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RESEARCH ARTICLE

Miceller catalyzed oxidative deamination and decarboxylation of L-alanine by acidic permanganate: A kinetic and mechanistic study

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Abstract

A Kinetic investigation of oxidation of L-alanine by acidic permanganate in presence of surfactant as catalyst has been carried out spectrophotometrically. The reaction is double process in which first stage is followed by second fast stage process. The rate shows a first order dependence on each oxidant, substrate and surfactant. The reaction is studied at different temperatures to evaluate usual kinetic and activation parameters such as rate constant, temperature coefficient, energy of activation, entropy of activation, enthalpy, Gibbs free energy and probability factor. The possible effect of the increasing ionic strength on the rate was also analysed and mechanism in concordance with the experimental findings is proposed for catalytic pathway.

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Introduction

The oxidation of amino acids by permanganate ion in varieties of media under different conditions has been done by many workers¹⁻⁶. However, a careful survey of the literature reveals that the surfactant catalysed oxidative decarboxylation by permanganate in acidic media has received very little attention. On the present work the micellar catalysed oxidation of L-alanine has been carried out from the mechanistic point of view by acidic permanganate.

Amino acids make up 75% of human body and are vital to every part of human function. The kinetic investigation of the oxidation of amino acids are important because of their biological significance and a precise understanding of the mechanism of such biological redox reactions help in the synthesis of reaction products.

The oxidation of L-alanine by permanganate ion in aqueous phosphate buffers is autocatalysed by the inorganic reaction product, a soluble form of colloidal manganese dioxide temporarily stabilized in solution by adsorption of phosphate ion on its surface. Kinetics and mechanisms of the oxidation by permanganate of L-alanine was studied by Andres et al⁷. Permanganate Oxidation of L-Alanine in Acidic Solvent which is autocatalysis by Intermediate Mn(IV) Species investigated by Insausti et al⁸.

Kinetics and mechanism of the silver(I) ion catalysed oxidation of α -alanine by peroxydisulphate was investigated by Chandra and coworkers⁹ while Mahadevappa et al¹⁰ studied oxidation of alanine and phenylalanine by sodium N-chlorobenzene sulfonamide (chloramine-B) in hydrochloric acid medium. Oxidation of alanine was reported by Rossiter¹¹.

Shrivastava and co-workers¹² studied the kinetics of Ru(III) catalysed oxidation of glycine and alanine by N-bromoacetamide (NBA) in perchloric acid media in the presence of mercury(II) acetate as a scavenger. Katre et al¹³ studied the oxidation of L-Alanine by N-bromophthalimide in the presence of sodium dodecyl sulfate. Oxidation of β -alanine by Ag(III) complex in alkaline medium and Oxidation of Glycine and Alanine by Bis(dihydrogentellurto)argentite(III) Ion in Alkaline Medium studied by Huo et al¹⁴⁻¹⁵.

Literature survey reveals that permanganate ions are widely used as oxidizing agent in synthetic and analytical chemistry¹⁶⁻¹⁷. It has several advantages as an analytical reagent. It is strong and vividly coloured. In acidic medium it exists in different forms as HMnO_4 , HMnO_4^+ , HMnO_3 , Mn_2O_7 and one depending on the nature of the reductant¹⁸.

Amphiphilic compounds are chemical compounds having dual affinity for water and oil. They have distinct nonpolar (lipophilic or hydrophobic) and polar (hydrophilic or hydrophobic) reactions in their molecules. They exhibit a special property in solution manifesting characteristic self-organization as association called 'micelle' formation and can be potentially used for surface chemical works. They are termed as SURFace ACTive AgENTS as SURFACTANTS^(19,20,21). A threshold concentration is required for the formation of micelle, that is known as 'Critical Micelle Concentration' or CMC. Many reactions have been found influenced by micellar medium.

Number of oxidation reactions have been carried out by different surfactants. Oxidation of glycine by quin-quevalent vanadium in the presence of CTAB surfactant was studied by M. Choubey et al.²² while S. Dubey and coworker²³ studied the oxidation of L-glutamine by Vanadium(V) in presence of CTAB. Gaur²⁴ has studied the sodium dodecyl sulphate catalysed oxidation of series of DL-isomers of amino acids by permanganate. So in order to gain further insight into the nature and mechanism of oxidation of alanine following study has been carried out. In the present work an anionic surfactant i.e. Sodium Lauryl Sulphate is used as micellar catalyst.

Material and Methods

All reagents used were of AnalaR and G.R. grade. Permanganate solution was prepared and tested as given by Vogel⁵. Doubly distilled water was used to prepare all the solutions.

Kinetic experiments were carried out in a thermostat in which the temperature is controlled within $\pm 0.1^\circ\text{C}$. The reactions were usually followed upto 70% of completion. The reaction was initiated by adding requisite amount of pre equilibrated solution of permanganate to an equilibrated mixture of substrate (L-alanine), surfactant and sulphuric acid solutions. The zero time of the reaction was noted when half of the permanganate solution was added. The total volume of the reaction mixture was always kept 50 ml.

