavincatalysed oxidations of α -amino acids¹³ by non-enzymatic means. These studies were found to yield the corresponding non aldehyde by oxidative decarboxylation of α -amino acids¹⁴⁻¹⁵. The kinetic investigation of the α -amino acids

by a variety of oxidants has been carried out under different experimental conditions¹⁶⁻²¹. In many cases it was reported that amino acids undergo oxidative decarboxylation. The study of the oxidation of amino acids becomes important because of their biological significance and selectivity towards oxidants.

L-aspartic acid is one of the essential amino acid in life and it finds applications in medicines and pharmaceutical. L-aspartic acid bears two acid groups and is of interest to verify the nature of active species of permanganate ion, actual site of oxidation and change in mechanism etc. Therefore this reaction has been carried out in order to elucidate the redox chemistry of permanganate in acid media and to derive at a plausible mechanism.

EXPERIMENTAL

Oxidation of L-aspartic acid by KMnO₄

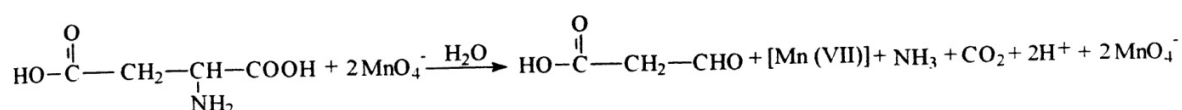
Reactions were carried out in glass-stoppered flasks immersed in a water-bath thermostated at $\pm 0.1^\circ\text{C}$. All the ingredients of the reaction mixture except KMnO₄ were taken in a flask and the reaction was initiated by adding requisite volume of pre-equilibrated solution of KMnO₄ in to the reaction mixture. The time was recorded when half of the pipette contents were released into the reaction mixture. An aliquot of the reaction mixture was withdrawn at different intervals of time and then quenched in an iodide solution.

Reaction order

The order of the reactants was determined from the slopes of $\log k_{\text{graph}}$ versus $\log (\text{concentration})$ plots by varying the concentration of L-aspartic acid and perchloric acid in turn, while keeping concentration of others constant.

Stoichiometry and product analysis

The reaction mixtures containing an excess permanganate concentration over L-aspartic acid and 1 mol dm⁻³ perchloric acid was allowed to react for 24 hours at 323⁰K. After completion of the reaction, solid KI was added followed by acidification with 10% H₂SO₄. The remaining MnO₄⁻ was then titrated against standard sodium thiosulphate²²⁻²³.



The result indicates that two moles of MnO₄⁻ consumed by one mole of L-aspartic acid. Product identified is aldehyd²⁴ by spot test, ammonia²⁵ by Nessler's reagent and CO₂ was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water²⁶. The quantitative estimation of aldehyde by 2,4- DNP derivative²⁷. It was further observed that the aldehyde does not undergo further oxidation, under present kinetic conditions.

Effect of Potassium Permanganate

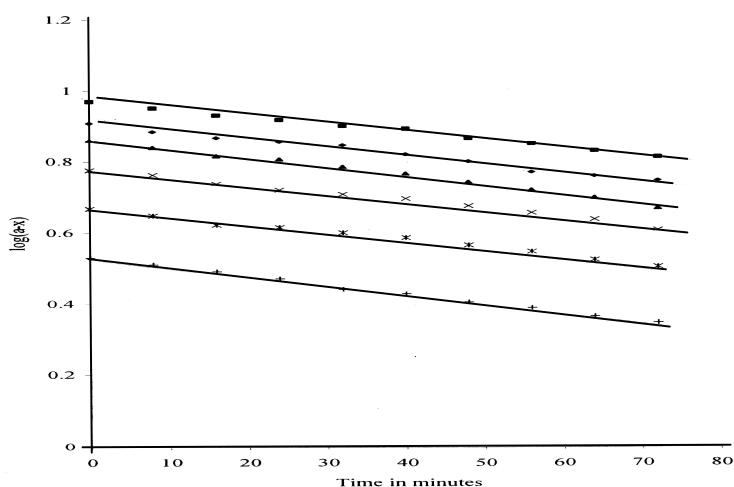
The concentration of potassium permanganate was varied from 1.0 to 4.0 x 10⁻³ mol dm⁻³ keeping fixed concentration of other reaction ingredients, for example [L-aspartic acid] = 5 x 10⁻² mol dm⁻³, [HClO₄] = 1.0 mol dm⁻³ at 318 ⁰K Pseudo first order conditions were maintained and the pseudo first order plots yielded parallel to each other, indicating the order with respect to potassium permanganate is one (Table 1 & Fig. 1).

