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# MICELLAR EFFECT IN THE OXIDATION OF HMBA BY Mn(VII)

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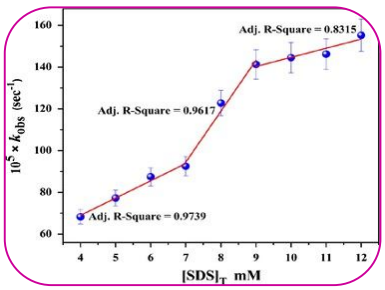
## ABSTRACT

*Kinetics of oxidation of 2- Hydroxy- 2- methyl butyric acid (HMBA) by Mn(VII) in aqueous $H_2SO_4$ medium in absence and presence of sodium lauryl suphate (NaLS) follows a route conforming to Michaelis-Menten Kinetics.Rate data in presence of $[H^+]$ show an acid dependent and acid independent path. The oxidation is catalysed by NaLS and the catalysis has been rationalized by Menger and Portnoy as well as Berezin model. The rate enhancement is attributed to binding of the substrate and oxidant to the micellar phase, the former through the hydrophobic interaction and the latter by electrostatic binding to the micelle.*




**KEYWORD :** *Michaelis-Menten Kinetics , Menger and Portnoy.*

## INTRODUCTION

2-Hydroxy-2-methyl butyric acid (HMBA) has been successful used to establish the intermediacy of Cr (V) in the Cr (VI) oxidation of isopropanol by Mohapatro et al.[1,2] The reaction essentially involves formation of a reversible complex between Cr(V) and HMBA followed by rate limiting decomposition of the complex. In continuation of study of the oxidation reactions in organized assemblies[3-6] and of hydroxyl acids by $MnO_4^-$ study of the kinetics of oxidation of HMBA by $KMnO_4$ in aqueous medium is available, an attempt has also been made to report the kinetics in aqueous medium in absence of NaLS .

## MATERIALS AND METHOD

All the chemicals are of A.Rgrade.2-Hydroxy- 2- methylbutric acid (Aldrich) and potassium permanganate were used as such. The surfactant sodium lauryl suphate (NaLS) was used after recrystallisation. All solutions were prepared in deionised water. Stock solutions of the surfactant (0.5 Mol.dm-$^3$) and Mn(VII) (appro.0.1 Mol. dm$^{-3}$) were prepared and diluted to the required concentration. Surfactant was always added to the oxidant flask. The reaction was initiated by mixing both the reactants thermally equilibrated for 45 minutes at the desired temperature and the progress of the reaction was followed by withdrawing 5ml of the aliquots of the reaction mixture at different time intervals and dumped into a constant excess of standard oxalic acid. Left over oxalic acid was titrated against a standard $KMnO_4$ solution which helping to follow the kinetics of the reaction. As $KMnO_4$ was not very stable in the presence of NaLS, blank readings were taken at initial stage and corrections were taken at initial stage and corrections were applied while computing the final rate constant. The results were reproducible with the limits of experimental error.

## RESULTS AND DISCUSSINS

**Oxidation of 2-Hydroxy- 2- methyl butyric acid in the absence of surfactant:** Potassium permanganate was found to oxidize 2-hydroxy-2-methyl butyric acid at moderate acid concentration maintained by $H_2SO_4$ with case at ambient temperature. At constant acid concentration and temperature disappearance of $MnO_4^-$ << 2-Hydroxy -2- methy1 butyric acid followed first order kinetics.

**Dependence on salt concentration:** In order to examine the influence of added [Salt] on the oxidation, the rates were measured in the presence of varying potassium sulphate and sodium perchlorate concentrations. The data are collected in Table- 1. From the rate data it is observed that the pseudo first order rate constants are constant, which indicates that the oxidation rate is not affected by the change of ionic strength of the medium. Hence in subsequent experiments no attempt was made to maintain the ionic strength.

**Dependence on 2- Hydroxy-2-methyl butyric acid:**

Pseudo first order rate constants measured at constant oxidant and acid concentration range 0.004-0.015 mol $dm^{-3}$ are included in Table-1.

It is seen that the rate increases with increase in Substrate concentration with a tendency to attain a limiting value at high substrate concentration. Plot of $K_{obs}$ against 2-Hydroxy-2-methyl butyric acid shows a curve of concave nature and plot of $K_{obs}^{-1}$ against [2-Hydroxy-2-methyl butyric acid]$^{-1}$ is linear with a positive intercept and positive slope. This observation indicates Michaelis Menten behaviour and formation of a complex preceding the rate limiting step as observed in the Cr(V) oxidation of HMBA[1].

