IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 7, Issue 5 Ver. I. (May. 2014), PP 45-53
www.iosrjournals.org

Kinetic studies in the surfactant catalyzed oxidative deamination and decarboxylation of L-Valine by permanganate in sulphuric acid medium

Nameeta S. Bende [1]*, Kirti Yadav [1] ,Vijay R.Chourey [1] and Anand G.Fadnis [2]
Department of Chemisrty,[1]Govt. Holkar Autonomous Science College,A.B.Road,Indore-17(M.P),India
[2]SCM,institute of professional studies,70 Ganesh Ganj,Indore(M.P.)India

Abstract: *A Kinetic investigation of oxidation of L-Valine by acidic permanganate in presence of surfactant as catalyst has been carried out spectrophotometrically. The reaction is double stage process in which first stage is followed by second fast stage process. The rate shows a first order dependence on each oxidant and substrate. 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, Gibb's free energy and probability factor. The possible effect of the increasing ionic strength on the rate was also analyzed and mechanism in concordance with the experimental findings is proposed for catalytic pathway.*

Keywords*: Surfactant, Catalysis, Rate constant, Kinetic parameters, Ionic strength, Oxidation, Spectrophotometer.*

I. Introduction

A great deal of work has been done on the oxidation of amino acids by permanganate ion in varieties of media under different conditions[1-6]. 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 miceller catalysed oxidation of L-valine 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.

Oxidation of valine by N-Bromophthalimide in presence of chlorocomplex of Pd(II),as Iridium (III) Chloride and Ruthenium(III) Chloride homogenous catalyst studied by Singh et al[7,8,9].

Deamination and decarboxylation in the chromium(III)-catalysed oxidation of L-valine by alkaline permanganate and analysis of chromium(III) in microscopic amounts by a kinetic method was studied by Kulkarni and coworkers[10].Kinetic and mechanistic studies of oxidation of glycine and valine by N-bromosuccinimide using chloro complex of Rh(III) in its nano-concentration range as homogeneous catalyst investigated by Singh et al[11].Kinetics and mechanisms of the permanganate oxidation of L-valine in neutral aqueous solutions was studied by Perez-benito et al[12].

Bahrami[13] had investigated kinetics and mechanism of the oxidation of L-amino-n-butyric acid in moderately concentrated sulfuric acid medium.Studies in the kinetics of oxidation of some amino acids like glycine, alanine, phenylalanine, serine, threonine, aspartic and glutamic acid by $KMnO_4$ in a moderately concentrated H_2SO_4 medium in the presence and absence of Ag^+ has been carried out by number of workers[14-15].

Literature survey reveals that permanganate ions are widely used as oxidizing agent in synthetic and analytical chemistry[16-17].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 reductant[18].Glycine being a simplest amino acids and mild reductant requires powerful oxidants for studying its kinetic behavior[19] due to this permanganate is assigned as oxidant in the present investigation.

Amphiphilies are chemical compounds having dual affinity for water water and oil. They have distinct nonpolar(lipophilic or hydrophobic) and polar(liophobic or hydrophilic) 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 are termed as SURFace ACTive AgeNTS as SURFACTANTS[20,21,22].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. Mechanistic investigations on the oxidation of L -valine by diperiodatocuprate(III) in aqueous alkaline medium was carried out by Deganatti et al[23] while S Dubey and coworker[24] studied the oxidation of L-glutamine by Vanadium(V) in presence of CTAB. Gaur[25] 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 glyine following studied has been carried out.In the present work an anionic surfactant i.e. Sodium Lauryl Sulphate is used as miceller catalyst.

II. Experiment

1.Material and method

L-valine and potassium permanganate used were from AnalaR (BDH).All other reagents used were of AnalaR and G.R. grade. Permanganate solution was prepared and tested as given by Vogel[5]. 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 ± 0.1^0C. The reactions were usually followed up to 70% of completion. The reaction was initiated by adding requisite amount of pre equilibrated solution of permanganate to an equilibrated mixture of substrate (L-valine),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 was 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 $<2^0$C) in the optic cell. The values of the absorbance due to unreacted permanganate at given times were read out directly from the spectrophotometer.

