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RESEARCH ARTICLE

Miceller catalysed oxidative decarboxylation of iso-butyric acid by acidic permanganate

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Abstract

A kinetic study of oxidation of iso-butyric acid has been investigated in presence and absence of sodium lauryl sulphate (NaLS) an anionic micelle. The reaction proceeds in two stages, in which first stage is followed by second fast stage process. Role of micelle is observed as positive catalyst. A first order kinetics is observed with respect to substrate and oxidant. The data has been examined in the light of Zucker-Hammett, Bunnett and Bunnett-Olsen criteria of reaction mechanism. The stoichiometry was observed in terms of mole ratio of permanganate ion and iso-butyric acid consumed. Effect of specific ions on the reaction rate has also been reported. Activation parameters for the reaction are evaluated and the mechanism pertinent to the observed data has been suggested.

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INTRODUCTION

Now a day's surfactant has attracted considerable interest in theoretical and experimental fields due to their catalytic efficiency at a certain concentration in solution. Their monomers associate to form longer aggregates known as micelles¹⁻⁶. In present work an anionic surfactant i.e. sodium lauryl sulphate is used as miceller catalyst. The oxidation kinetics of carboxylic acids and other substituted acids have been examined by number of workers⁷. Since little work has been reported on the miceller catalysed oxidation of carboxylic acid by acidic permanganate⁸⁻¹², hence the present work described the detailed study on the miceller catalysed oxidation of iso-butyric acid by acidic permanganate. The oxidation by permanganate has also been compared with potassium dichromate¹³⁻¹⁶.

Due to the several advantages of permanganate ions as an analytical oxidizing agent in synthetic and analytical works it is used in the present investigation. Attempts have also been made to elucidate the type of reaction mechanism based on the influence of H⁺ ion and neutral salts on the rate of the reaction. The involvement of water molecule in the reaction mechanism has been explained in the light of Zucker-Hammett, Bunnett and Bunnett-Olsen hypotheses.

Experimental:

The standard solution of iso-butyric acid (BDH) and sodium lauryl sulphate (BDH) were prepared in doubly distilled water. H₂SO₄ (Analar) was used as a source of hydrogen ion. Permanganate solution was prepared as given by Vogel¹⁷. Potassium dichromate solution of Analar grade from Rankem was used. Standard salt solutions were made by dissolving known amount of the solute in a given volume of distilled water. Kinetic procedure is same as already given in paper⁶.

Result and discussion:

(A) Dependency of reaction rate on permanganate concentration and dichromate concentration:

Dependency of reaction rate on permanganate has been studied by varying its initial concentration at constant concentration of other reactants. It shows that rate constant does not alter with oxidant concentration. 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. The oxidation has also been carried out by potassium dichromate from the comparative point of view. The

reaction is single stage process. The second slow stage process disappear in this case. It has been observed that values of pseudo first order rate constant doesnot alter with the oxidant concentration.

It has also been observed the rate of oxidation by dichromate is comparatively fast than by permanganate and it observed at very low concentration.

(B) Dependency of reaction rate on substrate concentration:

Experiments were also performed at 308K with different initial concentration of iso-butyric acid, keeping the concentration of all other reactants as constant. The rate both in uncatalysed and catalysed reaction was found to increase with the concentration of iso-butyric acid. Table 1.1(A), 1.1(B).

Plot of logarithm of [iso-butyric acid] with logarithm of rate constant (k_1 and k_1') give straight line approximately of unit gradient in both the stages. These show that the order of reaction with respect to iso-butyric acid is one for each stages and plots of $1/k_1$, $1/k_1'$ against $1/\text{Substrate concentration}$ (i.e. Michaelis-Menten plots) give straight lines passing through the origin for both the first and second stages. These confirm the first order dependence of reaction rate with respect to iso-butyric acid, in both the stages and there is no kinetic evidence for intermediate complex formation between iso-butyric acid and permanganate¹⁸. However if any complex is formed, its formation constant would be extremely small¹⁹

(C)i: Effect of the variation of the $[H^+]$ concentration :

The variation of the $[H^+]$ concentration on the reaction rate has been investigated between 2.0 mol dm^{-3} to 4.5 mol dm^{-3} concentration range of the sulphuric acid and 0.75 mol dm^{-3} to 2.5 mol dm^{-3} concentration range of the perchloric acid medium. The experimental results obtained at constant concentration of substrate and oxidant are summarized in table 1.2 and 1.3

(D) Dependency of reaction rate on NaLS concentration:

It has been observed clear that the pseudo first order rate constant for the given concentration range of NaLS increases with the increase in NaLS Concentration at given temperature (Table 1.6). In the present study, the formation of premicellar aggregates are responsible for the miceller catalysis²⁴⁻²⁷.