**Table-1**

**Pseudo first order rate constants for the oxidation of HMBA by $MnO_4^-$ in absence of SLS.**

| $10^2$[HMBA] mol.$dm^{-3}$ | 102[$H^+$] mol.$dm^{-3}$ | $10^3$[$NaClO_4$] mol.$dm^{-3}$ | $10^2$Kψ $min^{-1}$ |
|---|---|---|---|
| 1.0 | 10.0 | --------- | 2.40 |
| | | 5.0 | 2.42 |
| | | 10.0 | 2.44 |
| | | 15.0 | 2.45 |
| | | 20.0 | 2.41 |
| | | 25.0 | 2.46 |
| | | 30.0 | 2.50 |
| | | 40.0 | 2.49 |
| 4.0 | 15.0 | ----- | 1.45 |
| 6.0 | | | 2.10 |
| 8.0 | | | 2.35 |
| 10.0 | | | 2.56 |
| 12.0 | | | 2.75 |
| 15.0 | | | 3.09 |
| 1.0 | | | 3.09 |
| | 5.0 | | 1.23 |
| | 15.0 | | 2.59 |
| | 25.0 | | 2.80 |
| | 30.0 | | 3.50 |
| | 40.0 | | 4.30 |
| | 50.0 | | 4.80 |

**Acid dependence:**

Oxidation rates at different [$H_2SO_4$] were measured by keeping constant oxidant, substrate and temperature. Rate data are collected in Table- 2. It is observed that rate increases with increase in the [$H^+$] concentration. To arrive at a correlation the rate data were plotted against [$H^+$]. The nature of the plot is linear with a small positive intercept and positive slope suggesting that the oxidation involves an acid independent and acid dependent step. The overall observed rate is therefore the sum of the rates in acid dependent path and can be expressed as

$$K_{obs} = a + b[H^+]$$

**Table-2**

Pseudo first order rate constants for the oxidation of HMBA by $MnO_4^-$ in presence of NaLS. Temperature=35$^0$C, Solvent= Aq.medium.

| $10^3$[SLS] mol.dm$^{-3}$ | $10^2$ [$H_2SO_4$] Mol.dm$^{-3}$ | $10^4$[$MnO_4^-$] mol.dm$^{-3}$ | $10^3$[HMBA] Mol.dm$^{-3}$ | 103[$N_aClO_4$] Mol.dm$^{-3}$ | $10^2K_\psi$ Min$^{-1}$ |
|---|---|---|---|---|---|
| 8.0 | 15.0 | 5.0 | 10.0 | | 4.90 |
| | | 705 | | | 4.95 |
| | | 10.0 | | | 4.96 |
| | | 12.5 | | | 4.92 |
| | | 15.0 | | | 4.99 |
| 8.0 | 15.0 | 10.0 | 10.0 | | 4.81 |
| | | | | 5.0 | 5.05 |
| | | | | 10.0 | 4.95 |
| | | | | 20.2 | 4.48 |
| | | | | 30.0 | 4.92 |
| | | | | 40.0 | 5.01 |
| 8.0 | 15.0 | 10.0 | 5.0 | | 3.30 |
| | | | 7.5 | | 4.1 |
| | | | 10.0 | | 4.96 |
| | | | 12.5 | | 5.80 |
| | | | 15.0 | | 6.12 |
| 4.0 | 5.0 | 10.0 | 10.0 | | 2.81 |
| | 15.0 | | | | 4.61 |
| | 25.0 | | | | 7.20 |
| | 30.0 | | | | 8.53 |
| | 40.0 | | | | 12.01 |
| | 50.0 | | | | 13.23 |

**EFFECT OF RADICAL TRAPPING AGENTS:**

When the reaction mixture was allowed to stand in presence of acrylonitrile neither any precipitate nor turbidity was observed. This observation indicates the absence of participation of any radical during the oxidation and this rule out one electron transfer in the rate limiting step.

**PRODUCT OF OXIDATION:**

HMBA and $KMnO_4$ in the ratio of 1:5 were equilibrated in presence of 0.1 (M) $H_2SO_4$. The reaction mixture was neutralized by dilute alkali and extracted with ether. The product obtained for ether extract yielded positive test with 2,4- dinitro phenylhydrazine. Melting point of the derivative agreed with 2,4-DNP

derivative of known 2-butanone confirming that HMBA is oxidized to 2-butanone as observed in Cr(V) oxidation of HMBA[1].