2.Kinetic studies

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 determined[26].

III. Result and Discussion

Nature of reaction:-

Though the reaction have studied by number of investigators 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-valine. In the present study, it has been observed that the oxidation of L-valine 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_1^1) indicates linearity of both the stages.

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 L-valine in both the stages. They are found to be fairly constant. It 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-1)

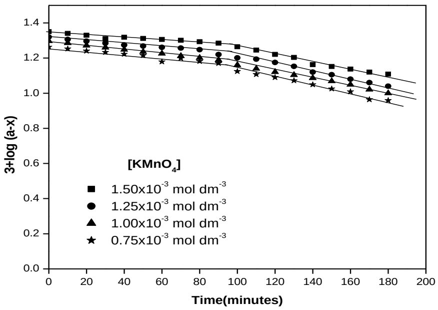

Figure 1:-variation of [permanganate]

Summary Table -1

Dependence of Rate on Oxidant Concentration (Figure-2)

$[H_2SO_4]$ = 2 mol dm $^{-3}$ [L-Valine] = 0.01 mol dm $^{-3}$

[NaLS] =1x10^{-4} mol dm $^{-3}$ Temp. = 303K

[KMnO4 x10^{-3}] mol dm $^{-3}$	k_1 x10^{-3} min^{-1} For I stage		k_1^1 x10^{-3} min^{-1} For II stage	
	By Integration	By Graphical	By Integration	By Graphical
0.75	2.3839	1.3856	4.9721	4.6635
1.00	2.7625	2.1379	4.4799	4.9284
1.25	2.5207	2.7492	4.0387	4.5056
1.50	2.7625	2.3755	4.4799	4.9848

2. Substrate variation

The reaction was studied at different concentrations of L-valine with and without addition of surfactant within the range 0.1to 0.5mol dm^{-3}concentrations. The plot of velocity constant "k" against L-valine concentration is found linear showing the first order dependency of the rate on L-valine 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(Figure-2) and 3(Figure-3).The graph between 1/k and 1/[L-valine] i.e. Michaelis Menten plot,[Figure 4(uncatalysed)],[Figure 5(catalysed)]have straight lines showing that the reaction is first order with respect to each stages and also confirms that there is no any intermediate complex formation, if there any complex is formed, its formation constant should be very small.

Summary Table -2

Dependence of rate on substrate concentration (uncatalysed) (Figure-3)

$[KMnO_4]$ = 1x10^{-3} mol dm^{-3} $[H_2SO_4]$ = 2 mol dm^{-3}

Temp. = 303K

[L-Valine] mol dm^{-3}	k_1 x10^{-3} min^{-1} For I stage			k_1^1x10^{-3} min^{-1} For II stage		
	By equation	By Graphical	By least square	By equation	By Graphical	By least square
0.010	2.0341	2.7625	2.0865	3.6681	3.7293	3.7293
0.015	3.0264	3.0777	3.0777	5.3490	5.6117	5.6117
0.020	3.7891	3.8837	3.8837	7.2019	7.2025	7.2025
0.025	4.8327	4.2353	4.2353	8.8855	8.8132	8.8132
0.030	5.5825	5.4254	5.4254	10.4514	10.5091	10.5091
0.035	6.4518	6.4171	6.4171	12.1922	12.5790	12.5790
0.040	7.3520	7.2295	7.2295	13.7883	13.8545	13.8545

Summary Table -3

Dependence of rate on substrate concentration (catalysed) (Figure 4)

$[KMnO_4]$ = 1x10^{-3} mol dm^{-3} $[H_2SO_4]$ = 2 mol dm^{-3}

[NaLS] = 1x10^{-4} mol dm^{-3} Temp. = 303K

[L-Valine] mol dm^{-3}	k_1 x10^{-3} min^{-1} For I stage			k_1^1x10^{-3} min^{-1} For II stage		
	By equation	By Graphical	By least square	By equation	By Graphical	By least square
0.010	2.7625	2.7625	2.7493	4.4799	4.5457	4.5057
0.015	4.1426	4.1519	4.1519	6.7028	6.6911	6.6800
0.020	5.5386	5.4083	5.4083	8.9449	9.1091	9.0808
0.025	6.9011	6.9353	6.9353	11.0519	11.2533	11.2533
0.030	8.3228	8.3444	8.3444	13.3841	13.4617	13.4617
0.035	9.5879	9.5273	9.5273	15.6099	15.7404	15.7404
0.040	11.1116	11.0345	11.0345	17.7045	17.5907	17.5907

