



Miceller catalysed oxidation of L-aspartic acid by acidic permanganate ---- A kinetics and mechanistic studies

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Abstract: Permanganatic oxidation of L- aspartic acid has been investigated at 303K in acidic medium using spectrophotometric technique. Both catalytic and non catalytic processes were found first order with respect to aspartic acid and permanganate ions. The oxidation is a double stage process, both stages are linear. The line corresponding to each of the stage intersect at a point. This point is an initial point for second stage process. k_1 and k_1' represent the pseudo first order rate constants corresponding to the faster of the two stages i.e. the first stage and the second, slower stage of the process respectively. These are the average rate constant for oxidation reaction.

Index Terms – L- Aspartic acid, permanganate oxidation, miceller, surfactant.

INTRODUCTION

The kinetic studies of the oxidation reactions provide valuable information regarding the mechanism of several reactions, which help in understanding, predicting and controlling many time dependent important chemical processes. Studies of oxidation processes have many advantages not only in the living system but also in analytical, commercial, synthetic and in industrial field. Silver catalysed oxidation of DL-Isomer of amino acids was studied by Chourey et al^{1,2} in acidic medium. Oxidation of L-aspartic acid by acidic permanganate was studied by Sahu et al³. Oxidation of L-glutamine by Vanadium was studied by Dubey et al⁴. Autocatalytic oxidation of alanine, phenylalanine and valine in alkaline medium was investigated by Kambo and coworkers⁵. Effect of CTAB Micelle on the oxidation of L-Leucine by N-Bromophthalimide was carried by Katre et al⁶. Kinetics and mechanism of oxidation of L-cysteine in aqueous and micellar media was observed by Senpati and coworkers⁷. Kinetics of oxidation of L-Leucine by mono and bimetallic gold and silver nanoparticles in hydrogen peroxide solution was studied by Venkatesan and coworkers⁸. Oxidation of amino acids, peptides and proteins by ozone and beta-cyclodextrine catalysed oxidation of some alpha-amino acids by chloramine-T in alkaline medium was carried out by Sharma et al⁹. Kinetics and mechanism of the autocatalysed oxidation of theophylline by permanganate in aqueous perchloric acid medium was investigated by Hosahalli et al¹⁰. Kinetics and mechanism of oxidation of fluorenone hydrazone by permanganate ion in different acidic medium was studied by Althagafi and coworkers¹¹. Singh et al¹² had studied Rh(III) complex in its nano concentration range as homogeneous catalyst. Methionine oxidation in a yeast peroxiredoxin mutant was investigated by Sideri et al¹³. R. Hassan and coworkers¹⁴ had studied kinetics of oxidation of bromothymol blue by oxyanion potassium permanganate as a strong oxidizing agent in acid solution. The present investigation reports the oxidation of L aspartic acid by potassium permanganate under pseudo first order condition in acidic medium.

MATERIAL AND METHODS

All chemical used for kinetic study were from Sigma Aldrich. All reagent are analytical grade and their solution were prepared by dissolving the requisite amount of sample in doubly distilled water. All weighing was performed on a electronic balance. Kinetic investigation were performed under pseudo first order conditions at 303 K. Requisite amount of solution of substrate, H₂SO₄ and water were equilibrated. A measured amount of KMnO₄ was rapidly added to the reaction mixture with stirring. The progress of the reaction was monitored by double beam UV-Visible spectrophotometer at its maximum absorption at 526nm.

Dependence of rate on substrate concentration(Uncatalysed)

$[\text{H}_2\text{SO}_4] = 0.75 \text{ mol dm}^{-3}$
Temp = 303K

$[\text{KMnO}_4] = 0.75 \times 10^{-3} \text{ mol dm}^{-3}$

[aspartic acid] mol dm ⁻³	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1^1 \times 10^{-3} \text{ min}^{-1}$
0.05	2.64	1.76
0.065	3.11	2.15
0.080	4.35	3.45
0.095	5.80	4.31

The plot of logarithm of aspartic acid with logarithm of rate constants (k_1 and k_1^1) gives straight line of approximately unit gradient in both the stages. These shows that the order of reaction with respect to aspartic acid is one for each stage.

