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Research Article

Kinetic and Mechenistic Study of Surfactant Catalysed Oxidation of L-Valine by Permanganate in Perchloric Acid Medium

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Abstract

A spectrophotometric investigation have been carried out on the miceller catalysed oxidation of L isomer of amino acid by permanganate in perchloric acid medium.Kinetic parameters and activation parameters have been determined.Temperature coefficients were determined by varying temperatures. Salt effects have been also analysed by keeping anion common and varying cation.

Keywords: Micelles, Perchloric acid, Kinetic parameters and Temperature coefficients.

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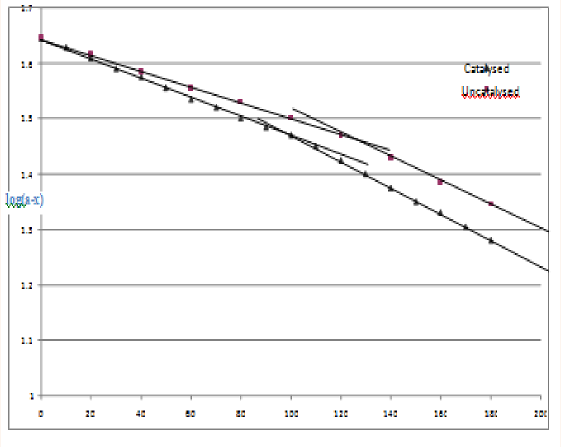

Typical Run of the reaction

Introduction

Oxidation of L isomers of amino acid(L-Valine) by potassium permanganate has been done in presence of miceller i.e.sodium lauryl sulphate in presence of acidic medium which is of perchloric acid. Literature survey reveals that the kinetic investigation of the oxidation of amino acids are important because of their biological significance. The precise understanding of the mechanism of such biological redox reactions help in the synthesis of reaction products. Many of researchers used alkaline medium for oxidation of amino acids.

The ruthenium(III)[1], chromium(III)[2] and Copper(III)[3] catalyzed oxidative deamination and decarboxylation of L-valine by alkaline permanganate were studied by few researchers. Oxidation of L-Asparagine[4] and L-α-amino-n-butyric acid[5] in a Moderately Concentrated Sulfuric Acid Medium were also been studied. Oxidation by permanganate in sulphuric acid medium of different amino acids was also taken in consideration[6-15].

However, miceller effect on oxidation of amino acids have been much less explored, it is therefore proposed to conduct systematic work on the surfactant catalyzed oxidation of L-valine by acidic permanganate.

Experimental

Material and Method

The kinetics of oxidative decarboxylation of L-valine by acidic permanganate in the presence of surfactant (Sodium Lauryl Sulphate - NaLS) have been reported. For finding out the kinetic parameters, the Ostwald's Isolation method was applied**[16]**.

Requisite amount of the solutions of L-valine, Surfactant (NaLS), Perchloric Acid and water (to maintain the total volume constant for all the runs) were taken in black painted glass stopper bottles to avoid any photochemical effect from outside and were thermo stated (of ±0.1°C accuracy) at constant required temperature. A measured amount of permanganate solution at the same temperature was added to the reaction mixture. The reaction mixture was then shaken well. The zero time of the reaction was noted when half of the permanganate solution was added. 2ml of the reaction mixture was withdrawn at known intervals of the time and the reaction was quenched by adding it into known excess of ice cold water in the optical cell. The progress of the reaction was measured in terms of the absorbance spectrophotometrically at 515nm band on CHEMILINE DIGITAL CL 320 Spectrophotometer. The reactions were studied almost upto 60-80% completion.

Results and Discussion

Kinetic studies of the oxidation decarboxylation and deamination of L-valine by Permanganate in Perchloric Acid medium in the presence of surfactant was performed under pseudo first order condition by varying the reactant concentration and keeping with large and excess of the other reactant concentrations.

It has been observed from the plot of logarithm of optical density (a-x) of unreacted Permanganate against time (in minutes), that the oxidation reaction is a double stage process (**Figure 1**).