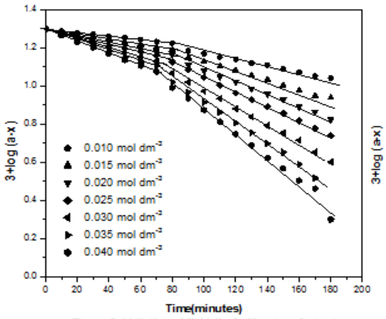

Figure 2-Vatiation of [L-Valine]without surfactant

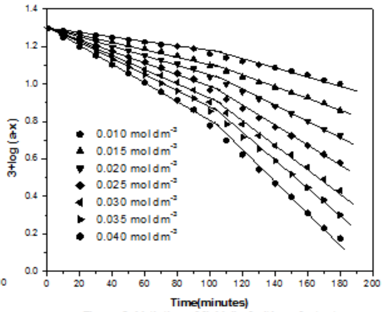

Figure 3:-Vatiation of [L-Valine] with surfactant

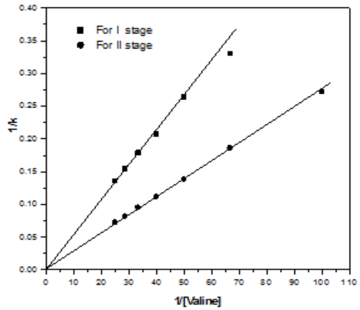

Figure 4-Michaelis Menten plot(uncatalysed)

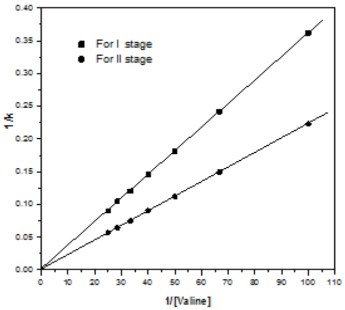

Figure 5:- Michaelis Menten plot(catalysed)

3. Surfactant (NaLS) variation

The reaction was also studied at different concentrations of the anionic surfactant Sodium Lauryl Sulphate (NaLS) within the range 1 x 10^{-4} to 5 x 10^{-4} mol dm^{-3} (Table – 4). It has been observed that the rate of reaction increases with surfactant concentration showing catalytic function of surfactant in the given reaction(Figure-6).The catalytic constant $\mathbf{k_c}$ was determined by the equation are reported in the Table-4 are fairly constant confirming its catalytic action.

$$\mathbf{k_c} = \frac{\mathbf{k_{catalysed}} - \mathbf{k_{uncatalysed}}}{[\mathbf{catalyst}]}$$

The reaction rate have been found increase with the increase in the NaLS concentration i.e.from 1x 10^{-4} M to 5x10^{-4} mol dm^{-3} .The reported CMC of NaLS is 8.1x10^{-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 premicellar catalysis[27].

In the theoretical treatment for pre-micellar catalysis a graph is plotted between n=log[k_{obs}-k_0]/log[k_m-k_{obs}] and log[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-7)The above plot is a good straight line with slope value 1.35 and 1.28 for first and second stage processes respectively.Both values are in between the expected value for premicellar catalysis i.e.between 1 to 6.Lower value suggest the premicellar 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.

Summary Table -4

Dependence of rate on catalyst concentration.