The catalysis by the concentration of micelle which is below their cmc (i.e. critical micelles concentration) value is also possible as reported in the literature. It is termed as premiceller catalysis. It has been determined graphically by plotting a Piszkiwicz graph between $\log [k_{\text{obs}} - k_o] / [k_m - k_{\text{obs}}]$ and $\log [\text{NaLS}]$. Here k_o is the velocity constant in absence of NaLS, k_{obs} is the velocity constant at different NaLS concentration, while k_m is the maximum velocity constant in presence of NaLS used. The concentration of NaLS varied from 5.0×10^{-4} to $9.0 \times 10^{-4} \text{ mol dm}^{-3}$. Its maximum concentration used is $9.0 \times 10^{-4} \text{ mol dm}^{-3}$. This is well below the reported cmc of sodium lauryl sulphate which is reported in the literature as $8.1 \times 10^{-3} \text{ mol dm}^{-3}$ at 298K. This confirms that the observed phenomenon is a case of premicellar catalysis.

In present case the plot is good straight line. The slope value 'n' obtained from this graph for first and second stages are 1.89 and 1.82. These are between the expected value for premiceller catalysis i.e. between 1 to 6, while in the case of miceller catalysis this value should be more than 20. This is according to the binding parameters as suggested by Piszkiwicz²⁸.

The result have been reported in the table 1.6 for both the stages. The 'n' value of positive cooperativity also supports the substrate promoted micellization which is analogous to positive cooperativity in case of enzymatic reactions²⁹⁻³¹

(E) Effect of variation of temperature :

The reaction was studied at different temperature i.e. 303, 308, 313 and 318K in order to observe the effect of temperature on reaction rate at the constant concentration of all the reactants. The result have been recorded in the table 1.7:

From the temperature variation studies, the various kinetic and activation parameters such as Energy of activation ΔE^\ddagger , Enthalpy of activation ΔH^\ddagger , Entropy of activation ΔS^\ddagger , Frequency factor pZ and Free Energy ΔG^\ddagger have been calculated by their standard equations and reported in the table 1.8. The values of energy of activation have also been obtained from the slopes of Arrhenius plots³² and have been reported in the respective table.

(F) Effect of Neutral salt and specific ionic effects on reaction rates:

In the case of oxidation of iso-butyric acid by potassium permanganate in the sulphuric acid medium, the primary kinetic salt effect was not observed by adding the neutral salts within the concentration limits as demanded for the applicability of Bronsted-Bjerum equation³³. Hence the results obtained in term of specific ionic effect.

Specific effect of cations and anions:

In order to know the specific effect of cations, sulphates and nitrates of cations were taken at their identical molar concentrations and in order to know the specific effect of anions, sodium salt of anions were taken at their identical molar concentration. The order of the effectiveness of univalent, bivalent and trivalent ions has been found as:

For cations $Al^{3+} > Zn^{2+} > Mg^{2+} > Na^+$ (as their sulphate)

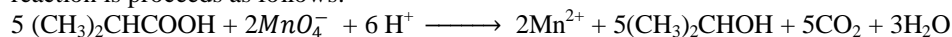
$Na^+ > K^+$ (as their nitrates)

For anions $NO_3^{2-} > SO_4^{2-}$

It has been observed that the CH_3COO^- and F^- anions have the negative effect on the reaction velocity. The rate of both the stages decreases with the increases in the concentration of CH_3COO^- and F^- in the order $F^- > CH_3COO^-$.

(G) Stoichiometry and product analysis:

Stoichiometry of the reaction was determined by analytical method. In this method the reaction mixture containing known excess of $KMnO_4$ over the substrate i.e. iso-butyric acid were allowed to stand at room temperature for a sufficiently long time (36 hours). After that the amount of unreacted permanganate was estimated iodometrically using starch as an indicator. It has been found that the five mole of substrate consumes one mole of potassium permanganate. On the basis of literature available and the work performed, the catalysed reaction is proceeds as follows:



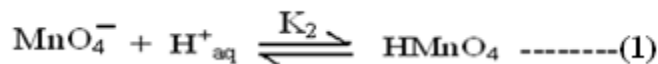
iso propyl alcohol was identified by spot test method as given by Figel³⁴ and Carbon dioxide have been determined by routine test as the end products. The formation of intermediate free radical is confirmed by induced reduction of mercuric chloride. Low value of energy of activation also supports the same.

