



Kinetics and mechanism of the micellers catalysed Permanganatic oxidation of L-Glutamic acid in acidic medium

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Abstract : Permanganatic oxidation of L-Glutamic acid has been investigated at 303⁰K in acidic medium using spectrophotometric technique. Both catalytic and non catalytic processes were found first order with respect to L-Glutamic 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.

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 Senapati 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- Glutamic acid by potassium permanganate under pseudo first order condition in acidic medium.

RESEARCH METHODOLOGY

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 303⁰K. 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 oxidant concentration

$[H_2SO_4] = 2.0 \text{ mol dm}^{-3}$

$[L\text{-Glutamic acid}] = 0.1 \text{ mol dm}^{-3}$

Temp = 303K

[KMnO ₄ × 10 ⁻³] mol/dm ³	$k_1 \times 10^{-3} \text{ min}^{-1}$		$k_1^1 \times 10^{-3} \text{ min}^{-1}$	
	By Equation	By Graphical method	By Equation	By Graphical method
0.75	1.513	1.514	1.301	1.312
1.0	1.514	1.512	1.303	1.310
1.25	1.510	1.521	1.321	1.321
1.5	1.516	1.523	1.322	1.317

The plot of log of optical density i.e. log (a-x) and time exhibit double stage process each being linear indicating that the order with respect to permanganate is one for each stages in acidic medium.

Dependence of rate on substrate concentration (uncatalysed)

$[KMnO_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$

Temp = 303K

$[H_2SO_4] = 2.0 \text{ mol dm}^{-3}$

[L-Glutamic acid] mol dm ⁻³	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1^1 \times 10^{-3} \text{ min}^{-1}$
0.10	1.51	1.30
0.15	2.04	1.88
0.20	2.66	2.41
0.25	3.40	2.87

Dependence of rate on substrate concentration (catalysed)

$[KMnO_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$

$[H_2SO_4] = 2.0 \text{ mol dm}^{-3}$

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

Temp. = 303K

[L-Glutamic acid] mol dm ⁻³	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1^1 \times 10^{-3} \text{ min}^{-1}$
0.10	1.84	1.53
0.15	2.97	2.59
0.20	3.81	3.27
0.25	4.61	4.13

The plot of logarithm of L-Glutamic 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 L-Glutamic acid is one for each stage.

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

$[H_2SO_4] = 2.0 \text{ mol dm}^{-3}$

$[L\text{-Glutamic acid}] = 0.1 \text{ mol dm}^{-3}$

$[KMnO_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$

Temp = 303K

[NaLS] mol dm ⁻³	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_c \times 10^{-3} \text{ min}^{-1}$	$k_1^1 \times 10^{-3} \text{ min}^{-1}$	$k_c^1 \times 10^{-3} \text{ min}^{-1}$
Uncatalysed	1.51		1.30	
1.0×10^{-4}	1.84	3.30	1.53	2.30
2.0×10^{-4}	2.21	3.50	1.83	2.65
3.0×10^{-4}	2.60	3.63	2.08	2.60
4.0×10^{-4}	3.01	3.75	2.39	2.72
Average		3.54		2.56

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 and calculation of Temperature coefficients

$[L\text{-Glutamic acid}] = 0.1 \text{ mol dm}^{-3}$

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

$[KMnO_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$

$[H_2SO_4] = 2.0 \text{ mol dm}^{-3}$

Temperature (K)	For uncatalysed		For catalysed	
	For stage one $k_1 \times 10^{-3} \text{ min}^{-1}$	For stage Two $k_1 \times 10^{-3} \text{ min}^{-1}$	For stage one $k_1 \times 10^{-3} \text{ min}^{-1}$	For stage Two $k_1 \times 10^{-3} \text{ min}^{-1}$
303	1.51	1.30	1.84	1.53
308	2.12	1.81	2.91	2.28
313	3.24	2.85	3.89	3.66
318	4.51	3.88	6.95	4.64

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	2.14	2.19	2.11	2.39
308-318	2.12	2.14	2.38	2.03

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 for uncatalysed and catalysed reaction

Parameters	For first stage		For second stage	
	Calculated	Graphical	Calculated	Graphical
ΔE^\ddagger (Kcal mol ⁻¹)	14.336	12.3895	15.012	14.850
Pz^\ddagger (dm ³ mol ⁻¹ min ⁻¹)	2.789×10^7	1.97×10^6	1.03×10^8	1.93×10^7
S^\ddagger (cal mol ⁻¹ kelvin ⁻¹)	-24.39	-24.1253	-24.016	-24.01
ΔH^\ddagger (Kcal mol ⁻¹)	13.736	12.86	14.401	13.967
ΔG^\ddagger (Kcal mol ⁻¹)	6.118	5.950	4.5011	4.5023