Table 1
Effect of Oxidant concentration

Time in minutes	[KMnO ₄] x 10 ³ mol dm ⁻³					
	1.0	2.0	2.5	3.0	3.5	4.0
	Volume of hypo used in ml					
0	3.40	4.66 (0)	5.98(0)	7.24(0)	8.10(0)	9.30(0)
8	3.26	4.46 (7)	5.80(8)	6.90(9)	7.68(8)	8.92(7)
16	3.12	4.26 (14)	5.48(16)	6.54(18)	7.38(16)	8.52(14)
24	2.96	4.14 (21)	5.24(24)	6.40(27)	7.16(24)	8.28(21)
32	2.76	3.98 (28)	5.10(32)	6.10(36)	7.00(32)	7.96(28)
40	2.68	3.86 (35)	4.96(40)	5.84(45)	6.60(40)	7.72(35)
48	2.54	3.68 (42)	4.74(48)	5.54(54)	6.40(48)	7.36(42)
56	2.45	3.54 (49)	4.54(56)	5.24(63)	5.90(54)	7.08(49)
64	2.32	3.36 (56)	4.36(64)	5.00(72)	5.76(64)	6.76(56)
72	2.22	3.22 (72)	4.08(72)	4.68(81)	5.60(72)	6.50(63)
k _{graph} x 10 ⁴ s ⁻¹	9.90	9.64	9.94	9.64	9.64	9.67
k _{eq} x 10 ⁴ s ⁻¹	9.82	9.71	8.33	8.42	8.74	9.33

Fig. 1

First Order Plot



Effect of L-aspartic acid

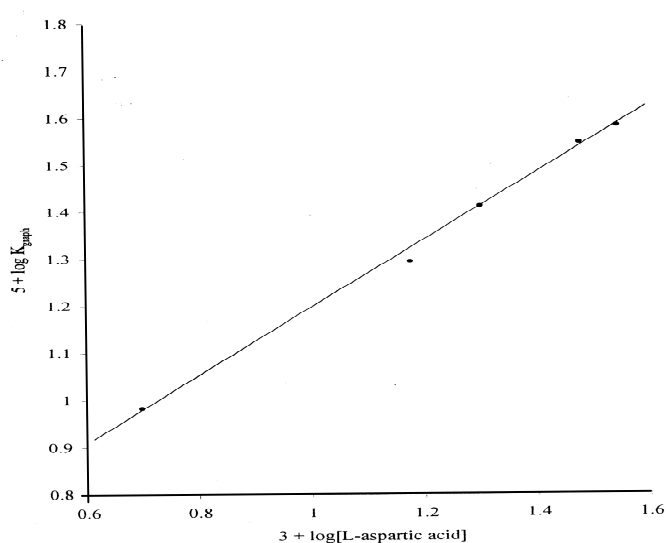
The concentration of L-aspartic acid was varied from 5.0 to $9.0 \times 10^{-2} \text{ mol dm}^{-3}$ at fixed concentration of other ingredients. For example $[\text{KMnO}_4] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{HClO}_4] = 1 \text{ mol dm}^{-3}$. The rate increases with increasing concentration of L-aspartic acid. The order of [L-aspartic acid] is fractional. The slope of the plot of $\log k_{\text{graph}}$ against $\log [\text{L-aspartic acid}]$ gives the order of reaction.