[H_2SO_4] = 2 mol dm^{-3} [L-Valine] = 0.01mol dm^{-3}

[$KMnO_4$] = 1x10^{-3} mol dm^{-3} Temp. = 303K

[NLSx10^{-4}]	k_1x10^{-3} min^{-1}	k_c X 10^{-3} Litre $mole^{-1}$ min^{-1}	$k_1^{\prime}$x 10^{-3} min^{-1}	$k_c^{\prime}$ X 10^{-3} Litre $mole^{-1}$ min^{-1}
uncatalysed	2.0300		3.6700	
1x10^{-4}	2.7625	7.3252	4.4799	8.0994
2x10^{-4}	3.4961	7.3307	5.2628	7.9640
3x10^{-4}	4.4026	7.9089	6.0900	8.0668
4x10^{-4}	5.0699	7.5998	6.8141	7.8604
5x10^{-4}	5.7315	7.4031	7.5667	7.7935
Average		**7.5136**		**7.9568**

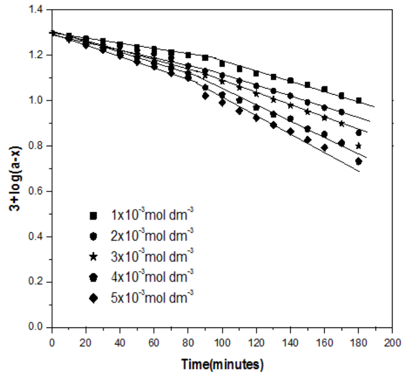

Figure-6:-variation of surfactant concentration

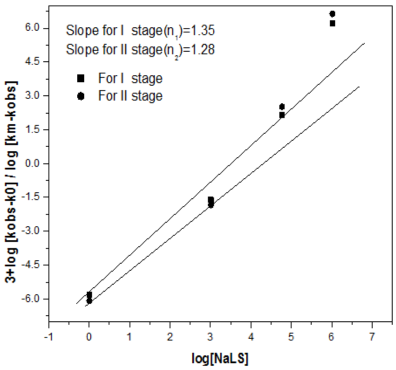

Figure-7:-Piszkiewicz Plot

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-valine in both stages (Table 5). It is most probably due to the protonation of the oxidant in accordance with the equilibrium $MnO_4^- + H^+ \leftrightarrows HMnO_4$ supported by the spectral studies[28]. 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 - Hammett[29] 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)(Figure-8 and Figure-9).In the view of these departures from ideal slope value, Bunnett[30] and Bunnett Olsen[31] hypothesis were tested(Figure-10 and Figure-11). 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_o and log a_{H_2O} values corresponding to given acid concentration have been collected from Paul and Long[32] and Bunnett respectively[3] .

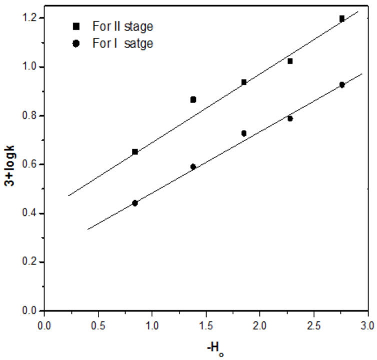

Figure-8:-Zucker-Hammett Plot-1

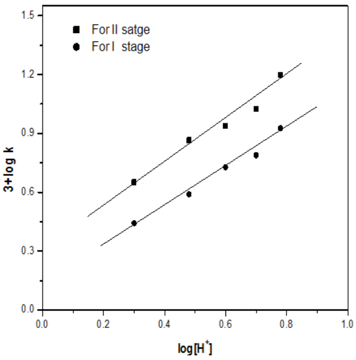

Figure-9:- Zucker-Hammett Plot-2

Summary Table -5

Dependence of Rate on sulphuric acid concentration [H$^+$]

[NaLS] = 1x10^{-4} mol dm^{-3} [L-Valine] = 0.01mol dm^{-3}

[KMnO$_4$] = 1x10^{-3} mol dm^{-3} Temp. = 303K

S.No.	[H$^+$] mol dm^{-3}	k_1 X 10^{-3} min^{-1}	k_1^1X 10^{-3} min^{-1}
1	2.0	2.76	4.47
2	3.0	3.89	7.34
3	4.0	5.34	8.67
4	5.0	6.14	10.56
5	6.0	8.45	15.76