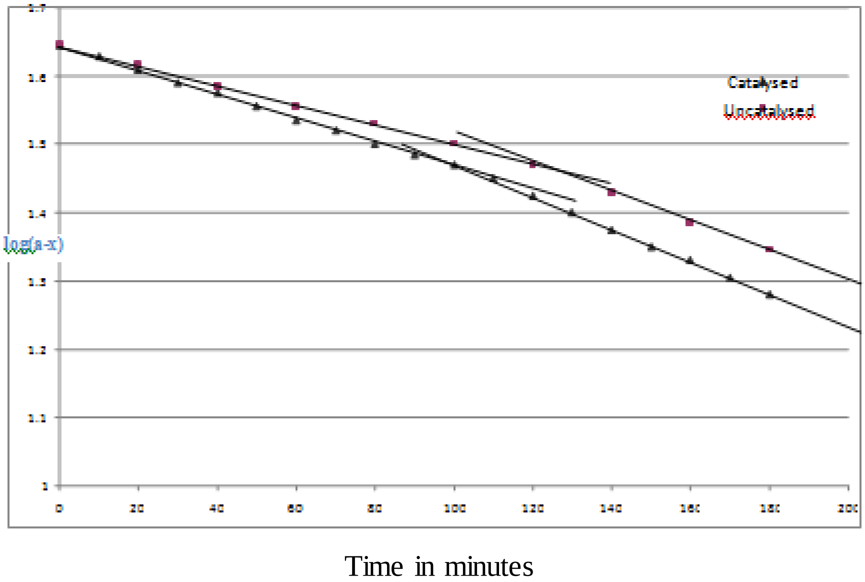

Figure 1 Typical run for the oxidation reaction

Table 1 [$KMnO_4$] Variation

[L-valine] = 0.1M
[NaLS] = $1.0x10^{-5}$M

[$HClO_4$] = 2.0M
Temperature = 308 K

Concentration [$KMnO_4$]	**$k_1 x 10^{-3} min^{-1}$**	**$k_1^{I} x 10^{-3} min^{-1}$**
$1.0x10^{-3}$ M	4.1246	5.6736
$1.25x10^{-3}$ M	4.0072	5.7575
$1.5x10^{-3}$ M	4.1661	5.7575

Order of the reaction with respect to potassium permanganate

The order of reaction with respect to potassium permanganate was determined by varying the potassium permanganate, concentration and keeping the concentration of L-valine, perchloric acid and sodium lauryl sulphate in excess and constant throughout the progress of reaction. The value of pseudo first order rate constant does not after significantly. This confirms that the reaction is first order with respect to $KMnO_4$. From the obtained kinetic data the order has been determined by Ostwald methods under pseudo first order condition.

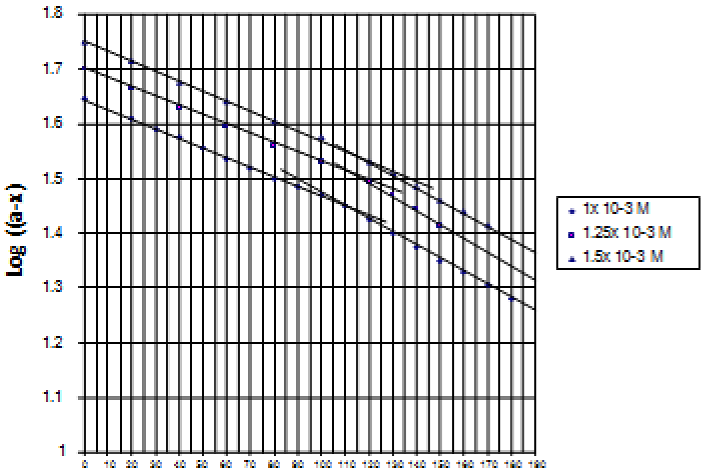

Figure 2 [$KMnO_4$] Variations

Order of reaction with respect to substrate [L-valine] and effect of variation of L-valine concentration

For the determination of order with respect to substrate i.e. L-valine, experiment were performed at 308K with different initial concentration of L-valine , keeping the concentration of other reactant constant. The perusal of these tables shows that the values of pseudo first order rate constant for both the stages increases with the increase in the concentration of L-valine (**Figure 3**).