All kinetic measurements were conducted under pseudo first order conditions where the amino acid was maintained in a large excess over the permanganate ion concentration. Kinetic studies were performed by using Systronics 106 spectrophotometer at 525 nm i.e. at absorbance maximum of permanganate. It was verified that there is no interference from other reagents at this wavelength. 2 ml of the aliquot of reaction mixtures were withdrawn at known intervals of time and the reaction was quenched by adding it to a known excess of ice-cold distilled water (temperature $< 2^\circ\text{C}$) in the optic cell. The values of the absorbance due to unreacted permanganate at given times were read out directly from the spectrophotometer.

The work is performed on the determination of dependence of the rate on substrate, surfactant and oxidant concentration. The reaction is studied at different temperatures and evaluation of usual kinetic and activation parameters such as rate constant, temperature coefficient, energy of activation, entropy of activation, enthalpy and probability factor have been determined²⁵.

Result and Discussion

Nature of reaction:-

Though the reaction has been studied by number of workers by different oxidant and in different medium. But the results reported are available upto the completion of first stage process only in case of oxidation of L-alanine. In the present study, it has been observed that the oxidation of L-Alanine by permanganate in presence of anionic surfactant i.e. sodium lauryl sulphate is a linear double stage process, first stage is followed by second fast stage process. Velocity constant of both the stages (first stage shown by k_1 and second one is shown by k_1') indicates linearity of both the stages. (figure-1).

1. Oxidant variation

The reaction was studied at various concentration of the potassium permanganate in the presence of the surfactant for study the effect of oxidant on the reaction. It has been observed that the increase in the permanganate concentrations does not alter the rate of oxidation of alanine in both the stages. They are found to be fairly constant. It is shown that rate of oxidation is independent of concentration of oxidant and order of reaction with respect to permanganate is confirmed to be one. (Table-1, Figure-2).

2. Substrate variation

The reaction was studied at different concentrations of L-alanine with and without addition of surfactant within the range 0.1 to 0.5 mol dm⁻³ concentrations. The plot of velocity constant "k" against L-alanine concentration is found linear showing the first order dependency of the rate on L-alanine concentration in the given range for both stages. It has been observed that the rate of reaction increases with substrate concentration in both i.e. in absent and in presence of surfactant. Velocity constants calculated by different methods are given in Table – 2 and 3. (Figure-3 for uncatalysed and Figure-4 for catalysed)

The graph between $1/k$ and $1/[\text{Alanine}]$ i.e. Michaelis-Menten plot, [Figure 5(uncatalysed)], [Figure 6(catalysed)] have straight lines showing that the reaction is first order with respect to each stage and also confirms that there is no any intermediate complex formation, if there any complex is formed, its formation constant should be very small.

3. Surfactant (NaLS) variation

The reaction was also studied at different concentrations of the anionic surfactant Sodium Lauryl Sulphate (NaLS) within the range 1×10^{-4} to 5×10^{-4} mol dm⁻³ (Table – 4 and Figure-7). The plot of velocity constant “ k ” against surfactant concentration is found linear showing the first order dependency of the rate on surfactant concentration in the given range for both stage. It has been observed that the rate of reaction increases with surfactant concentration showing catalytic function of surfactant in the given reaction. The catalytic constant k_c was determined and are reported in the Table 4, are fairly constant confirming its catalytic action.

The reaction rate have been found increase with the increase in the NaLS concentration i.e. from 1×10^{-4} M to 5×10^{-4} mol dm⁻³. The reported CMC of NaLS is 8.1×10^{-4} mol dm⁻³ at 25°C. These shown that catalysis below CMC is feasible. As per the literature available, it is a type of pre-micellar catalysis²⁶.

In the theoretical treatment for pre-micellar catalysis a graph is plotted between $n = \log[k_{\text{obs}} - k_0] / \log[k_m - k_{\text{obs}}]$ and $\log[\text{NaLS}]$. Here k_0 is the velocity constant without NaLS, k_{obs} is the velocity constant at different NaLS concentration while k_m is the maximum velocity constant in presence of NaLS used. (figure-8) The above plot is a good straight line with slope value 1.2026 and 1.3128 for first and second stage processes respectively. Both values are in between the expected value for pre-micellar catalysis i.e. between 1 to 6. Lower value suggest the pre-micellar catalysis. For micellar catalysis these values should be more than 20. In the present study NaLS is catalysing the reaction below its CMC in the given range of concentrations used.

4. Variation of $[H^+]$

The reaction was studied at various concentration of the sulphuric acid in the presence of the surfactant to observe the activity of hydrogen ion in the reaction. It has been observed that the increase in the acid concentrations increases the rate of oxidation of L-alanine in both stage (Table 5). It is most probably due to the protonation of the oxidant in accordance with the equilibrium $\text{MnO}_4^- + \text{H}^+ \rightleftharpoons \text{HMnO}_4$ supported by the spectral studies²⁷. It has also been observed that the rate of oxidation is strictly proportional to the concentration of the substrate indicates that HMnO_4 oxidizes the substrate directly.