Dependence of rate on substrate concentration (Catalysed)

$[\text{KMnO}_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$
 $[\text{NaLS}] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$

$[\text{H}_2\text{SO}_4] = 0.75 \text{ mol dm}^{-3}$
Temp. = 303K

[aspartic acid] mol dm ⁻³	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1^1 \times 10^{-3} \text{ min}^{-1}$
0.05	2.91	1.93
0.065	3.63	2.69
0.080	4.84	3.89
0.095	6.18	4.81

Dependence of rate on NaLS concentration and catalytic constant (k_c)

$[\text{H}_2\text{SO}_4] = 0.75 \text{ mol dm}^{-3}$
 $[\text{KMnO}_4] = 0.75 \times 10^{-3} \text{ mol dm}^{-3}$

[aspartic acid] = 0.05 mol dm⁻³
Temp = 303K

[NaLS] mol dm ⁻³	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_c \times 10^{-3} \text{ min}^{-1}$	$k_1^1 \times 10^{-3} \text{ min}^{-1}$	$k_c^1 \times 10^{-3} \text{ min}^{-1}$
1.0x10-4	3.27	6.30	2.10	3.40
2.0x10-4	3.86	6.12	2.48	3.60
3.0x10-4	4.51	6.23	2.75	3.30
4.0x10-4	5.14	6.25	3.10	3.35
Average		6.22		3.41

The value of catalytic constant k_c and k_c^1 obtained for first and second stage process are almost constant within the limits of experimental error.

Dependence of rate on temperature, Temperature coefficients

[aspartic acid] = 0.05 mol dm⁻³
 $[\text{KMnO}_4] = 0.75 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{NaLS}] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$
 $[\text{H}_2\text{SO}_4] = 0.75 \text{ mol dm}^{-3}$

Temperature (K)	For uncatalysed		For catalysed	
	For stage one $k_1 \times 10^{-3} \text{ min}^{-1}$	For stage Two $k_1^1 \times 10^{-3} \text{ min}^{-1}$	For stage one $k_1 \times 10^{-3} \text{ min}^{-1}$	For stage Two $k_1^1 \times 10^{-3} \text{ min}^{-1}$
303	2.64	1.76	2.87	1.90
308	3.41	2.32	3.78	2.89
313	5.38	3.87	5.99	4.04
318	7.45	5.14	7.97	6.24

Temperature range(K)	Temperature coefficient For k_1	Temperature coefficient For k_1^1	Temperature coefficient For k_1	Temperature coefficient For k_1^1
303-313	2.03	2.19	2.09	2.13
308-318	2.18	2.21	2.11	2.16

In order to study the effect of temperature on the reaction rate, the reaction both catalysed and uncatalysed, have been studied at various temperature keeping the concentration of all the reactants constant.

Various thermodynamic parameters

Parameters	For first stage		For second stage	
	Calculated	Graphical	Calculated	Graphical
ΔE^\ddagger (Kcal mol ⁻¹)	13.43	13.3895	14.87	14.19
Pz^\ddagger dm ³ mol ⁻¹ min ⁻¹	1.38x10 ⁷	1.47x10 ⁷	1.03x10 ⁸	1.09x10 ⁸
S^\ddagger (cal mol ⁻¹ kelvin ⁻¹)	-25.80	-25.12	-21.82	-21.01
ΔH^\ddagger (Kcal mol ⁻¹)	12.83	12.86	14.27	13.93
ΔG^\ddagger (Kcal mol ⁻¹)	20.65	19.78	20.88	20.50

Dependence of rate on sulphuric acid concentration [H⁺]