Table 2
order of L-aspartic acid

[L-aspartic acid] 10^2 mol dm^{-3}	$3+\log[\text{L-aspartic acid}]$	$k_{\text{graph}} \times 10^4 \text{ s}^{-1}$	$5+\log k_{\text{graph}}$
0.5	0.6989	0.96	0.9822
1.5	1.1760	1.56	1.1931
2.0	1.3010	1.82	1.26
3.0	1.4771	3.52	1.5465
3.5	1.5440	3.83	1.5831

Fig. 2

Order of L-aspartic acid



Effect of Perchloric acid

The concentration of hydrogen ion was varied employing perchloric acid at fixed concentrations of other reaction ingredients, for example $[\text{KMnO}_4] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{L-aspartic acid}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$. The rate of the reaction increasing with increasing hydrogen ion concentration.

Effect ionic strength

The ionic strength effect was studied by varying the concentration of sodium perchlorate. The ionic strength of the reaction mixtures was varied from 0.25 to 1 mol dm^{-3} at constant concentrations of $[\text{KMnO}_4] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{L-aspartic acid}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $[\text{HClO}_4] = 1 \text{ mol dm}^{-3}$. The rate of the reaction is not affected by the ionic strength.

Effect of temperature

The reaction was studied at 313, 318 and 323°K with the conditions as given in Table. Thermodynamic parameters were calculated from the plot of $\log k_{\text{graph}}$ vs. $1/T$ (Table 4 Fig. 3).

Table 3
Effect of Perchloric acid

Times in minutes	[HClO ₄] mol dm ⁻³			
	2.00	1.50	1.00	0.50
0	5.50	5.30	4.40	5.30
10	4.40	4.40	3.92	4.74
20	3.20	4.10	3.58	4.42
30	1.90	3.68	3.22	4.22
40	1.58	3.08	2.90	3.70
50	0.00	2.84	2.76	3.20
60	0.00	2.22	2.10	2.80
70	0.00	2.00	0.00	2.68
$k_{\text{graph}} \times 10^4 \text{s}^{-1}$	5.85	2.63	1.77	1.34
$k_{\text{eq}} \times 10^4 \text{s}^{-1}$	6.00	2.33	1.78	1.30

Table 4
Effect of temperature

Temp ⁰ K	1 / T x 10 ⁻³	$k_{\text{graph}} \times 10^4 \text{S}^{-1}$	log k_{graph}
313	3.1948	0.96	-4.0177
318	3.1446	1.43	-3.7391
323	3.0959	2.87	-3.5421