The two Zucker-Hammett²⁸ plots were found to be linear. This shows that the reaction is acid catalysed. However none of the plots produces the ideal slope value of unity. (Table 6)

In the view of these departures from ideal slope value, Bunnett²⁹ and Bunnett Olsen³⁰ hypothesis were tested. The slope values of these plots indicate that the water molecule should be act as a proton abstracting agent in the rate determining step. The related $-H_0$ and $\log a_{\text{H}_2\text{O}}$ values corresponding to given acid concentration have been collected from Paul and Long³¹ and Bunnett respectively³.

5. Temperature variation

For determination of various thermodynamic parameters the reaction have been studied at different temperatures with and without surfactant. (Table-8). All kinetic and activation parameters were determined in absence and presence of surfactant³². The slope value of a plot between $\log k$ and $1/T$ i.e. Arrhenius plot (Figure 13 for uncatalysed and Figure 14 for catalysed) has also been used to determine activation energy. All parameters have been reported in Table-7 for uncatalysed and for catalysed reaction.

The temperature coefficients for two different temperature range, have been given for first and second stage process (k_1 & k_1') for uncatalysed and catalysed reaction in Table-8.

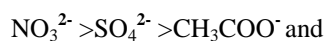
The values of energy of activation are fairly within the range of activation energy for radical molecule reaction. Low and negative value of entropy of activation suggest that it is a normal reaction³³.

6. Effect of added neutral salts

The positive salt effect on the surfactant catalysed oxidation reaction confirms that the reaction is between a positive ion and a molecule in the rate determining step.

The specific effect of cations and anions on the reaction rate has also been studied by taking sodium salts of anions and sulphates of cations. Order of influence has been observed as follows:-

For Anions



For Cations



It has been observed that CH_3COO^- exerts retarding effect on the reaction.

7. Stoichiometry and product analysis

Product analysis:-

Under the condition employed, the products of oxidation were identified as acetaldehyde, ammonia and carbon dioxide.

Identification of aldehyde as reaction product analysed by thin layer chromatography(TLC).The reaction mixture was kept for 24 hours, then it was applied on TLC plates(silica gel plates),and placed in TLC chamber containing petroleum ether/diethyl ether (90/10,v/v) for few minutes.Solution containing 0.4% 2,4-dinitrophenylhydrazine(w/v) in 2M HCl, were then sprayed over TLC plate.Yellow spots were found confirming Acetaldehyde as a reaction product³⁴.

Identification of carbon dioxide is carried out by lime water test. Reaction mixture turns milky within 3 to 6 hours due to the evolution of carbon dioxide.

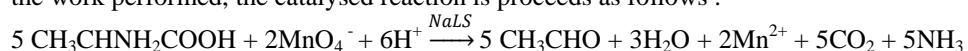
The ammonia as ammonium ion was identified by Nessler's test.

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 the polymerization³⁵⁻³⁶. This confirms presence of free radical during the progress of reaction.

Stoichiometry:-

Stoichiometry of the reaction was determined by analytical method. In this method the reaction mixture containing excess of KMnO_4 over the L-alanine were allowed to stand at 35°C for a sufficiently long time(36 hours).The amount of unreacted permanganate was estimated iodometrically.It has been found that the five molecules of L-alanine recognise two molecules of permanganate for complete oxidation. On the basis of literature available¹⁸ and the work performed, the catalysed reaction is proceeds as follows :



The above stoichiometric equation is consistent with the results of product analysed.

Figure-1:Typical run(catalysed and uncatalysed reactions)