(J) Mechanism :

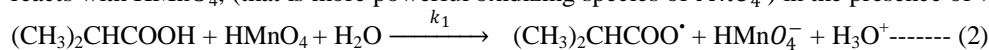
On the basis of the results of kinetic measurements facts and discussion the following mechanism for the oxidation reaction of iso-butyric acid in the absence and presence of sodium lauryl sulphate as catalyst has been suggested.

(1) Mechanism and rate law for uncatalysed oxidation:

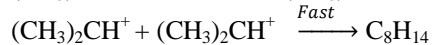
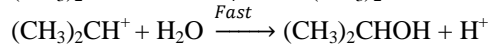
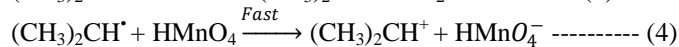
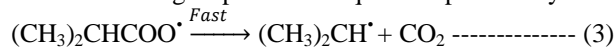
The mechanism proceeds with the formation of molecular $HMnO_4$ in sulphuric acid medium



This step is consistent with the spectroscopic evidence of existence of molecular $HMnO_4$. Now substrate reacts with $HMnO_4$, (that is more powerful oxidizing species of MnO_4^-) in the presence of water molecule.



This three body collision is difficult and thus explains the cause of slowness in the slowest reaction. It is rate determining step. All subsequent steps are very fast and not of kinetic importance, are as follows;



The above mechanism leads to suggest the rate expression as follow for uncatalysed reaction; in which the concentration of hydrogen ion and water have been withdrawn from main equation.

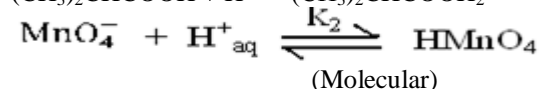
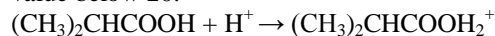
$$-\frac{d[MnO_4^-]}{dt} = K_s [(CH_3)_2CHCOOH] [MnO_4^-]$$

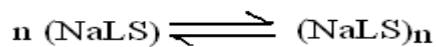
Where

$$K_s = \frac{k_1 K_1 K_2 [H^+]^2 [H_2O]}{\{ 1 + K_2 [H^+] \}}$$

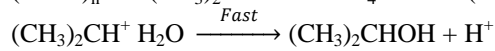
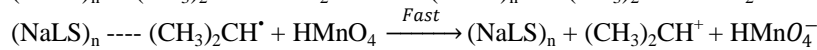
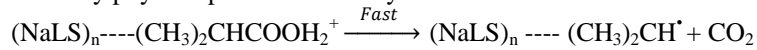
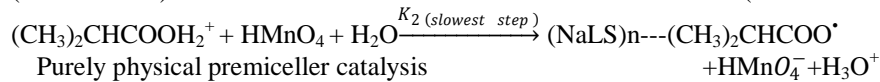
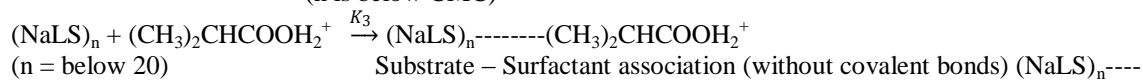
(2) Mechanism and rate law for catalysed reaction:

The reaction rates have been found substantially increased in presence of anionic sodium lauryl sulphate surfactant. It is assumed that due to the electrostatic interaction between iso-butyric acid and micelles of surfactant leads the increase in effective concentration which is responsible for the increase in reaction rate. The very low number 'n' of surfactant molecules i.e. below 20 is expected in micelles. The mechanism proposed, therefore involve the substrate – surfactant interaction, with the premicellar catalysis phenomenon as the n, calculated has the value below 20.