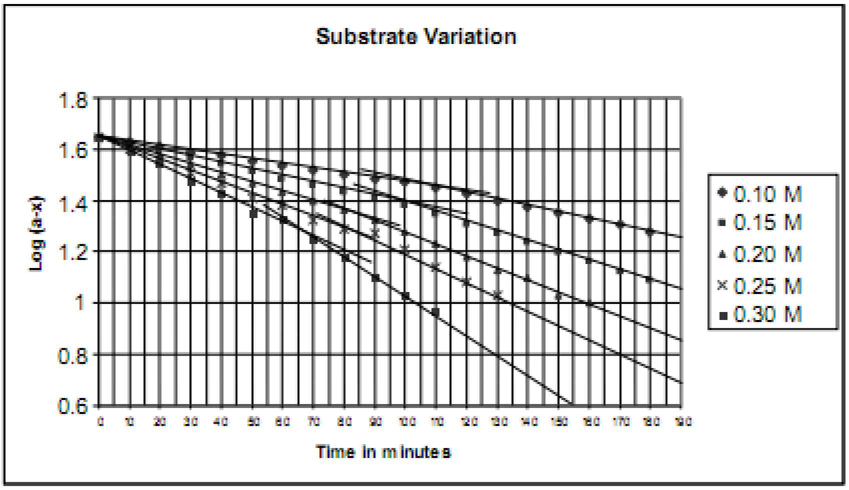

Figure 3 L-valine concentration

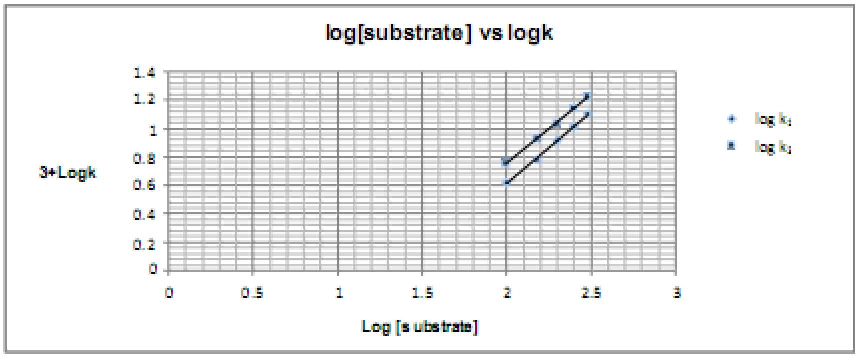

Figure 4 log[substrate] Vs log k

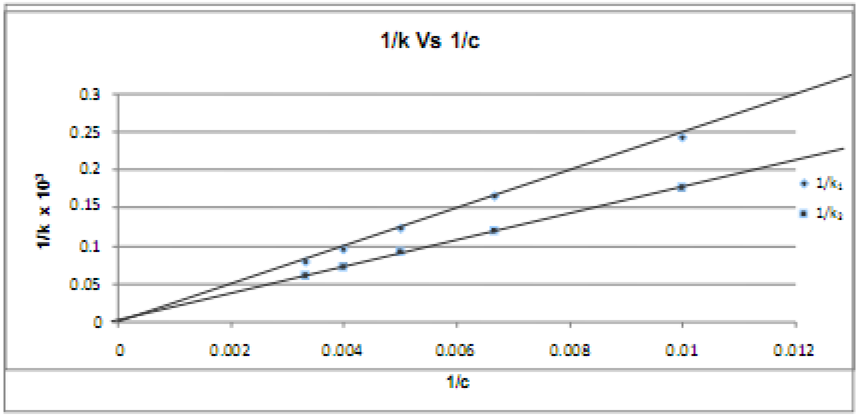

Figure 5 1/k Vs 1/c

Table 2 L- valine variations

$[HClO_4]$ = 2M $[KMnO_4]$=1.0x10^{-3}M		$[NaLS]$ = 1.0x10^{-5}M Temperature = 308 K
Concentration L-valine	**k_1x 10^{-3}min^{-1}**	**k_1^A x 10^{-3}min^{-1}**
0.1M	4.124	5.673
0.15M	6.078	8.383
0.2M	8.170	10.862
0.25M	10.431	13.847
0.3M	12.702	16.600

Order of reaction with respect to surfactant and effect of variation of surfactant concentration

In order to determine the effect of surfactant concentration on the reaction rate, the oxidation reaction have been carried out at various initial concentration of anionic surfactant that is Sodium Lauryl Sulphate (NaLS) by keeping the other reactant constant at given constant temperature.

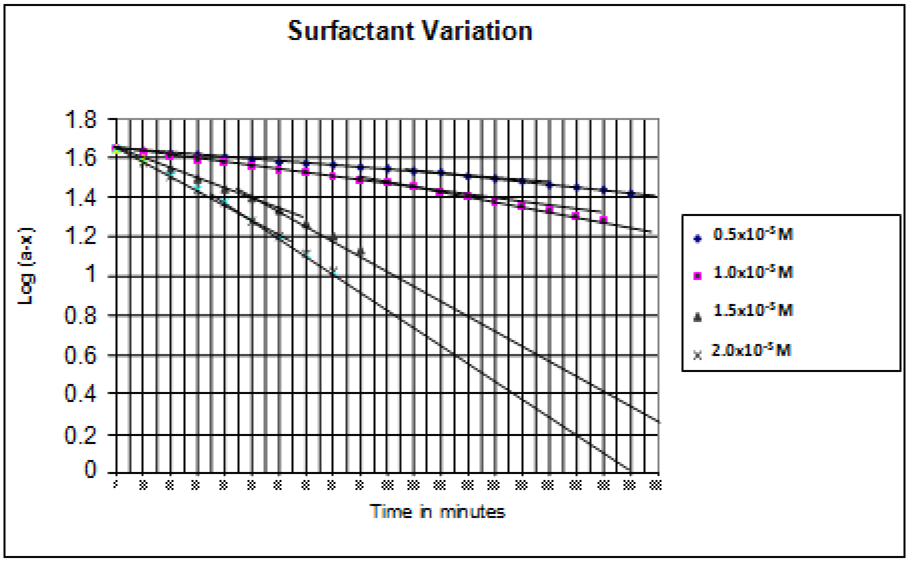

Figure 6 variation of surfactant concentration

Table 3 [NaLS] Variation

[L-valine]=0.1M $[KMnO_4]=1X10^{-3}M$		$[HClO_4]=1X10^{-5}M$ Temperature = 308 K
Concentration [NaLS]	$k_1 x\ 10^{-3} min^{-1}$	$k_1{}^A\ x\ 10^{-3} min^{-1}$
$0.5x10^{-5}$ M	2.3758	3.4200
$1.0x10^{-5}$ M	4.1246	5.6736
$1.5x10^{-5}$ M	5.7750	7.7000
$2.0x10^{-5}$ M	7.5661	10.5145