Slope = -2291.66

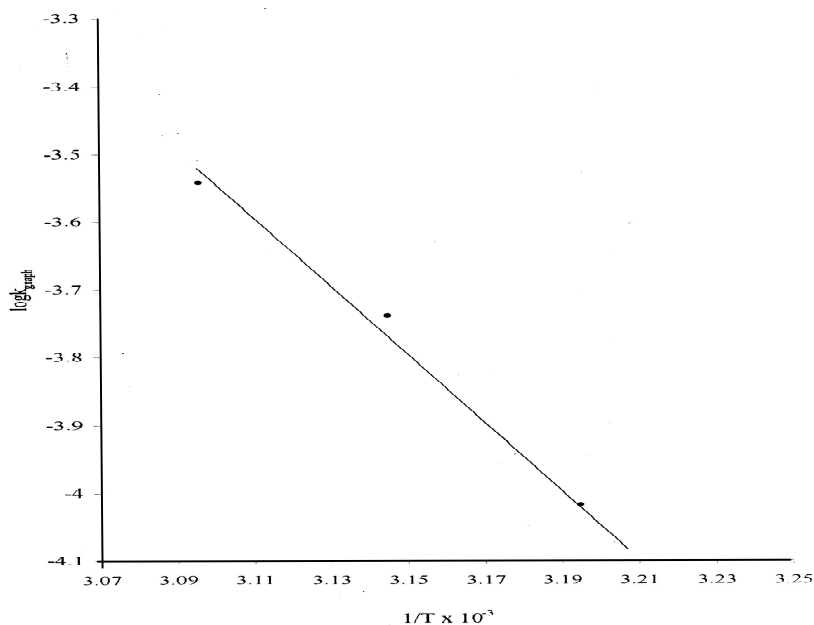
E_a = 43.90 kJ mole⁻¹

$$\Delta S^\ddagger = -187.07 \text{ kJ mole}^{-1} \quad \Delta H^\ddagger = 41.296 \text{ kJ mole}^{-1}$$

$$\Delta G^\ddagger = 99.85 \text{ kJ mole}^{-1}$$

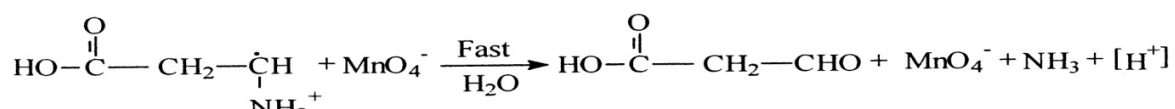
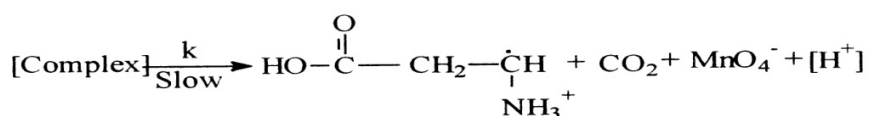
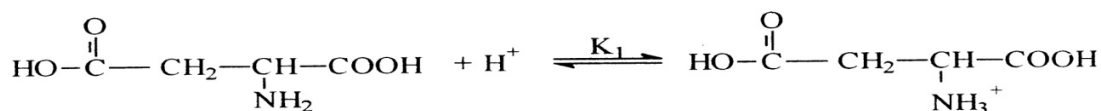
Fig. 3

Effect of Temperature



DISCUSSION

Oxidation of L-aspartic acid by potassium permanganate in perchloric acid. Potassium permanganate is a powerful oxidant in acid medium. Oxidation by permanganate has been extensively used in organic synthesis as it exhibits multivalent oxidation states. The reaction between permanganate and L -aspartic acid in acid medium has a stoichiometry 1:2 with first order dependence each in permanganate ion and L-aspartic acid concentration.



The formation of acid permanganate complex is supported by the observed fractional order. In $[H^+]$ and Michelis Mentan plot which is linear with positive intercept. The formation of the complex is observed kinetically by the non-zero intercept of the plot of $1/k_{\text{graph}}$ versus $1/[L\text{-aspartic acid}]$. The presence of free radical was evidenced by the initiation of polymerization of acrylonitrile monomer, which is also observed in earlier works. Therefore, according to scheme 1.