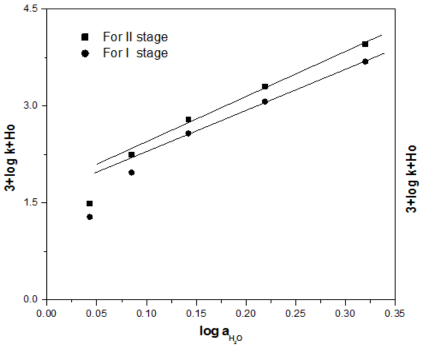

Figure-10:-Bunnett plot

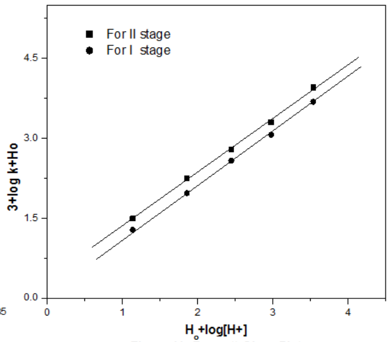

Figure-11:-Bunnett-Olsen Plot

Summary Table -6

Slope values from different hypotheses plots

[NaLS] = 1x10^{-4} mol dm^{-3} [L-Valine] = 0.01mol dm^{-3}
[KMnO$_4$] = 1x10^{-3} mol dm^{-3} Temp. = 303K

correlation	figure	parameters	1st stage (slope values)	2nd stage (slope values)
Zucker-Hammett Plots				
log k Vs H_o	Figure-6. 9	slope	0.2473	0.2649
(log k) Vs (log[H^+])	Figure-6.10	slope	0.9779	1.0469
Bunnett Plot				
(log k+ H_o)Vs(log a_{H_2O})	Figure-6.11	ω-slope	8.2995	8.4229
Bunnett-Olsen Plot				
(log k+ H_o)Vs (H_o+log[H^+])	Figure-6.12	ϕ-slope	0.9974	1.0115

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 surfactant[33]. The slope value of a plot between log k and 1/T i.e. Arrhenius plot has also been used to determine activation energy.

The temperature coefficients for two different temperature range, have been given for first and second stage process (k_1 & k_1^1) for uncatalysed and catalysed reaction in Table-7.

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 reaction [34].

Summary Table -7

Dependence of rate on Temperature

[L-Valine] = 0.01 mol dm^{-3} [NaLS] = 1x10^{-4} mol dm^{-3}
[KMnO$_4$] =1x10^{-3} mol dm $^{-3}$ [H$_2$SO$_4$] = 2 mol dm^{-3}

Temperature (K)	For uncatalysed		For catalysed	
	For I stage k_1 X 10^{-3} min^{-1}	For II stage k_1^1 X10^{-3} min^{-1}	For I stage k_1 X10^{-3} min^{-1}	For II stage k_1^1 X10^{-3} min^{-1}
303	2.03	3.67	2.76	4.47
308	3.44	5.64	3.78	6.98
313	4.32	7.77	5.78	9.12
318	6.91	12.76	7.37	16.45
Temperature Range(K)	Temperature coefficient for I stage	Temperature coefficient for II stage	Temperature coefficient for I stage	Temperature coefficient for II stage
303-313	2.13	2.11	2.09	2.03
318-328	2.00	2.26	1.94	2.35

Summary Table -8

Various thermodynamic Parameters for uncatalysed and catalysed reactions:-

[L-Valine] = 0.01 mol dm^{-3} Temp=303K
$[KMnO_4]$ =1x10^{-3} mol dm^{-3} $[H_2SO_4]$ =2.0 mol dm^{-3}

Uncatalysed (Zero NaLS)				
Parameters	For Ist Stage		For II Stage	
	Calculated	Graphical	Calculated	Graphical
$\Delta Ea^{\#}$ (K Cal mol^{-1})	14.2011	14.9021	14.0876	15.4790
$Pz^{\#}$ (dm^3mol^{-1} min^{-1})	$3.85x10^{10}$	$1.23x10^{11}$	$5.76x10^{10}$	$5.86x10^{11}$
$\Delta S^{\#}$ (K $Cal^{-1}mol^{-1}$)	-12.8802	-12.8779	-12.6234	-12.6188
$\Delta H^{\#}$ (K Cal mol^{-1})	13.6011	14.3021	13.4876	14.8791
$\Delta G^{\#}$ (K Cal mol^{-1})	3.9162	3.9162	3.8383	3.8383