It is clear from the pseudo first order rate constant for the given concentration range of NaLS increases with the increase of NaLS concentration.

Effect of the Variation of the Concentration of Percholric Acid

The effect of the acid concentration on the reaction rate has been investigated for 2.0M, 2.5M, 3.0M & 3.5M concentration range of the perchloric acid medium. The experimental results obtained on varying the concentrations of perchloric acid, at constant concentration of L-valine and potassium permanganate are summarized and tabulated. The values of 'H_0' are taken from Paul and Long and Bunnet respectively [16-17]. (Figure 7)

In the case of the oxidation of L-valine by potassium permanganate, the two Zucker-Hammett[18-19] relations i.e. (i) the plot of log k_1 against $-H_0$ and (ii) the plot of log k_1 against log $[HClO_4]$, show linear correlations of rate with the acid concentration (Figure 8 & 9). This shows that the reaction is acid catalysed. However, no straight line of Zucker-Hammett plot produces the ideal slope value of unity. Deviation from the ideal slope value of unity confirms that the water molecule involve as proton abstracting agent in the rate determining step. Though it further required for confirmation by applying Bunnet & Bunnet-Olsen linear free energy relationship[16-17].

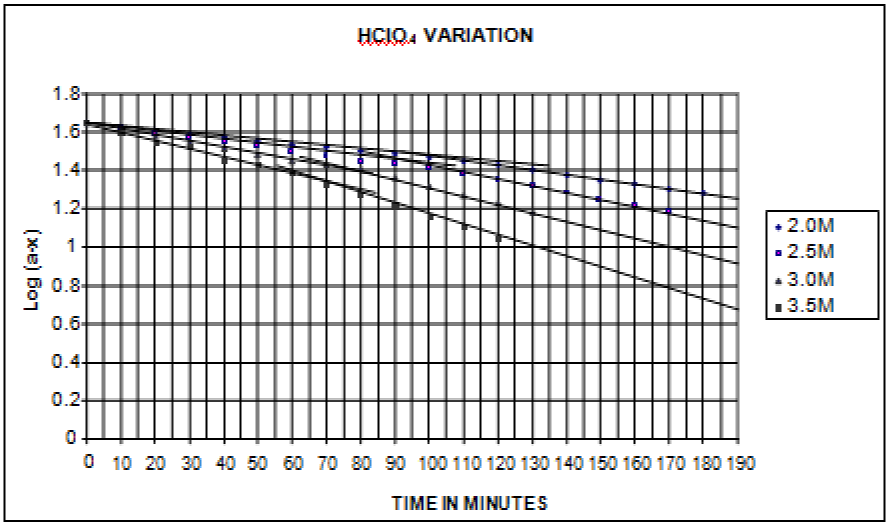

Figure 7 $HClO_4$ Variation

Table 4 $HClO_4$ Variation

[L-valine]=0.1M $[KMnO_4]=1.0x10^{-3}M$				$[NaLS]=1.0x10^{-5}M$ Temperature = 308 K
Concentration $HClO_4$	$-H_0$	Log $[HClO_4]$	k_1x $10^{-3}min^{-1}$	k_1^A x $10^{-3}min^{-1}$
2.0M	-0.78	0.3010	4.1246	5.6736
2.5M	-1.01	0.3979	5.5840	7.8542
3.0M	-1.23	0.4771	7.5661	10.5145
3.5M	-1.47	0.5440	10.4487	12.8328