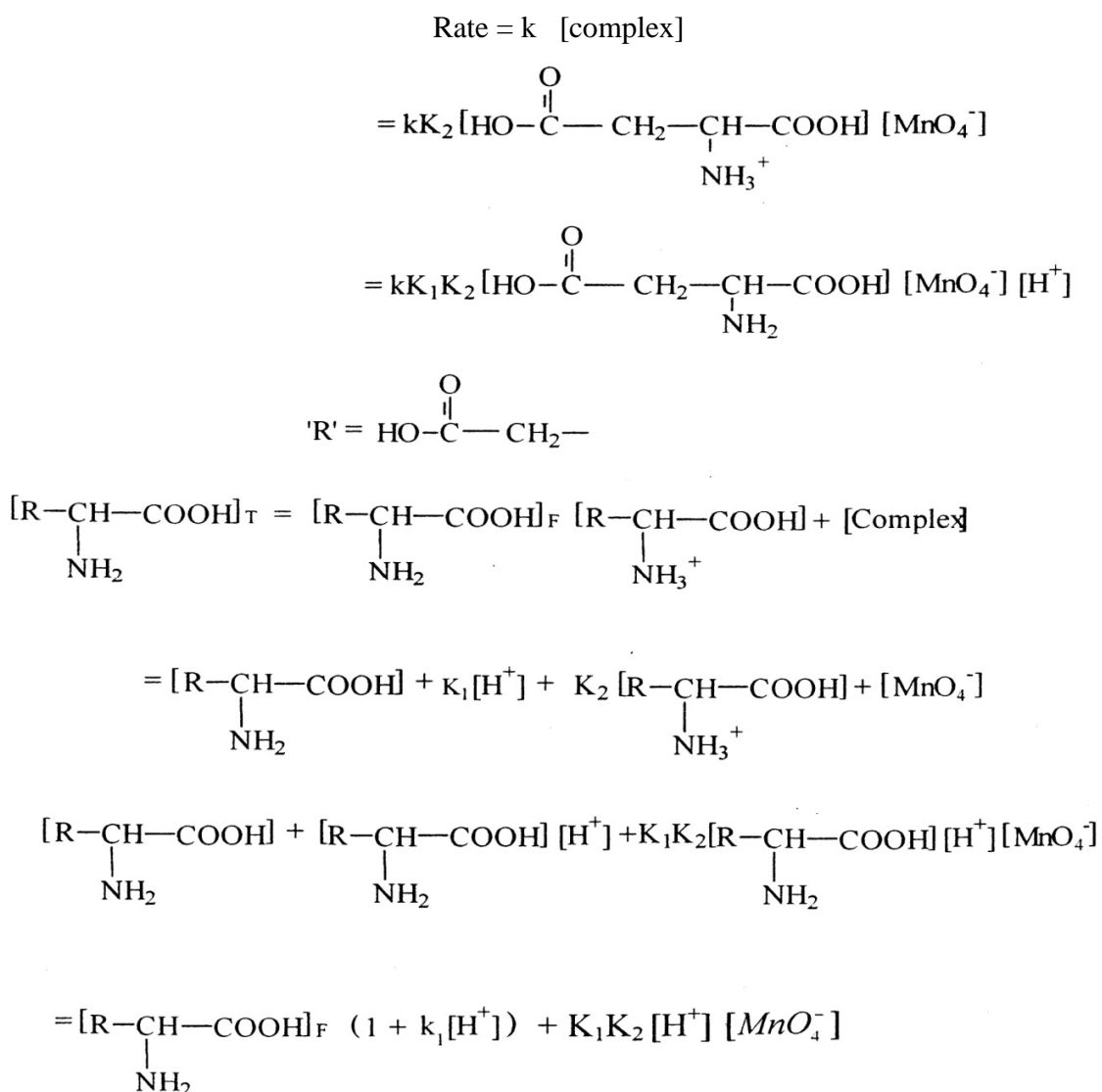


Table 5
Verification of Rate law

[L-aspartic acid] 10^2 mol dm^{-3}	1/[L-aspartic acid]	$k_{\text{graph}} \times 10^4 \text{ S}^{-1}$	$1/k_{\text{graph}} \times 10^3$	$K_{\text{cal}} \times 10^4 \text{ S}^{-1}$
0.5	200.00	0.96	1.041	0.52
1.5	66.66	1.56	6.411	1.56
2.0	50.00	1.82	5.494	2.07
3.0	33.33	3.52	2.845	3.08
3.5	28.57	3.83	2.613	3.57

$$[\text{R}-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}]_{\text{F}} = \frac{[\text{R}-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}]_{\text{T}}}{1 + k_1[\text{H}^+] + k_1 k_2 [\text{H}^+][\text{MnO}_4^-]} \quad \text{.....(1)}$$