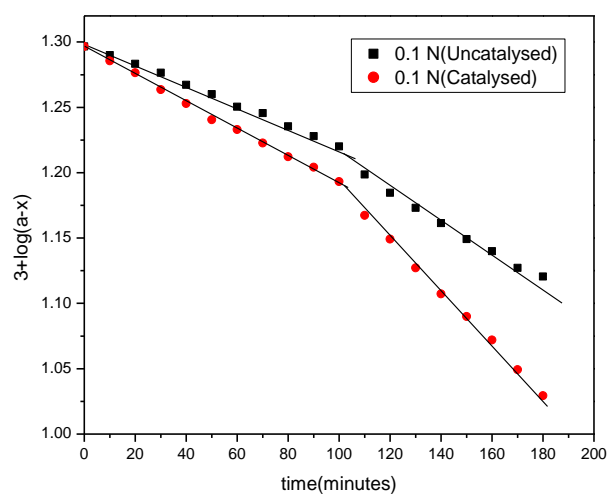


Figure-2:-Permanganate variation

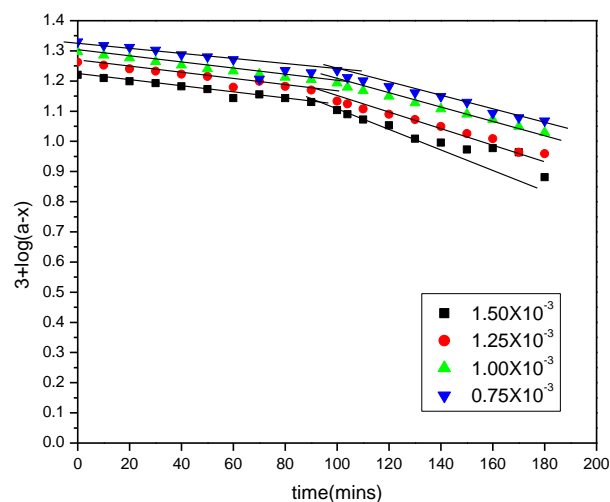


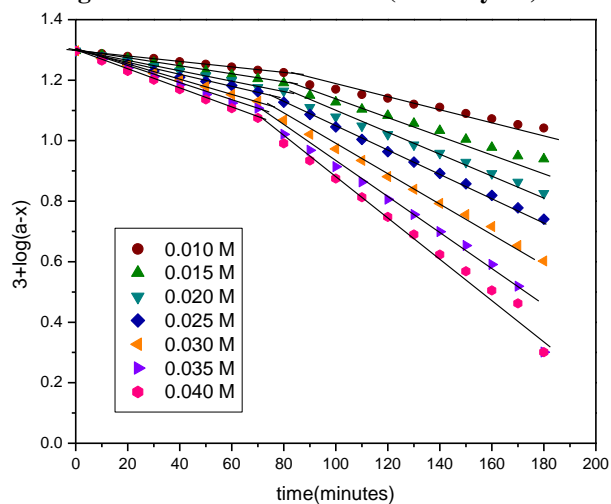
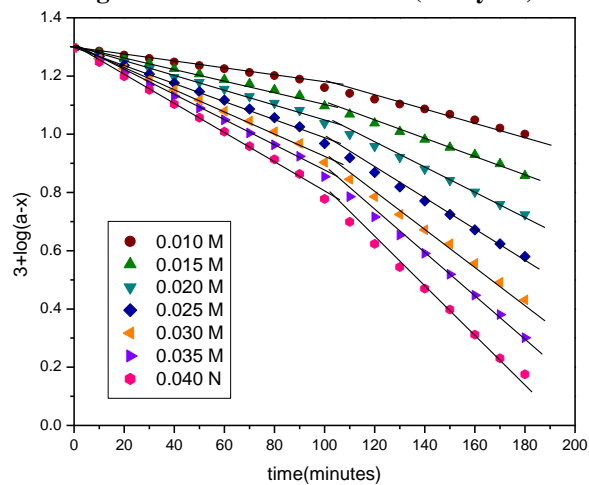
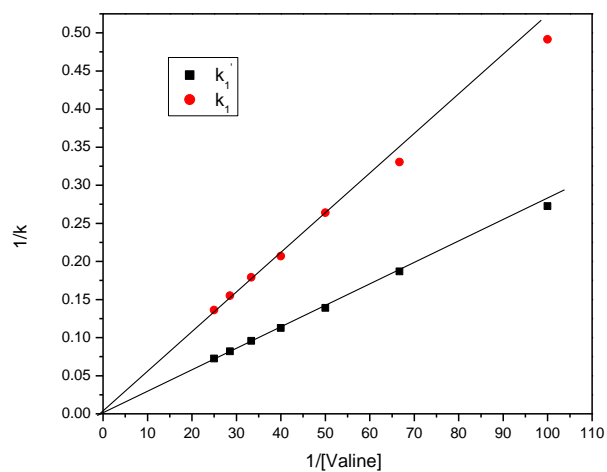
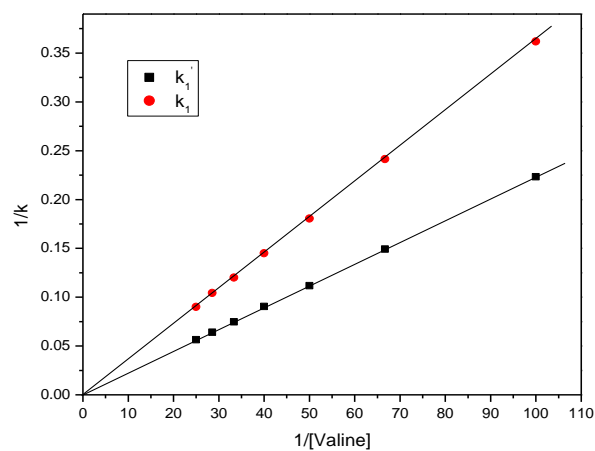
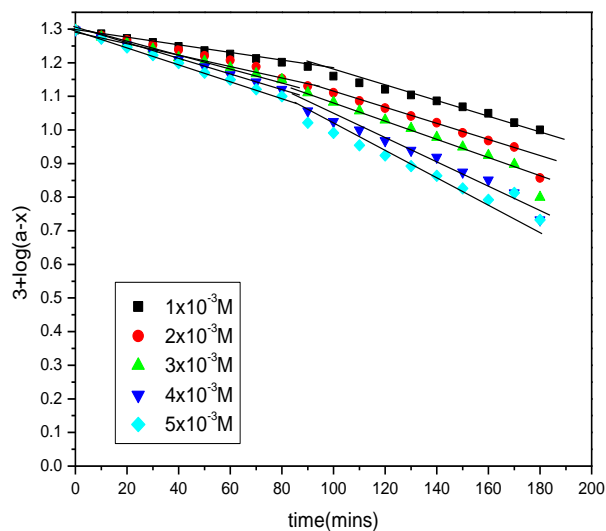
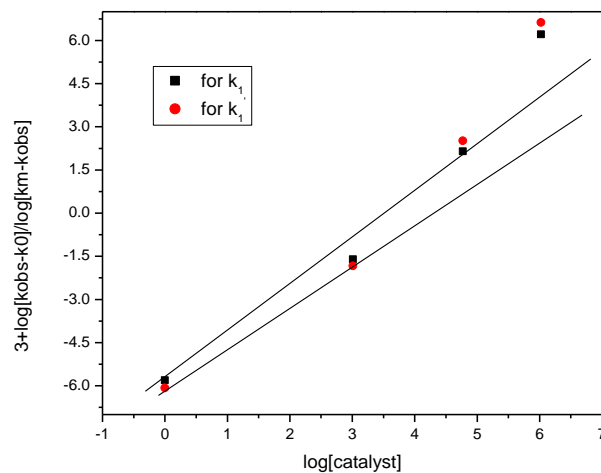
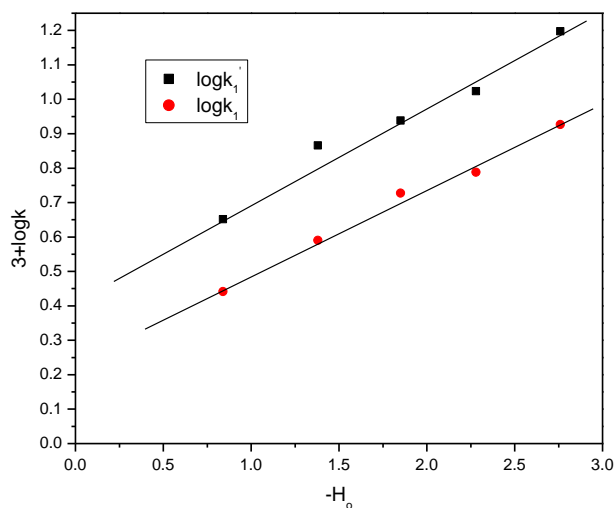
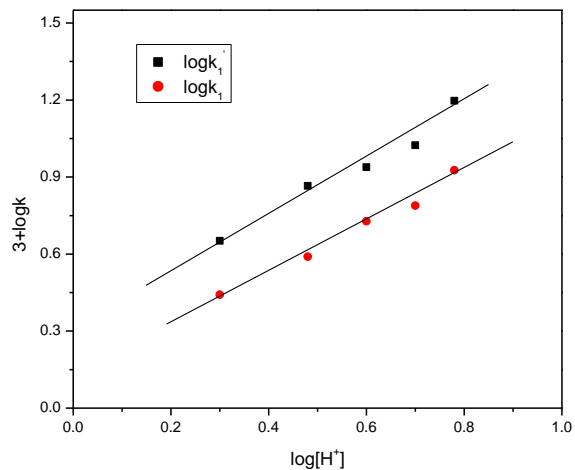