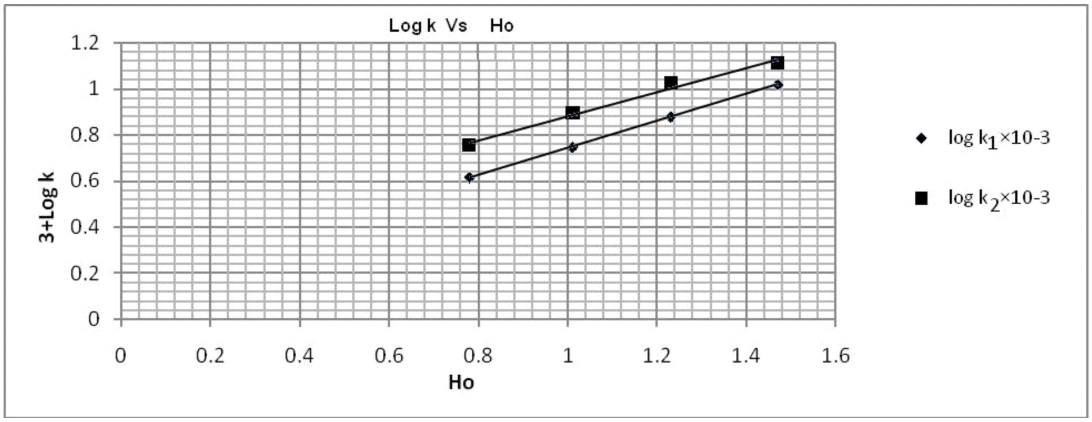

Figure 8 Zucker-Hammett Plot (a)

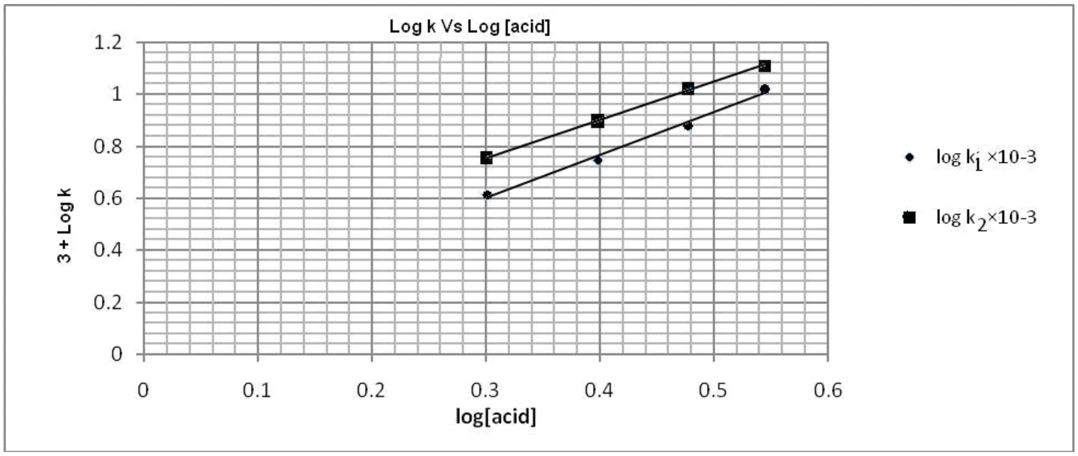

Figure 9 Zucker-Hammett Plot (b)

Table 5 Slope values of Two Zucker-Hammett Plots

Correction	Slope Values	
Zucker-Hammett Plots	**For I Stage**	**For II Stage**
a) H_0 against log k	0.625	0.50
b) log [$HClO_4$] against log k	0.875	0.50

Temperature variation: Kinetic and Activation Parameters

In order to determine various kinetic and activation parameters, such as temperature coefficient, frequency factor (Pz), energy of activation $\Delta E^{\#}$, heat of activation $\Delta H^{\#}$ and entropy of activation $\Delta S^{\#}$ and Gibbs free energy $\Delta G^{\#}$ the reaction has been studied at 308K, 313K, 318K & 323K) (Figure 10 & 11). For both catalysed and uncatalysed reactions.

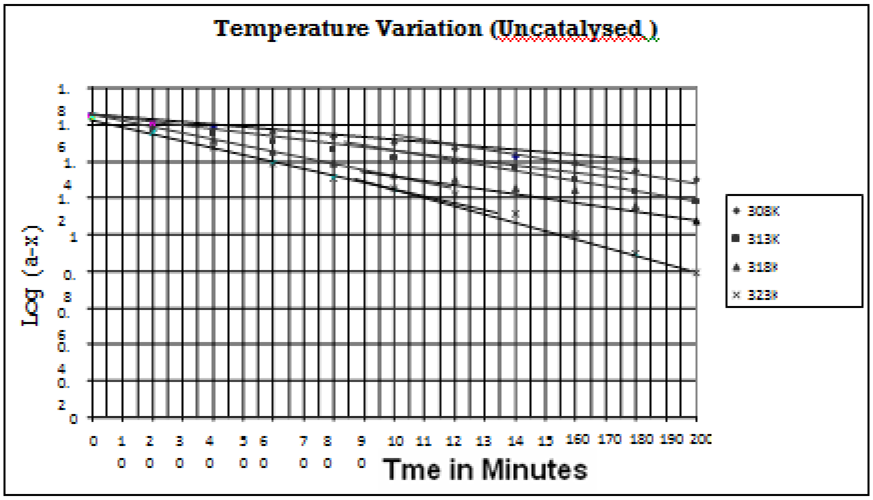

Figure 10 Temperature variation(Uncatalysed)