Catalysed (1x10-4 mol dm-3NaLS)				
Parameters	For Ist Stage		For II Stage	
	Calculated	Graphical	Calculated	Graphical
$\Delta Ea^{\#}$ (K Cal mol^{-1})	13.8655	12.8617	13.3510	15.8921
$Pz^{\#}$ (dm^3mol^{-1} min^{-1})	$2.99x10^{10}$	$5.62x10^{9}$	$2.06x10^{10}$	$1.42x10^{12}$
$\Delta S^{\#}$ (K $Cal^{-1}mol^{-1}$)	-12.7475	-12.7508	-12.5392	-12.5308
$\Delta H^{\#}$ (K Cal mol^{-1})	13.2656	12.2617	12.7510	15.2922
$\Delta G^{\#}$ (K Cal mol^{-1})	3.8757	3.8757	3.8121	3.8121

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 NO_3^{2-} >SO_4^{2-} >CH_3COO^- and
For Cations Zn^{2+} >Mg^{2+} >NH_4^+ >Na^+ >K^+
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 Isoveleraldehyde, 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-dinitophenylhydrazine(w/v) in 2M HCl were then sprayed over TLC plate. Yellow spots were found confirming Isoveleraldehyde as a reaction product [35].

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 Nesseler'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 polymerization[19,36] .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-valine were allowed to stand at 35°C for a sufficiently log time(36 hours).The amount of unreacted permanganate was estimated iodometrically. It has been found that the five molecules of L-valine recognise two molecules of permanganate for complete oxidation. On the basis of literature available[18] and the work performed, the catalysed reaction is proceeds as follows :

$$5NH_2CH(CH_3)_2CHCOOH + 2MnO_4^- + 6H^+ \xrightarrow{NaLS} 5CH(CH_3)_2\,CHCHO + 3H_2O + 2Mn^{2+} + 5CO_2 + 5NH_3$$

The above stoichiometric equation is consistent with the results of product analysed.
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[25,37] 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.

$$\mathrm{NH_2CH(CH_3)_2CHCOOH \leftrightarrows NH_3^+CH(CH_3)_2CHCOO^- \ldots\ldots\ldots\ldots\ldots.(1)}$$

$$\mathrm{K1}$$

$$\mathrm{NH_3^+CH(CH_3)_2CHCOO^- + H^+ \leftrightarrows NH_3^+CH(CH_3)_2CHCOOH \ldots\ldots\ldots\ldots.(2)}$$

$$\mathrm{K2}$$

$$\mathrm{MnO_4^- + H^+ \leftrightarrows HMnO_4 \ldots\ldots\ldots\ldots\ldots\ldots.(3)}$$

An Active Oxidizing species

$$\mathrm{Ks}$$

$$\mathrm{nNaLS \leftrightarrows (NaLS)_n} \text{………………………. (4)}$$

Monomers Micelles

$$\mathrm{KD}$$

$$\mathrm{(NaLS)_n + NH_3^+CH(CH_3)_2CHCOOH \leftrightarrows (NaLS)_n \ldots\ldots\ldots.NH_3^+CH(CH_3)_2CHCOOH \ldots\ldots\ldots.(5)}$$

$$\mathrm{(NaLS)_n \ldots..NH_3^+CH(CH_3)_2CHCOOH + H_2O + HMnO_4 \xrightarrow[\text{Slow (rds)}]{\text{Kr}}}$$

$$\mathrm{(NaLS)_n \ldots\ldots.NH_3^+CH(CH_3)_2CHCOO^\bullet + H_3O^+ + HMnO_4^-} \text{ ……….. ....(6)}$$

$$\mathrm{(NaLS)_n \ldots\ldots.NH_3^+CH(CH_3)_2CHCOO^\bullet \xrightarrow[\text{Decarboxylation}]{\text{Fast}}}$$

$$\mathrm{(NaLS)_n \ldots\ldots.NH_3^+CH(CH_3)_2CH^\bullet + CO_2 \uparrow} \text{…………….(7)}$$

$$\mathrm{(NaLS)_n \ldots\ldots\ldots NH_3^+CH(CH_3)_2CH^\bullet + HMnO_4 \xrightarrow{\text{Fast}}}$$

$$\mathrm{(NaLS)_n + NH_2^+ = CH(CH_3)_2CH + H^+ + HMnO_4^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(8)}$$

$$\mathrm{NH_2^+ = CH(CH_3)_2CH + H_2O \xrightarrow[\text{Deamination}]{\text{Fast}} CH(CH_3)_2CHCHO + NH_3 + H^+ \ldots\ldots\ldots\ldots.(9)}$$