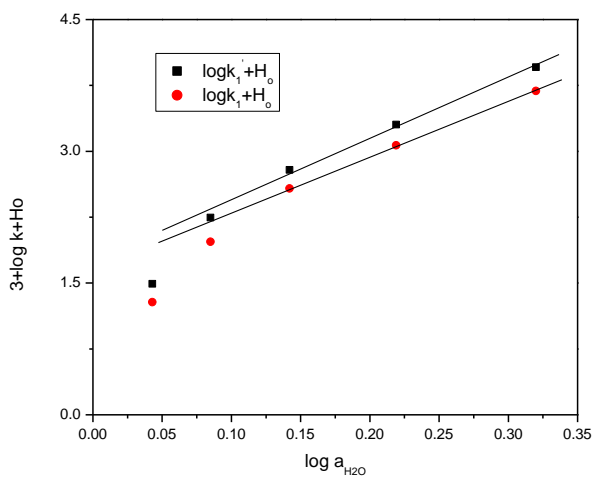
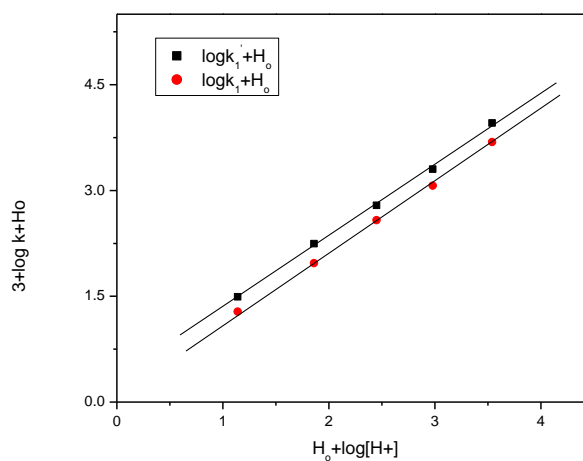
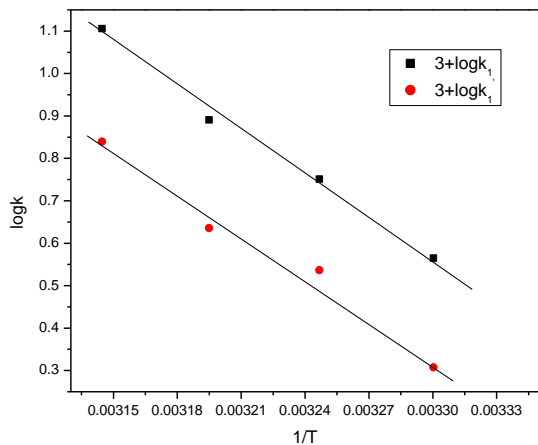
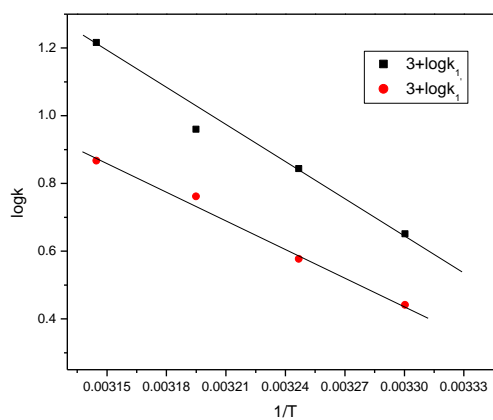
Figure 3:-Substrate variation(uncatalysed)**Figure 4:- Substrate variation(catalysed)****Figure 5:-Michaelis Menten plot(uncatalysed)****Figure 6:- Michaelis Menten plot(catalysed)****Figure 7:-Surfactant Variation****Figure 8:-Premiceller catalysis**