Dependence of rate on sulphuric acid concentration [H⁺]

[KMnO₄] = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$
[NaLS] = $1.0 \times 10^{-4} \text{ mol dm}^{-3}$

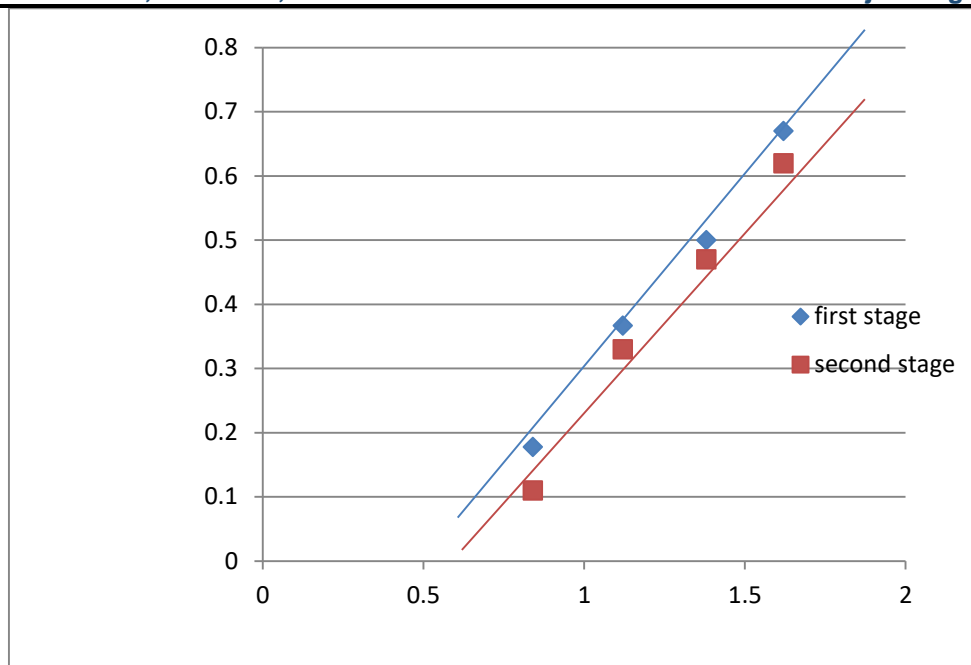
[L-Glutamic acid] = 0.1 mol dm^{-3}
Temp = 303K

[H ⁺] mol dm ⁻³	-H ₀	-log a _{H₂O}	$k_1 \times 10^{-3}$	$k_1^1 \times 10^{-3}$
2.0	0.84	0.043	1.51	1.30
2.5	1.12	0.063	2.33	2.13
3.0	1.38	0.085	3.15	2.96
3.5	1.62	0.111	4.74	4.19

To investigate the role of H⁺ ion on the oxidation reaction, various hypotheses have been applied. The two Zucker-Hammett¹⁵ relations i.e.

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

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.



Plot of (log k) against (H₀)

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 logk₁ and logk₁⁻¹ have been drawn

Specific effect of cations

[L-Glutamic acid] = 0.1 mol dm⁻³
[H₂SO₄] = 2 mol dm⁻³

[KMnO₄] = 1.0x 10⁻³ mol dm⁻³
Temp = 303K

ZnSO ₄			MgSO ₄			(NH ₄) ₂ SO ₄		
μ	k ₁ x10 ⁻³	k ₁ ⁻¹ x10 ⁻³	μ	k ₁ x10 ⁻³	k ₁ ⁻¹ x10 ⁻³	μ	k ₁ x10 ⁻³	k ₁ ⁻¹ x10 ⁻³
1x10 ⁻³	1.70	1.3	1x10 ⁻³	1.69	1.28	7.5x10 ⁻⁴	1.65	1.20
2x10 ⁻³	1.71	1.40	2x10 ⁻³	1.72	1.30	1.5x10 ⁻⁴	1.69	1.22
3x10 ⁻³	1.80	1.44	3x10 ⁻³	1.78	1.35	2.25x10 ⁻³	1.71	1.28
4x10 ⁻³	1.83	1.46	4x10 ⁻³	1.81	1.40	3x10 ⁻³	1.76	1.26