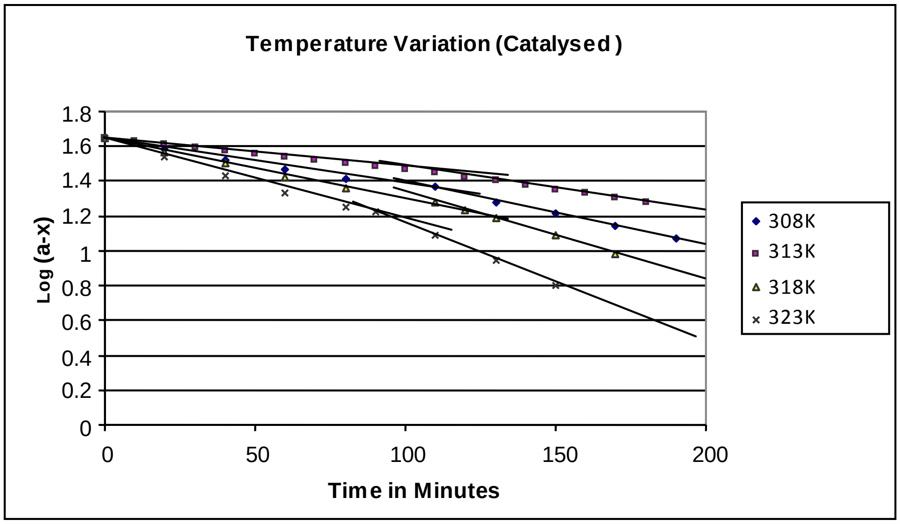

Figure 11 Temperature variation(Catalysed)

Table 6 Temperature Variation (Uncatalized)

[L-valine]=0.1M		[HClO$_4$]=2M
Temperature	k$_1$x 10^{-3}min^{-1}	k$_1$^{A} x 10^{-3}min^{-1}
308K	3.4240	4.7980
313K	5.4426	7.2023
318K	7.5057	9.3914
323K	9.7800	12.4900

Table 7 Temperature Variation (Catalyzed)

[L-valine]=0.1M [NaLS]=1X10^{-5}M		[HClO$_4$]=2.OM
Temperature	k$_1$x 10^{-3}min^{-1}	k$_1$^{A} x 10^{-3}min^{-1}
308K	4.1246	5.6736
313K	6.8130	8.8881
318K	8.4683	10.4146
323K	11.8447	15.9802

The results of various kinetic and activation parameters, such as temperature coefficient, frequency factor (Pz), energy of activation $\Delta E^{\#}$, heat of activation $\Delta H^{\#}$, entropy of activation $\Delta S^{\#}$ and Gibbs free energy $\Delta G^{\#}$ for the reaction have been calculated for both catalysed & uncatalysed, and for both the stages in each case. The results of temperature coefficient have been given in the Table 8 while others activation parameters have been summarized in the Table 9.

The values of temperature coefficient for 10°C rise in temperature are summarized in following table

Table 8 Temperature Coefficients

S.No.	Temperature Range	Temperature Coefficient for k_1	Temperature Coefficient for k_1^A
Catalysed			
1.	308-313K	2.05	1.83
2.	313-323K	1.73	1.79
Uncatalysed			
1.	308-313K	2.86	1.96
2.	313-323K	1.38	1.73

Table 9 Kinetic and Activation Parameters

[L-Valine]=0.1M [$HClO_4$]=2.0M
[NaLS]= $1.0\text{x}10^{-5}$M [$KMnO_4$]=$1.0\text{x}10^{-3}$M, Temp.=308K

For Catalysed

Stages	$\Delta E_a^\#$ Kcals. mol^{-1} Theoretical	$\Delta H^\#$ Kcals. mol^{-1} Theoretical	$\Delta G^\#$ Kcals. mol^{-1} Theoretical	Pz Litres $mol^{-1}min^{-1}$ Theoretical	$\Delta S^\#$ cals. $mol^{-1}K^{-1}$ Theoretical
For First Stage	9.6781	9.068	3.8884	$7.26\text{x}10^{39}$	-12.5953
For Second Stage	8.6565	8.046	3.8457	$4.64\text{x}10^{22}$	-12.46

For Uncatalysed

Stages	$\Delta E_a^\#$ Kcals. mol^{-1} Graphical	$\Delta H^\#$ Kcals. mol^{-1} Theoretical	$\Delta G^\#$ Kcals. mol^{-1} Graphical	Pz Litres $mol^{-1}min^{-1}$ Theoretical	$\Delta S^\#$ cals. $mol^{-1}K^{-1}$ Theoretical
For First Stage	11.675	8.327	3.9179	$3.27\text{x}10^{39}$	-12.5977
For Second Stage	12.368	7.223	3.8687	$4.07\text{x}10^{22}$	-12.4626

The Arrhenius plot has also been drawn between log k and 1/T to determine the energy of activation by slope measurement (Figure 12 & 13).