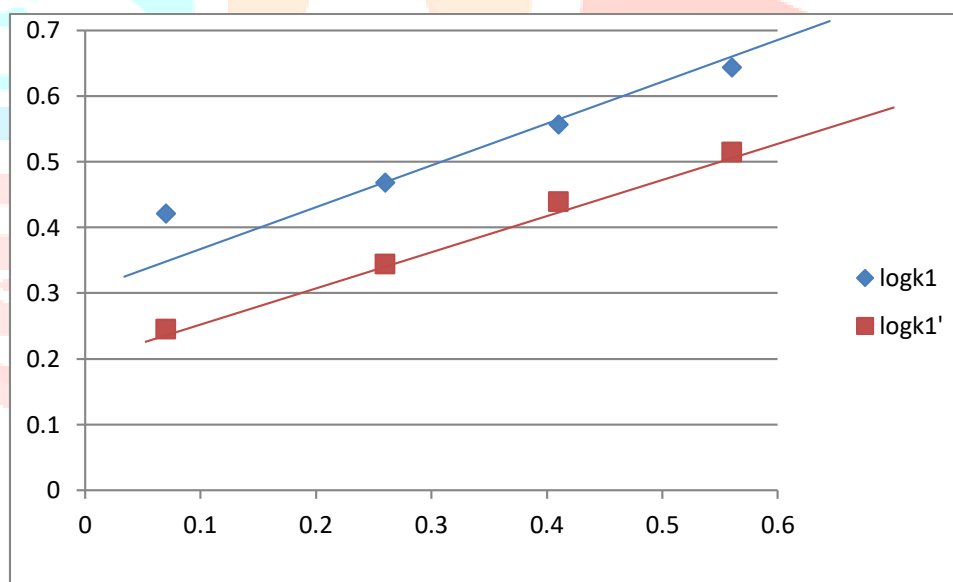
[KMnO₄] = 0.75x10⁻³ mol dm⁻³
[NaLS] = 1.0x10⁻⁴ mol dm⁻³

[aspartic acid] = 0.05 mol dm⁻³
Temp = 303K

[H ⁺] mol dm ⁻³	-H ₀	-log a _{H2O}	k ₁ x10 ⁻³	k ₁ ' x10 ⁻³
0.75	0.07	0.013	2.64	1.76
1.0	0.26	0.018	2.94	2.01
1.25	0.41	0.024	3.61	2.75
1.50	0.56	0.03	4.41	3.83

To investigate the role of H⁺ ion on the oxidation reaction, various hypotheses have been applied. The two Zucker-Hammett relations i.e.

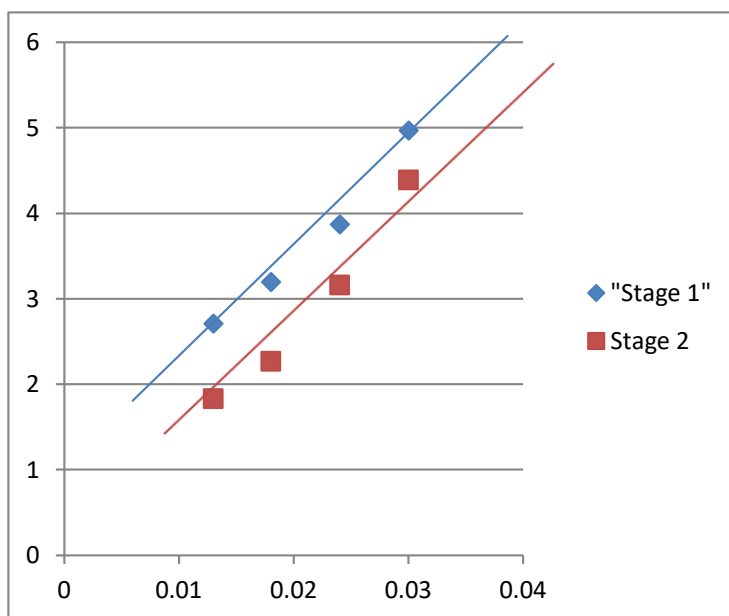
- The plot of (log k) against (H₀)
- The plot of (log k) against (log(acid))



Plot of (3+ (log k)) against (H₀)

Show linear correlation of rate with the sulphuric acid concentration confirming that the reaction is acid catalysed too. However no straight line of Zucker-Hammett plots produced ideal slope value of unity. Here H₀ is acidity function and a_{H2O} is a activity of water and their values corresponding the given sulphuric acid concentration have been collected from Paul, Long¹⁵ and Bunnett¹⁶. While Vibhuti Sohni et. al¹⁷ studied the kinetics and mechanism of micellar catalysed oxidation of glutamic acid.