Na ₂ SO ₄			K ₂ SO ₄		
μ	k ₁ x10 ⁻³	k ₁ ⁻¹ x10 ⁻³	μ	k ₁ x10 ⁻³	k ₁ ⁻¹ x10 ⁻³
7.5x10 ⁻⁴	1.67	1.37	7.5x10 ⁻⁴	1.70	1.31
1.5x10 ⁻⁴	1.73	1.42	1.5x10 ⁻⁴	1.74	1.49
2.25x10 ⁻³	1.78	1.45	2.25x10 ⁻³	1.81	1.51
3x10 ⁻³	1.80	1.47	3x10 ⁻³	1.84	1.53

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 logk₁ and logk₁⁻¹ have been drawn.

Specific effect of Anion

[L-Glutamic acid] = 0.1 mol dm⁻³
[H₂SO₄] = 2 mol dm⁻³

[KMnO₄] = 1.0x 10⁻³ mol dm⁻³
Temp. = 303K

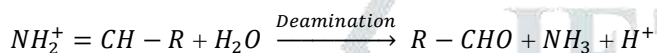
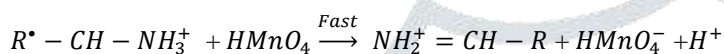
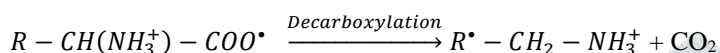
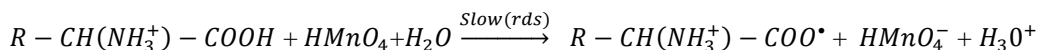
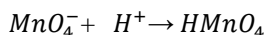
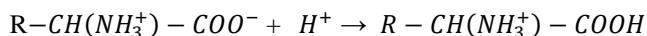
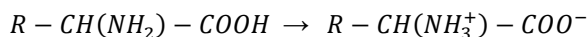
NaNO ₃			Na ₂ SO ₄			CH ₃ COONa		
μ	k ₁ x10 ⁻³	k ₁ ⁻¹ x10 ⁻³	μ	k ₁ x10 ⁻³	k ₁ ⁻¹ x10 ⁻³	μ	k ₁ x10 ⁻³	k ₁ ⁻¹ x10 ⁻³
2.5x10 ⁻⁴	2.70	1.32	7.5x10 ⁻⁴	1.67	1.37	2.5x10 ⁻⁴	1.43	1.30
5x10 ⁻⁴	4.75	3.58	1.5x10 ⁻⁴	1.73	1.42	5x10 ⁻⁴	1.32	1.21
7.5x10 ⁻⁴	6.80	5.82	2.25x10 ⁻³	1.78	1.45	7.5x10 ⁻⁴	1.17	1.10
1x10 ⁻³	8.86	7.46	3x10 ⁻³	1.80	1.47	1x10 ⁻³	1.08	1.03

RESULTS AND DISCUSSION

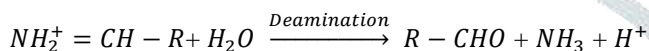
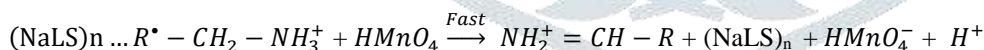
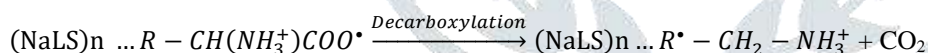
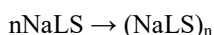
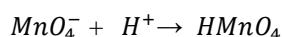
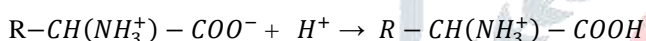
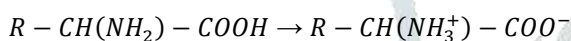
On the basis of kinetic result and observation of the studied reaction i.e. surfactant catalysed oxidation of L- Glutamic acid by acidic permanganate, following conclusion may be drawn.

HMnO_4 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)



Mechanism (in presence of miceller (NaLS))



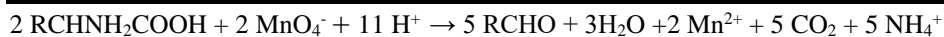
Free Radical Formation

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 confirm presence of free radical during the reaction. Presence of free radical also confirm by the formation of white precipitate of mercurous chloride by the reduction of mercuric chloride. Low value of activation energy also support the formation of free radical.

Identification Of Product

The Product of surfactant catalysed oxidation of L-Glutamic 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.



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