Figure 9:-Zucker-Hammett Plot-1**Figure 10:- Zucker-Hammett Plot-2****Figure 11:-Bunnett plot****Figure 12:-Bunnett-Olsen Plot****Figure 13:-Arrhenius Plot (uncatalysed)****Figure 14:- Arrhenius Plot (catalysed)**

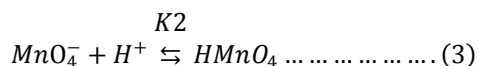
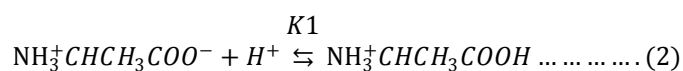
On the basis of the kinetic results are other evidences the following reaction mechanism is suggested from first stage process only. It is similar to the mechanism proposed by other workers for other amino acids.

Mechanism :-For catalysed pathway(In presence of NaLS,Catalyst)

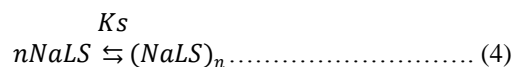
Sodium lauryl sulphate is an anionic surfactant. The reaction rate has been found to be substantially increased with increase in the effective concentration of NaLS. The reaction mechanism for surfactant catalysed reaction may be proposed on the basis of similar available work^{24,37} assuming formation of substrate-surfactant complex in the initial step, which is purely a physical catalysis and there is no covalent type of bond formation take place.



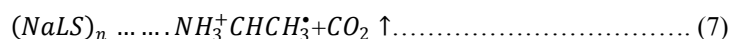
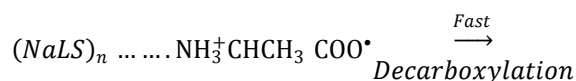
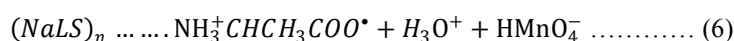
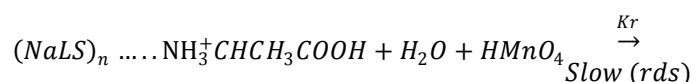
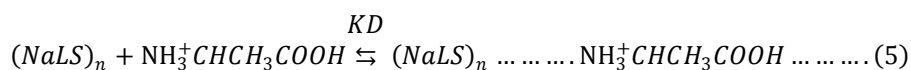
Zwitter Ion (Polar)

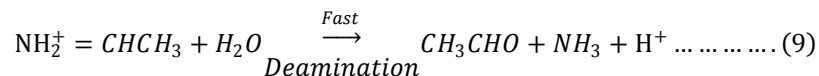
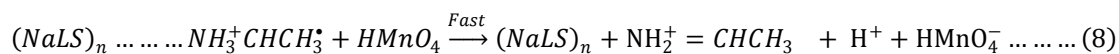


An Active Oxidizing species



Monomers Micelles





By applying the law of mass action to the steps 2 to 5, following step is generated;

(a) For step 2,

$$[NH_3^+CHCH_3COOH] = K_1[NH_3^+CHCH_3COO^-][H^+] \dots \dots (10)$$

(b) For step 3,

$$[HMnO_4] = \frac{K_2[H^+][MnO_4^-]}{1 + K_2[H^+]} \dots \dots (11)$$

(c) For step 4,

$$K_s = \frac{[NaLS]_n}{[n NaLS]} \dots \dots (12)$$

$$K_s[n NaLS] = [NaLS]_n \dots \dots (13)$$

(d) For step 5,

$$K_D = \frac{[(NaLS)_n \dots \dots NH_3^+CHCH_3COOH]}{[NaLS]_n[NH_3^+CHCH_3COOH]} \dots \dots (14)$$

$$[(NaLS)_n \dots \dots NH_3^+CHCH_3COOH] = K_D[(NaLS)_n][NH_3^+CHCH_3COOH] \dots \dots (15)$$