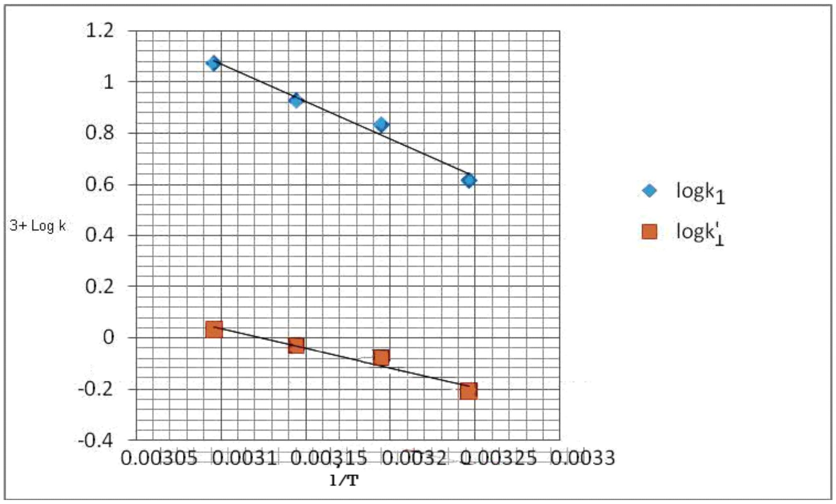

Figure 12 Arrhenius plot **[Catalysed]**

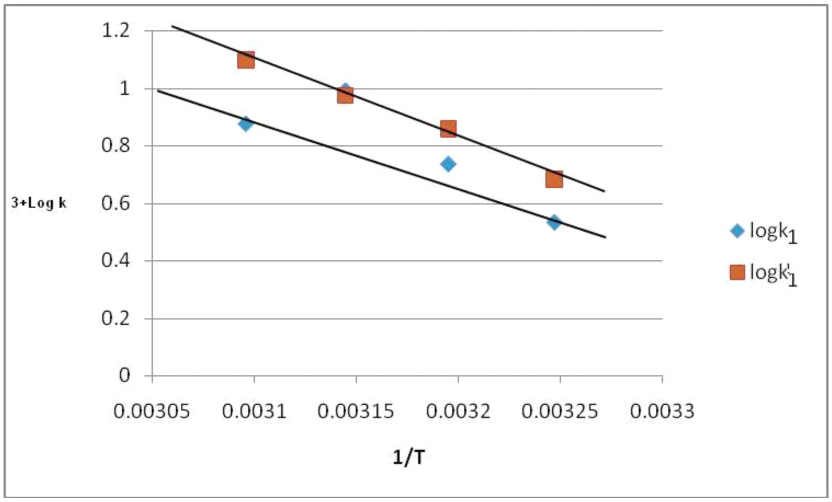

Figure 13 Arrhenius plot **[Uncatalysed]**

The Arrhenius plot has also been drawn between log k and 1/T to determine the energy of activation by slope measurement (Figure 12 & 13).

Effect of Neutral Salts

The reactions have been studied to observe the effect of neutral salts i.e. Na_2SO_4, MgSO4 and $MnSO_4$ on the reaction rate. The results have been reported in the following Tables 10. Effect of neutral salts with sufficient increase in reaction velocity indicates that interaction between one neutral molecule and a positive ion in the slow step (Figure 14).

The series for the order of the effectiveness of cations have been found as

$$Mn^{++} > Mg^{++} > Na^{+}$$

Table 10 Salt Effect

[L-valine]=0.1M		
[$HClO_4$]=2.0M	[NaLS]=1.0x 10^{-5}M	
[$KMnO_4$]= 1.0x10^{-3}M	Temperature =308K	
Salts	k_l x $10^{-3}min^{-1}$	k_1^A x $10^{-3}min^{-1}$
Without Salt	4.1240	5.673
Na_2SO_4 (0.4M)	7.1650	13.9350
$MgSO_4$(0.4M)	8.4850	13.1540
$MnSO_4$(1.0x10^{-4}M)	10.3640	14.2690