(n is below CMC)



The following rate law expression may be derived from above discussed steps considering that catalysed and uncatalysed reactions proceed simultaneously.

$$\frac{-d[\text{MnO}_4^-]}{dt} = \frac{k_1 k_2 K_1 K_2 K_3 [H^+]^2 [H_2O] [(CH_3)_2CHCOOH_2^+][\text{MnO}_4^-]}{\{1 + K_2 [H^+]\}}$$

$$\frac{-d[\text{MnO}_4^-]}{dt} = k'' [\text{NaLS}]_n (\text{CH}_3)_2\text{CHCOOH}_2^+ [\text{MnO}_4^-]$$

Here

$$k'' = \frac{k_1 k_2 K_1 K_2 K_3 [H^+]^2 [H_2O]}{\{1 + K_2 [H^+]\}}$$

Conclusion:

It is evident from the rate law that reaction is first order with respect to substrate and oxidant. The role of surfactant is only as premicellar physical catalyst with no covalent bond formation between surfactant – substrate association. Rate law involves the acid concentration term and water molecule which has been explained in the light of Zucker-Hammett, Bunnett’s and Bunnett-Olsen Hypotheses.

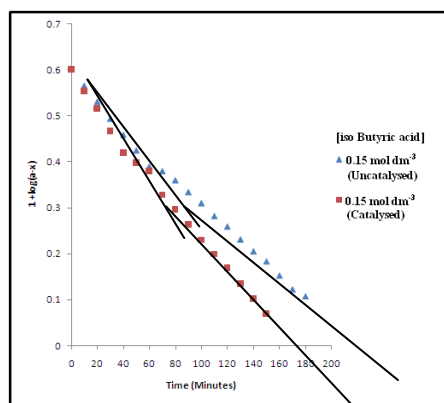


Figure – 1.1: Typical run for the oxidation reaction in sulphuric acid medium

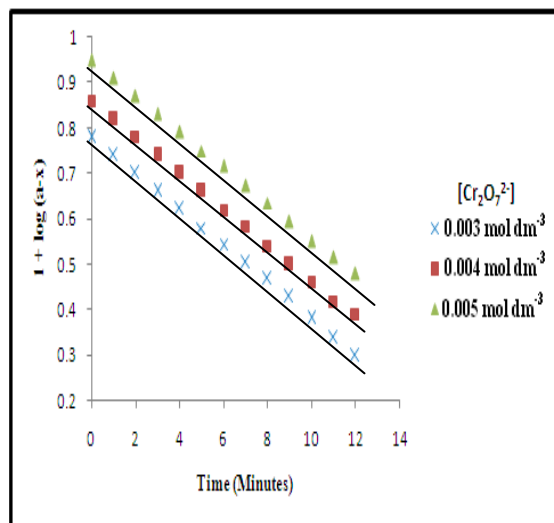


Figure - 1.2: variation of [Dichromate]

TABLE - 1.1 (A) :Variation of iso-butyric acid concentration (Uncatalysed)

[H ₂ SO ₄] = 4.0 mol dm ⁻³ Temperature = 308K		[KMnO ₄] = 1.0 × 10 ⁻³ mol dm ⁻³ [NaLS] = Nil		
[iso-butyric acid] mol dm ⁻³	k ₁ × 10 ⁻³ Min ⁻¹		k ₁ '' × 10 ⁻³ Min ⁻¹	
	By Differential method	By Graphical method	By Differential method	By Graphical method
0.05	3.17	3.18	2.30	2.30
0.10	5.78	5.17	4.28	4.20
0.15	8.21	8.14	6.02	5.95
0.20	10.96	10.68	8.42	8.35
0.25	14.09	13.88	10.06	10.16

TABLE 1.1 - (B) :Variation of iso-butyric acid concentration (Catalysed)

[H ₂ SO ₄] = 4.0 mol dm ⁻³ Temperature = 308K		[KMnO ₄] = 1.0 × 10 ⁻³ mol dm ⁻³ [NaLS] = 1.0 × 10 ⁻⁴ mol dm ⁻³		
[iso-butyric acid] mol dm ⁻³	k ₁ × 10 ⁻³ Min ⁻¹		k ₁ '' × 10 ⁻³ Min ⁻¹	
	By Differential method	By Graphical method	By Differential method	By Graphical Method
0.05	3.51	3.48	2.42	2.41
0.10	6.97	6.98	4.89	4.88
0.15	10.19	9.44	7.39	7.43
0.20	13.25	12.20	9.97	9.90
0.25	16.87	15.77	12.20	11.97