$$[\text{MnO}_4^-]_{\text{T}} = [\text{MnO}_4^-]_{\text{F}} + \text{Complex}$$

$$= [\text{MnO}_4^-] + K_2 [\text{R}-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}] [\text{MnO}_4^-]$$

$$= [\text{MnO}_4^-] + K_1 K_2 [\text{R}-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}] [\text{H}^+] [\text{MnO}_4^-]$$

$$[\text{MnO}_4^-]_{\text{T}} = [\text{MnO}_4^-]_{\text{F}} + (1 + K_1 K_2 [\text{R}-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}] [\text{H}^+]) \quad \text{---- (2)}$$

$$[\text{MnO}_4^-]_{\text{F}} = \frac{[\text{MnO}_4^-]_{\text{T}}}{1 + k_1 k_2 [\text{R}-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}] [\text{H}^+]} \quad \text{---- (3)}$$

Substituting (2) and (3) in equation (1)

$$\frac{-d[\text{MnO}_4^-]}{dt} = \frac{k_1 k_2 [\text{R}-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}] [\text{MnO}_4^-] [\text{H}^+]}{(1 + k_1 k_2 [\text{R}-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}] [\text{H}^+])}$$

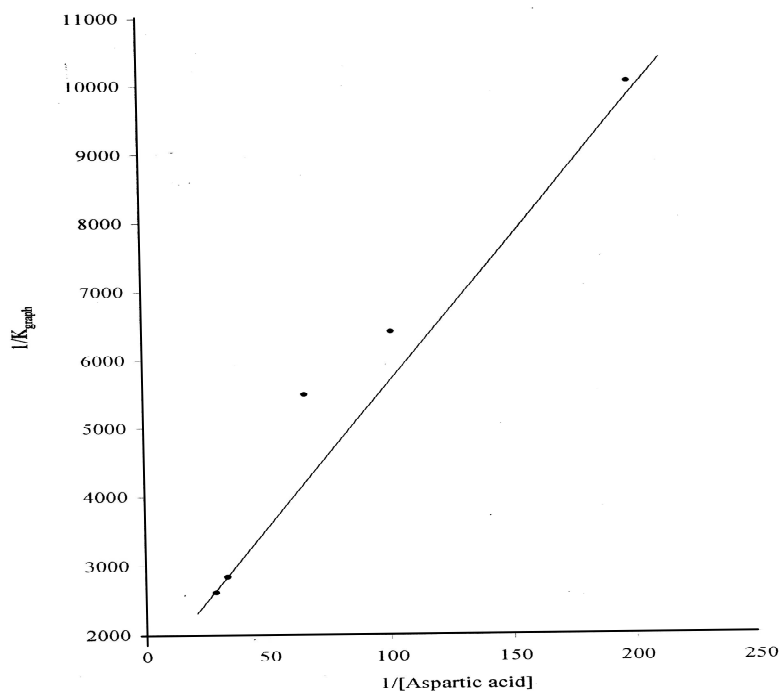
$$\frac{\text{Rate}}{[MnO_4^-]} \cdot k_{cal} = \frac{kK_1K_2[R-\overset{\overset{NH_2}{|}}{CH}-COOH][H^+]}{1 + K_1K_2[R-\overset{\overset{NH_2}{|}}{CH}-COOH][H^+]}$$

$$\frac{1}{k_{graph}} = \frac{1}{k_1k_2[R-\overset{\overset{NH_2}{|}}{CH}-COOH][H^+] } + \frac{1}{k} \dots\dots (4)$$

$\frac{1}{k_{graph}}$ versus $\frac{1}{[L - aspartic acid]}$

Fig. 4

Verification of Rate Law



According to equation (4) the plot of $1/k_{\text{graph}}$ versus $1/[\text{L-aspartic acid}]$ is linear which is verified. The slopes and intercepts of such plots lead to the values of kK_1 and K_2 using these values, the rate constants under different experimental conditions were calculated and compared with experimental data which is given in Table 5 and Fig.4. Experimental and calculated value agrees reasonably well supporting the assumptions of scheme 1.