(e) For step 6,

$$\frac{-d[MnO_4^-]}{dt} = k_r[(NaLS)_n \dots \dots NH_3^+CHCH_3COOH][H_2O][HMnO_4] \dots \dots (16)$$

Substituting the values of $[HMnO_4]$ from step (11) and of $[(NaLS)_n \dots \dots NH_3^+CHCH_3COOH]$ from step (15) to step 16.

$$\frac{-d[MnO_4^-]}{dt} = \frac{k_r K_D K_2 [(NaLS)_n] [NH_3^+CHCH_3COOH] [H^+] [MnO_4^-] [H_2O]}{1 + K_2 [H^+]} \dots \dots \dots (17)$$

In this step substituting the values of $(NaLS)_n$ from step,(13) and $[NH_3^+CHCH_3COOH]$ from step (10)

$$\frac{-d[MnO_4^-]}{dt} = \frac{k_r K_D K_5 K_1 K_2 [nNaLS] [NH_3^+CHCH_3COO^-] [H^+]^2 [MnO_4^-] [H_2O]}{1 + K_2 [H^+]} \dots \dots \dots (18)$$

$$\frac{-d[MnO_4^-]}{dt} = k [NH_3^+CHCH_3COO^-] [MnO_4^-] \dots \dots \dots (19)$$

Where $k = \frac{k_r K_D K_5 K_1 K_2 [nNaLS] [H^+]^2 [H_2O]}{1 + K_2 [H^+]}$

Details regarding occurrence of the two stages cannot be furnished at present. It might be assumed that the second stages are probably due to the creation of optimum concentration of some product of due to the autocatalysis as suggested by Levitt and coworkers³⁸.

CONCLUSION

The order of reaction has been confirmed by different methods. The total order of reaction was found three i.e; one with respect to each L-alanine, permanganate and sodium lauryl sulphate respectively.

On the basis of kinetic results and observations it has been confirmed that oxidation of L-alanine is catalysed by H^+ ion and the reaction rate also enhanced in the presence of micelles. On the basis of activation parameters like energy of activation and negative values of entropy of activation, it has been suggest that the studied reaction comes under the category of slow reactions.

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SUMMARY TABLES WITH THEIR CAPTIONS**SUMMARY TABLE -1**

Dependence of Rate on Oxidant Concentration

$[H^+] = 1 \text{ mol dm}^{-3}$

$[NaLS] = 1 \times 10^{-4} \text{ mol dm}^{-3}$

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

Temp. = 303K

S.no.	$[KMnO_4] \times 10^{-3} \text{ M}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$
		Integration	Graphical	Integration	Graphical
1	0.75	2.3280	2.2957	4.8307	5.3832
2	1.00	2.4588	2.3637	4.4836	4.5196
3	1.25	2.6086	2.6801	4.3784	4.5744
4	1.50	2.2593	2.0842	4.9505	3.3558

SUMMARY TABLE -2

Dependence of Rate on substrate concentration (uncatalysed)

$[KMnO_4] = 1 \times 10^{-3} \text{ mol dm}^{-3}$

$[NaLS] = 1 \times 10^{-4} \text{ mol dm}^{-3}$

$[H_2SO_4] = 1 \text{ mol dm}^{-3}$

Temp. = 303K

[L-alanine] M	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$
	theoretical	graphical	least sq.	theoretical	graphical	least sq.
0.1	1.6741	1.8096	1.8096	2.6717	2.5952	2.5952
0.2	3.1926	3.2346	3.2346	5.3217	5.2683	5.2683
0.3	4.7567	4.7338	4.7338	7.4719	7.2899	7.2899
0.4	6.0256	6.0629	6.0629	10.1190	10.1592	10.1592
0.5	7.6399	7.9321	7.9321	12.5268	11.4788	11.4788

SUMMARY TABLE -3

Dependence of Rate on Substrate Concentration (catalysed)

$[KMnO_4] = 1 \times 10^{-3} \text{ mol dm}^{-3}$

$[NaLS] = 1 \times 10^{-4} \text{ mol dm}^{-3}$

$[H_2SO_4] = 1 \text{ mol dm}^{-3}$

Temp. = 303K

[L-alanine] M	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$
	theoretical	graphical	least sq.	theoretical	graphical	least sq.
0.1	2.4588	2.3824	2.3637	4.4933	4.5196	4.5196
0.2	4.9508	4.9569	4.9573	8.9193	8.9282	8.3903
0.3	7.5650	7.2868	7.2228	13.5519	13.7978	13.7978
0.4	10.0570	10.0628	10.0645	17.8417	18.3043	18.3043
0.5	12.5672	12.5616	12.5533	22.4100	22.3486	22.3486