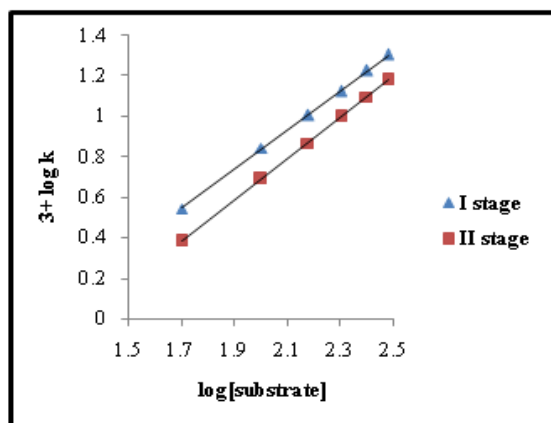


Figure - 1.3: log k Vs log [substrate] Catalysed

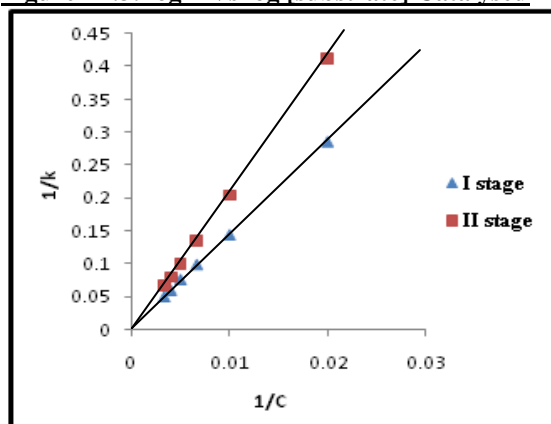


Figure - 1.4: Michaelis Menten plot (Catalysed)

TABLE - 1.2: Dependence of rate on sulphuric acid concentration $[H^+]$

[iso-butyric acid] = 0.20 mol dm^{-3} Temperature = 308K		[KMnO ₄] = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ [NaLS] = $1.0 \times 10^{-4} \text{ mol dm}^{-3}$		
$[H^+]$ mol dm ⁻³	-H ₀	$-\log a_{H_2O}$	$k_1 \times 10^{-3} \text{ Min}^{-1}$	$k_1'' \times 10^{-3} \text{ Min}^{-1}$
2.0	0.84	0.043	7.80	5.41
2.5	1.12	0.063	8.80	6.48
3.0	1.38	0.085	10.15	7.47
3.5	1.62	0.111	11.49	8.37
4.0	1.85	0.142	13.25	9.97
4.5	2.06	0.176	15.08	11.09

TABLE 1.3 : Dependence of rate on perchloric acid concentration $[H^+]$

[iso-butyric acid] = 0.15 mol dm^{-3} Temperature = 308K		[KMnO ₄] = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ [NaLS] = $1.0 \times 10^{-4} \text{ mol dm}^{-3}$		
$[H^+]$ mol dm ⁻³	-H ₀	$-\log a_{H_2O}$	$k_1 \times 10^{-3} \text{ Min}^{-1}$	$k_1'' \times 10^{-3} \text{ Min}^{-1}$
0.75	0.04	0.012	4.86	3.06
1.00	0.22	0.018	5.59	3.92
1.50	0.53	0.030	5.95	4.80
2.00	0.78	0.043	6.58	5.60
2.50	1.01	0.060	7.32	6.44

TABLE - 1.4 : Correlation of reaction rate with sulphuric acid concentration

[iso-butyric acid] = 0.20 mol dm ⁻³ Temperature = 308K		[KMnO ₄] = 1.0 × 10 ⁻³ mol dm ⁻³ [NaLS] = 1.0 × 10 ⁻⁴ mol dm ⁻³		
S.No.	Correlation	Parameters	Slope value	
			I stage	II stage
1.	Zucker-Hammett plot			
(a)	(log Rate constant) against -H ₀	Slope	0.235	0.254
(b)	(log Rate constant) against log [H ⁺]	Slope	0.814	0.88
2.	Bunnett's plots			
(a)	(log Rate constant + H ₀) against - log a _{H₂O}	(ω)	- 6.89	-6.74
(b)	(log Rate constant - log [H ⁺]) against log - log a _{H₂O}	(ω*)	a	a
(c)	(log Rate constant - log [H ⁺] - H ₀) against - log a _{H₂O}	Slope	8.62	8.77
3.	Bunnett-Olsen plot (L.F.E.R)			
(a)	(log Rate constant + H ₀) against (H ₀ + log [H ⁺])	(φ)	1.07	1.04