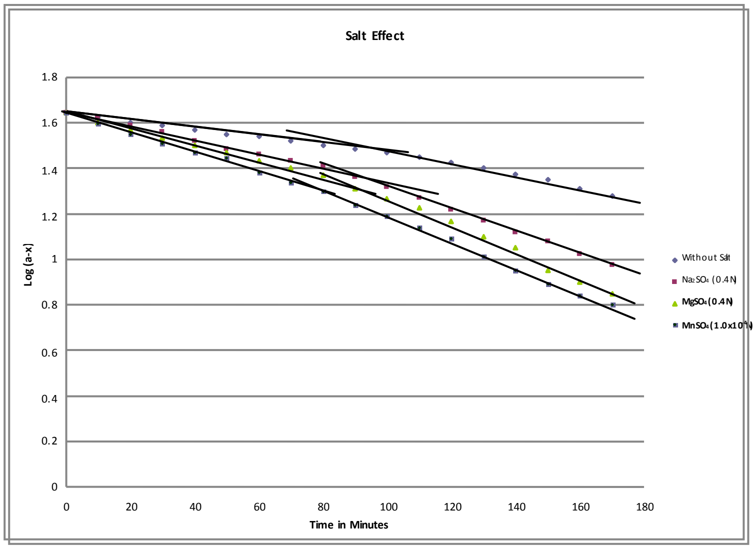

Figure 14 Salt Effect

Product Analysis

- Identification of CO_2 (Decarboxylation): For the identification of CO_2 lime water test was applied. It has been observed that the lime water turns milky within 4 to 5 hrs of oxidation. This confirms the evolution of CO_2 from the reaction mixture as one of the oxidation product.

- Ammonia has been detected as ammonium ions in solution as an oxidation product by routine Nessler's test.

- For the detection of Isobutyraldehyde in the reaction as an established oxidation product of L-valine following method was performed. 1ml of the acidic solution was heated for two minutes in a dry test tube in water bath at 85^oC. After cooling under the tap to 28^oC, a pinch of a solid p-hydroxydiphenyl is added, the mixture is swirled several times and left for 10-20 minutes. Red colour develops, confirms the formation of Isobutyraldehyde as an oxidation product[22].

Determination of Free Radical

Formation of some intermediate active organic free radicals has been confirmed by the formation of white precipitate of mercurous chloride as a result of induced reduction of mercuric chloride[22].

The Stoichiometry of the Reaction

The stoichiometry of the reaction was determined by analytical method. In this method the reaction mixture containing excess of $KMnO_4$ over the L-valine (1:0.8) were allowed to stand at 35°C for a sufficiently long time (36hrs.).

The amount of unreacted permanganate was estimated idometrically. It has been found that the five molecule of L-valine require two molecules of permanganate for complete oxidation. The overall reaction may be written as;

$$5RCHNH_2COOH+2MnO_4^-+11H^+ \xrightarrow{NaLS} 5RCHO+3H_2O+2Mn^{++}+5CO_2+5NH_4^+ \cdots$$

$$\begin{array}{lcl}
NH_2\,CHRCOOH & \rightleftharpoons & \overset{+}{N}H_3\,CHRCOO^- \\
\overset{+}{N}H_3\;CHRCOO^- + \overset{+}{H} & \overset{k_1}{\rightleftharpoons} & \overset{+}{N}H_3\,CHRCOOH \\
MnO_4^- + \overset{+}{H} & \overset{k_2}{\rightleftharpoons} & HMnO_4 \\
(nNaLS) & \overset{k_S}{\rightleftharpoons} & (NaLS)_n \\
\textbf{Molecular Surfactant} & & \textbf{Micelle} \\
(NaLS)_n + \overset{+}{N}H_3\,CHRCOOH & \overset{k_D}{\rightleftharpoons} & (NaLS)_n \cdots \overset{+}{N}H_3\,CHRCOOH \\
(NaLS)_n \cdots \overset{+}{N}H_3\,CHRCOOH + & \overset{k_T}{\rightarrow} & (NaLS)_n \cdots \overset{+}{N}H_3\,CHRCO\dot{O} + \\
H_2O + HMnO_4 & & \overset{+}{H_3}O + HMnO_4^- \\
 & & \textbf{(Rate determining stage)} \\
(NaLS)_n \cdots N^+H_3CHRCO\dot{O} & \overset{fast}{\rightarrow} & D_n \cdots \overset{+}{N}H_3\;C\dot{H}R + CO_2\uparrow \\
(NaLS)_n \cdots \overset{+}{N}H_3\,C\dot{H}R + HMnO_4 & \overset{fast}{\rightarrow} & (NaLS)_n + \overset{+}{N}H_2 = CHR + \overset{+}{H} \\
 & & +HMnO_4^- \\
\overset{+}{N}H_2 = CHR + H_2O & \overset{fast}{\rightarrow} & RCHO + NH_3 + \overset{+}{H}
\end{array}$$

$$where\; R = \; CH(CH_3)_2$$

The above stoichiometric equation is consistent with the results of product analysis.Though elucidation of the mechanism for the processes require further exhaustive and separate work, but here following steps have been adopted from the earlier work [20-22] carried out on other amino acids.

Conclusion

On the basis of kinetic results and observations it has been confirmed that oxidation of L-valine by permanganate is acid catalysed and the reaction rate also enhanced in the presence of micelles. The order of reaction has been confirmed by different methods.The total order of reaction was found three i.e.; one with respect to L-valine, permanganate and sodium lauryl sulphate respectively.

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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