Bunnett plot

Plot of $((3+\log k_1)+H_0)$ against $\log a_{H_2O}$

Specific effect of cations: - In order to know the specific effect of cations, sulphates of cations were taken at their identical molar concentrations. To show the effect of ionic strength, on the reaction velocity, the plot of ionic strength ' μ ' against the $\log k_1$ and $\log k_1^1$ have been drawn.

Specific effect of cations

$$[\text{KMnO}_4] = 0.75 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{aspartic acid}] = 0.05 \text{ mol dm}^{-3}$$

$$[\text{H}_2\text{SO}_4] = 0.75 \text{ mol dm}^{-3}$$

$$\text{Temp} = 303\text{K}$$

ZnSO ₄			MgSO ₄			NaHSO ₄		
μ	$k_1 \times 10^{-3}$	$k_1^1 \times 10^{-3}$	μ	$k_1 \times 10^{-3}$	$k_1^1 \times 10^{-3}$	μ	$k_1 \times 10^{-3}$	$k_1^1 \times 10^{-3}$
5.0×10^{-4}	4.32	2.96	5.0×10^{-4}	4.10	2.76	5.0×10^{-4}	3.13	2.32
7.5×10^{-4}	4.86	3.47	7.5×10^{-4}	4.52	3.21	7.5×10^{-4}	3.82	2.76
1.0×10^{-3}	5.46	4.21	1.0×10^{-3}	5.12	4.13	1.0×10^{-3}	4.18	3.21

Na ₂ SO ₄			K ₂ SO ₄		
μ	$k_1 \times 10^{-3}$	$k_1^1 \times 10^{-3}$	μ	$k_1 \times 10^{-3}$	$k_1^1 \times 10^{-3}$
5.0×10^{-4}	3.09	2.04	5.0×10^{-4}	3.91	2.83
7.5×10^{-4}	4.53	3.12	7.5×10^{-4}	4.64	3.23
1.0×10^{-3}	5.03	3.97	1.0×10^{-3}	5.12	4.03

Specific effect of anions

In order to know the specific effect of anions, sodium salt of anions were taken at their identical molar concentrations. To show the effect of ionic strength, on the reaction velocity, the plot of ionic strength ' μ ' against the $\log k_1$ and $\log k_1^1$ have been drawn.