TABLE - 1.5 : Correlation of reaction rate with perchloric acid concentration

[iso-butyric acid] = 0.15 mol dm ⁻³ Temperature = 308K		[KMnO ₄] = 1.0 × 10 ⁻³ mol dm ⁻³ [NaLS] = 1.0 × 10 ⁻⁴ mol dm ⁻³		
S.No.	Correlation	Parameters	Slope value	
			I stage	II stage
1.	Zucker-Hammett plot			
(a)	(log Rate constant) against -H ₀	Slope	0.168	0.318
(b)	(log Rate constant) against log [H ⁺]	Slope	0.312	0.593
2.	Bunnett's plots			
(a)	(log Rate constant) + H ₀) against - log a _{H₂O}	(ω)	a	a
(b)	(log Rate constant - log [H ⁺]) against - log a _{H₂O}	(ω*)	a	a
(c)	(log Rate constant - log [H ⁺] - H ₀) against - log a _{H₂O}	Slope	12.86	15.78
3.	Bunnett-Olsen plot (L.F.E.R)			
(a)	(log Rate constant +H ₀) against (H ₀ + log [H ⁺])	(φ)	1.78	1.47

Where 'a' is for absent

TABLE - 1.6 : Dependence of rate on NaLS Concentration and Catalytic Constant

[iso-butyric acid] = 0.10 mol dm ⁻³ [H ₂ SO ₄] = 4.0 mol dm ⁻³		[KMnO ₄] = 1.0 × 10 ⁻³ mol dm ⁻³ Temperature = 308K		
[NaLS] mol dm ⁻³	k ₁ × 10 ⁻³ Min ⁻¹	k _c × 10 ³ litre mol ⁻¹ Min ⁻¹	k ₁ " × 10 ³ Min ⁻¹	k _c " × 10 ³ litre mol ⁻¹ Min ⁻¹
Uncatalysed(Absent)	5.78	----	4.28	----
1.0 × 10 ⁻⁴	6.97	1.19	4.89	6.1
2.0 × 10 ⁻⁴	8.12	1.17	5.51	6.16

3.0×10^{-4}	9.11	1.11	6.04	6.15
4.0×10^{-4}	10.69	1.22	6.65	5.9
5.0×10^{-4}	11.91	1.22	7.33	5.92

TABLE - 1.7 : Effect of Temperature variation

[iso-butyric acid] = 0.15 mol dm^{-3} [H ₂ SO ₄] = 4.0 mol dm^{-3}		[KMnO ₄] = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ Temperature = 308 K		
Temperature (K)	Velocity constant for Uncatalysed NaLS = Nil		Velocity constant for Catalysed NaLS = $1.0 \times 10^{-4} \text{ M}$	
	$k_1 \times 10^{-3} \text{ Min}^{-1}$	$k_1 \times 10^{-3} \text{ Min}^{-1}$	$k_1'' \times 10^{-3} \text{ Min}^{-1}$	$k_1'' \times 10^{-3} \text{ Min}^{-1}$
303	4.01	5.00	5.00	3.48
308	5.78	6.97	6.97	4.89
313	8.47	10.16	10.16	6.97
318	12.00	13.84	13.84	9.60
Temperature Range (K)	Temperature coefficient for Uncatalysed		Temperature coefficient for Catalysed	
	I stage	II stage	I stage	II stage
303-313	2.11	2.25	2.03	2.00
308-318	2.07	2.16	1.98	1.96

TABLE - 1.8 : Thermodynamic and Activation Parameters (For Uncatalysed and Catalysed reaction)

[iso-butyric acid] = 0.15 mol dm^{-3} [H ₂ SO ₄] = 4.0 mol dm^{-3} Temperature = 308K			[KMnO ₄] = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ [NaLS] = $1.0 \times 10^{-4} \text{ mol dm}^{-3}$			
Kinetic Parameters						
Stages	Energy of activation (ΔE^\ddagger) KJ mol ⁻¹		Enthalpy of activation (ΔH^\ddagger) KJ mol ⁻¹	Entropy of activation (ΔS^\ddagger) J mol ⁻¹ K ⁻¹	Frequency factor (pZ) dm ³ mol ⁻¹ Sec ⁻¹	Free Energy of activation (ΔG^\ddagger) KJ mol ⁻¹
	Cal.	Gra.				
Uncatalysed I stage (Without NaLS)	59.493	61.267	52.580	-109.00	5.39×10^7	19.010
Uncatalysed II stage (Without NaLS)	62.764	65.097	62.536	-79.178	19.58×10^8	38.154
Catalysed I stage (With NaLS)	55.864	53.609	51.048	-112.419	35.94×10^6	16.423
Catalysed II stage (With NaLS)	54.938	55.141	54.878	-102.94	11.21×10^7	23.170

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