SUMMARY TABLE -4

Dependence of Rate on Catalyst Concentration.(Figure-7)

$$[H^+] = 1 \text{ mol dm}^{-3}$$

$$[KMnO_4] = 1 \times 10^{-3} \text{ mol dm}^{-3}$$

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

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

$[NLS \times 10^{-4}]$ mol dm^{-3}	$k_1 \times 10^{-3} \text{ min}^{-1}$	k_c	$k_1' \times 10^{-3} \text{ min}^{-1}$	k_c'
uncatalysed	1.67		2.67	
1.0	2.45	7.8885	4.48	18.1361
2.0	3.23	7.8308	6.45	18.9247
3.0	4.02	7.8372	8.081	18.0381
4.0	4.54	7.1958	10.23	18.9244
5.0	5.36	7.3916	12.10	18.8726
AVERAGE		7.6288		18.5792

SUMMARY TABLE -5Dependence of Rate on sulphuric acid concentration $[H^+]$

$$[KMnO_4] = 1 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[NaLS] = 1 \times 10^{-4} \text{ mol dm}^{-3}$$

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

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

S.No.	$[H^+] \text{ mol dm}^{-3}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1' \times 10^{-3} \text{ min}^{-1}$
1	2.0	2.45	4.48
2	3.0	3.67	5.89
3	4.0	4.55	7.67
4	5.0	5.87	9.33
5	6.0	6.87	13.76

SUMMARY TABLE -6

$$[KMnO_4] = 1 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[NaLS] = 1 \times 10^{-4} \text{ mol dm}^{-3}$$

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

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

s.no.	correlation	figure	parameters	1 st stage (slope values)	2 nd stage (slope values)
	Zucker-Hammett Plots				
1.	$\log k \text{ Vs } H_0$	Figure 9	slope	0.2320	0.2473
2.	$\log k \text{ Vs } \log[H^+]$	Figure 10	slope	0.9285	0.9632
	Bunnett Plot				
3.	$\log k + H_0 \text{ Vs } \log a_{H_2O}$	Figure 11	ω -slope	8.1761	8.3395
	Bunnett-Olsen Plot				
4.	$\log k + H_0 \text{ Vs } H_0 + \log[H^+]$	Figure 12	ϕ -slope	0.9857	0.9968

SUMMARY TABLE -7

Dependence of rate on Temperature

[L-alanine] = 0.1 mol dm⁻³[KMnO₄] = 1x10⁻³ mol dm⁻³[NaLS] = 1x10⁻⁴ mol dm⁻³[H₂SO₄] = 1 mol dm⁻³

S.No	Temperature (K)	For uncatalysed	For uncatalysed	For catalysed	For catalysed
		$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1' \times 10^{-3} \text{ min}^{-1}$	$k_1 \times 10^{-3} \text{ min}^{-1}$	$k_1' \times 10^{-3} \text{ min}^{-1}$
1.	303	1.67	2.67	2.45	4.48
2.	308	2.07	5.14	3.23	7.88
3.	313	4.33	7.03	5.24	9.56
4.	318	5.34	14.22	7.54	16.57
	Temperature Range(K)	Temperature coefficient for k_1	Temperature coefficient for k_1'	Temperature coefficient for k_1	Temperature coefficient for k_1'
1.	303-313	2.5928	2.6329	2.1310	2.1322
2.	318-328	2.5797	2.7665	2.3343	2.1027

SUMMARY TABLE -8

Various thermodynamic Parameters for uncatalysed and catalysed reactions:-

[L-alanine] = 0.1 mol dm⁻³[KMnO₄] = 1x10⁻³ mol dm⁻³[H₂SO₄] = 1 mol dm⁻³

Uncatalysed(Without NaLS)				
Parameters	For Ist Stage		For II Stage	
	Calculated	Graphical	Calculated	Graphical
$\Delta E_a(\text{KCal mol}^{-1})$	17.8939	16.1222	18.1825	20.3353
$P_z(\text{dm}^3 \text{mol}^{-1} \text{ min}^{-1})$	1.49×10^{13}	7.78×10^{11}	3.86×10^{13}	1.39×10^{15}
$\Delta S(\text{KCal}^{-1} \text{mol}^{-1})$	-12.9528	-12.9586	-12.7480	-12.7409
$\Delta H(\text{KCal mol}^{-1})$	17.2940	15.5223	17.5825	19.7353
$\Delta G(\text{KCal mol}^{-1})$	3.9419	3.9419	3.8802	3.8802
Catalysed(1×10^{-4} mol dm ⁻³ NaLS)				
Parameters	For Ist Stage		For II Stage	
	Calculated	Graphical	Calculated	Graphical
$\Delta E_a(\text{KCal mol}^{-1})$	14.2105	14.6615	14.2205	15.7028
$P_z(\text{dm}^3 \text{mol}^{-1} \text{ min}^{-1})$	4.7×10^{10}	1.00×10^{11}	8.79×10^{10}	1.04×10^{12}
$\Delta S(\text{KCal}^{-1} \text{mol}^{-1})$	-12.7969	-12.7954	-12.5360	-12.5311
$\Delta H(\text{KCal mol}^{-1})$	13.6105	14.0616	13.6206	15.1029
$\Delta G(\text{KCal mol}^{-1})$	3.8910	3.8910	3.8120	3.8120