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

$$\mathrm{[NH_3^+CH(CH_3)_2CHCOOH] = K_1[NH_3^+CH(CH_3)_2CHCOO^-][H^+] \ldots\ldots\ldots\ldots\ldots..(10)}$$

(b)For step 3,

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

(c)For step 4,

$$\mathrm{K_s = \frac{[NaLS]_n}{[n\ NaLS]} \ldots\ldots\ldots\ldots\ldots\ldots..(12)}$$

$$\mathrm{K_s[n\ NaLS] = [NaLS]_n \ldots\ldots\ldots\ldots.(13)}$$

(d)For step 5,

$$\mathrm{K_D = \frac{[(NaLS)_n \ldots\ldots.NH_3^+CH(CH_3)_2CHCOOH]}{[NaLS_n][NH_3^+CH(CH_3)_2CHCOOH]} \ldots\ldots\ldots\ldots\ldots\ldots.(14)}$$

$$\mathrm{[(NaLS)_n \ldots\ldots.NH_3^+CH(CH_3)_2CHCOOH] = K_D[(NaLS)_n][NH_3^+CH(CH_3)_2CHCOOH] \ldots\ldots\ldots\ldots\ldots\ldots(15)}$$

(e)For step 6,

$$\mathrm{\frac{-d[MnO_4^-]}{dt} = k_r[(NaLS)_n \ldots\ldots.NH_3^+CH(CH_3)_2CHCOOH][H_2O]\ [HMnO_4] \ldots\ldots\ldots\ldots\ldots\ldots\ldots.(16)}$$

Substituting the values of $\mathrm{[HMnO_4]}$ from step (11) and of $\mathrm{[(NaLS)_n \ldots\ldots.NH_3^+CH_2COOH]}$ from step (15) to the step (16)

$$\frac{-\mathrm{d}[\mathrm{MnO_4^-}]}{\mathrm{dt}} = \frac{\mathrm{k_r K_D K_2 [(NaLS)_n]\ [NH_3^+CH(CH_3)_2CHCOOH][H^+][MnO_4^-][H_2O]}}{1 + \mathrm{K_2[H^+]}} \ldots\ldots\ldots\ldots (17)$$

In this step substituting the values of $\mathrm{(NaLS)_n}$ from step (15),(13) and$\mathrm{[NH_3^+CH_2COOH]}$ from step (10)

$$\frac{-\mathrm{d}[\mathrm{MnO_4^-}]}{\mathrm{dt}} = \frac{\mathrm{k_r K_D K_S K_1 K_2\ [nNaLS][NH_3^+CH(CH_3)_2CHCOO^-][H^+]^2[MnO_4^-][H_2O]}}{1 + \mathrm{K_2[H^+]}} \ldots\ldots . (18)$$

$$\frac{-\mathrm{d}[\mathrm{MnO_4^-}]}{\mathrm{dt}} = \mathrm{k[NH_3^+CH(CH_3)_2CHCOO^-]\ [MnO_4^-]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots..\ldots (19)$$

Where $\mathrm{k} = \frac{\mathrm{k_r K_D K_S K_1 K_2\ [nNaLS][H^+]^2[H_2O]}}{1+\mathrm{K_2[H^+]}}$………………………...............…(20)

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 coworkers [38].

IV. 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-valine and permanganate respectively.

On the basis of kinetic results and observations it has been confirmed that oxidation of L-valine 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.

Acknowledgment

One of the author (Nameeta Bende) is thankful to the Principal and Head of the Department (Chemistry) of Govt. Holkar Science College, Indore(M.P.)India for providing necessary laboratory facilities.

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