Specific effect of Anion

[aspartic acid] = 0.05 mol dm⁻³

[KMnO₄] = 0.75x 10⁻³ mol dm⁻³

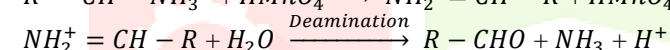
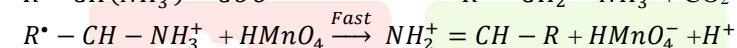
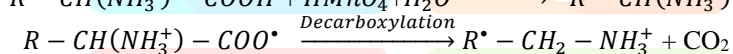
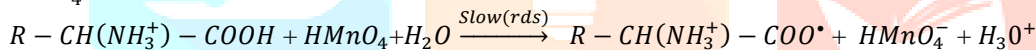
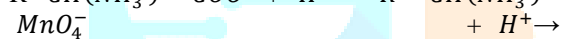
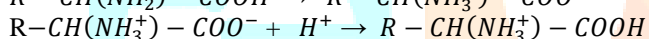
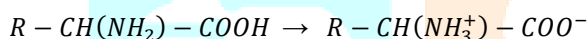
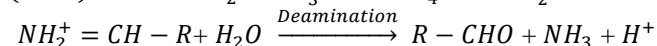
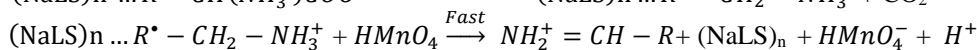
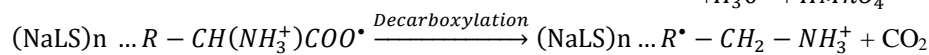
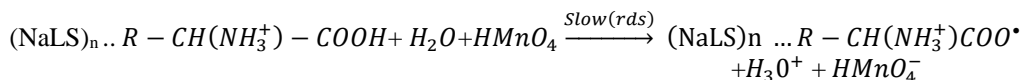
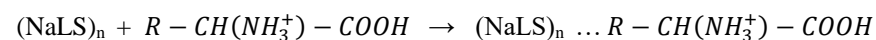
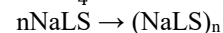
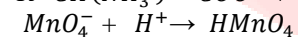
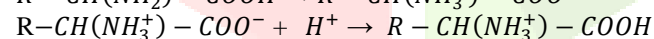
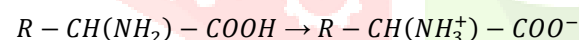
[H₂SO₄] = 0.75 mol dm⁻³

Temp. = 303K

Anions	k ₁ x10 ⁻³	k ₁ ¹ x10 ⁻³	Variation in reaction rate
In absence of anions	2.64	1.76	-
ClO ₄ ⁻	3.81	2.54	44%
HSO ₄ ⁻	3.13	2.32	18%
SO ₄ ⁻	3.09	2.04	17%

RESULTS AND DISCUSSION

On the basis of kinetic result and observation of the studied reaction i.e. surfactant catalysed oxidation of L- aspartic acid by acidic permanganate, following conclusion may be drawn. HMnO₄ is suggested as active oxidizing species. It has been also supported by Stewart and other similar type of work. Acid catalysis has been confirmed by applying the Zucker-Hammett hypothesis. Deviation of slope value of two Zucker-Hammett plots were explained by applying the Bunnett hypothesis. It has been confirmed from Bunnett parameter that water molecule is involved in the reaction in the rate determining step.

Mechanism (in absence of miceller)HMnO₄**Mechanism (in presence of miceller (NaLS))****Free Radical Formation**

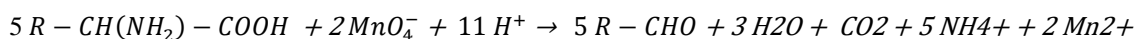
For the identification of free radical formation, acrylonitrile was added in the reaction mixture. After few minutes the filter paper covering the solution, turns yellow due to polymerization of acrylonitrile. This confirms presence of free radical during the reaction. Presence of free radical also confirms by the formation of white precipitate of mercurous chloride by the reduction of mercuric chloride. Low value of activation energy also supports the formation of free radical.

Identification Of Product

The Product of surfactant catalysed oxidation of aspartic acid are carbon dioxide, ammonia as ammonium ion and aldehyde respectively. Identification of carbon dioxide is carried out by lime water test. Ammonium ions confirm by Nessler's test. Formation of aldehyde confirmed by thin layer chromatography. The reaction mixture kept for 24 hours, for the completion of oxidation was then applied on activated TLC plate and placed in TLC chamber containing petroleum ether for few minutes, then plate was sprayed with reagent 2,4-dinitrophenylhydrazine(w/v) in 2 mol dm⁻³ HCl. A yellow spot appears, it confirms the formation of aldehyde.

Stoichiometry

Stoichiometry of the reaction was determined by analytical method. In this method the reaction mixture containing known excess of KMnO₄ over the substrate (L- aspartic acid) and mixture is allowed to stand at room temperature for a sufficiently long time (36 hours). After that the amount of unreacted permanganate was estimated iodometrically. It has been found that the five molecule of aspartic acid require two molecule of permanganate for complete oxidation.



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