REFERENCES

1. A. Y. Drummond and W. A. Waters, J. Chem. Soc, 1953,435.
2. J. W. Ladburry and C. F. Cullis, Chem. Rev. 1958.58,403
3. J. S. F. Pode and W. A. Waters, J. Chem. Soc. 1956,717.
4. J. Szamrner, M.Jaky and O. V. Gernasirnov, Int. J. Chem. Kinet., 1992, 24,145.
5. R. Stewart, "Oxidations in Organic Chemistry", edited by K.B. Wiberg. Academic Press, New York, Part A. Chapt.I.
6. R.G.Panari, A.L.Harihar and S.T.Nandibewoor, J.Phys.Org. Chem. 1999, 12,340.
7. R. G. Panari, R. B. Chougale and S. T. Nandibewoor. J. Phys. Org. Chem. 1998, 11, 448.
8. L. I. Sirnandi, M. Jaky, C.R. Savage and Z.A. Schelly, J. Am. Chem. Soc. 1985, 107,4220.
9. M. Jaky, Szewerehyi & L. I. Sirnandi, Inorg., Chem. Acta 1991, 186, 33; P.L. Tirnrnanagoudar, G.A. Hirernath and S.T. Nandibewoor, Trans Met. Chem. 1997, 22, 193;P.L. Timmanagoudar, G.A. Hirernath and S.T. Nandibewoor, Polish J. Chem. 1996,70, 1459;S. Nadirnoalli, R. Rallabandi and L.S. A. Dikshitula ,Trans. Met. Chem. 1993, 18,510.
10. C.Walsh, Ace.Chem. Res 1980, 13, 148. T.C. Bruica, Ace. Chem. Res. 1980, 13,' 256.
11. B.Kawale, M. Thirupathirao and M. Adinarayana Indian J.Chem. 1996,35 A, 667.
12. A. J. L. Coop, J. Z. Gions and A. Meister, Chem. Rev. 1983, 83, 321.
13. N. A. Hampson, J. B. Lee, J. Movely and B. Round Seanlow, J. Chem. Soc. 1970, (C) 815.
14. R. G. R. Baccon, W. H. W. Hanna and D.Stewart, J. Chem. Soc. 1966 (C), 1388.
15. M. R. Kembhavi, A. L. Harihar And S. T. Nandibewoor Oxidn. Comm., 2000, 23, 304.

16. M. R. Kembhavi, A. L. Harihar and S. T. Nandibewoor. Inorg. React. Mech., 2000 (In press).
17. A. L. Harihar, M. R. Kembhavi and S. T. Nandibewoor Manatshette for Chemic. 2000, 131, 734,
18. D. S. Mahadevappa, S. Ananda, A. S. A. Murthy and K. S. Rangappa. Indian J. Chem. 1984. 23 A. 17.
19. B. T. Gowda and R. Vijaylakshmi, Oxidn. Comm., 1988, 11, 45.
20. B. T. Gowda and R. Vijaylakshmi, Indian Chem. Soc. 1987,64,403.
21. M. Iyengar, I. V. Koxhevník and V. Hott. Int. J. Chem. Kinet. 1992,24,1055.
22. R.G.Panari,A.I. Harihar & S.T.Nandibewoor 1. Phy. Organ. Chem. 1999, 12,340.
23. F. Feigl, "Spot Test in Organic Analysis". Elsevier New York, 1975, P.195.
24. M. R. Kembhavi, A. L. Harihar And S. T. Nandibewoor Oxidn. Comm., 2000, 23, 674.
25. A. K. Das and M. Das, 1. Chem. Soc. Dalton Trans 1995,483.
26. A. I. Vogel, "A Test Book of Practical Organic Chemistry including Qualitative Organic Analysis" 3 rd edn, Longman, London, 1973, 332. J. Volhard, Ann, 198, 1879.