## STOICHIOMETRY:

HMBA and $KMnO_4$ in different proportions in 0.1 (M) $H_2SO_4$ were made to react. After equilibrium brown solid particles were observed which is considered to be $MnO_2$. Estimation of residual $KMnO_4$ and 2-butanone formed show a stoichiometry of more than 1:1 but less than 1:2.

## Mechanism of the oxidation:

In order to propose the mechanism of oxidation of HMBA by $KMnO_4$, the following kinetic features need to be taken into consideration.

1. Dependence in $KMnO_4$ is unity.
2. Dependence in HMBA follows Michaelis Menten Kinetics.
3. Dependence in $H_2SO_4$ is fractional.
4. No salt effect is observed.
5. Test for free radical is negative.

Thus one can propose the following steps for the oxidation of HMBA by $KMnO_4$ in presence of acid.

$$MnO_4^- + H^+ \underset{}{\overset{K_n^+}{\rightleftharpoons}} HMnO_4 \qquad \ldots\ldots 1$$

$$HMBA + HMnO4 \underset{}{\overset{k_1}{\rightleftharpoons}} \text{Complex } (C^*) \ldots\ldots 2$$

$$\text{Comp (c)} + \underset{K1}{\overset{\text{Slow}}{\longrightarrow}} Mn(v) + \text{Product} \qquad \ldots 3$$

$$Mn(V) + HMB \xrightarrow{\text{Fast}} Mn(III) + \text{Product} \qquad \ldots 4$$

$$Mn(III) + Mn(V) \xrightarrow{\text{Fast}} 2\,Mn(IV) \qquad \ldots 5$$

The rate expression in presence of acid can be deduced as

$$-\frac{d[KMnO_4]}{dt} = \frac{k_1 K_1 [HMBA][HMnO_4]}{1 + K_1[HMBA]} \qquad \ldots\ldots 6$$

In Presence of $[H^+]$, whole of the $KMnO_4$ will be present as $HM_nO_4$ and acid independent step will be negligible. The rate expression (eq.6) satisfies the kinetic features observed confirming the mechanism.

## OXIDATION OF HMBA IN PRESENCE OF SLS:

Oxidation of HMBA by $MnO_4^-$ in the presence of constant sodium lauryl sulphate concentration has similar kinetic features as those in the absence of SLS. The kinetic data are collected in Table-2. The order with respect to $MnO_4^-$, $H^+$, and HMBA is same as that in absence of SLS. At the same time it is observed that the rate of the reaction in not affected by added salts and radical trapping agents. These observations confirm the reaction pathway in presence and absence of SLS to be similar.

## EFFECT OF VARIATION OF SLS CONCENTRATION:

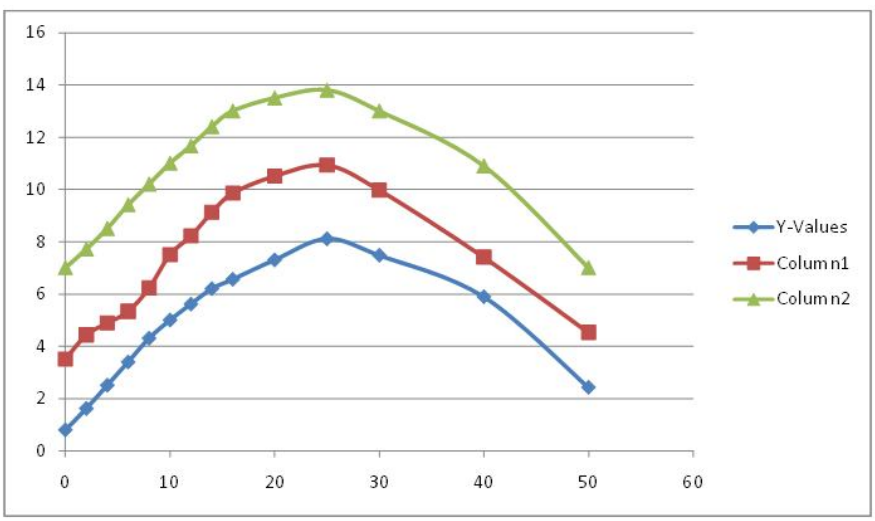
The pseudo first order rate constants ( $k_\psi$ $min^{-1}$) for the oxidation of HMBA by $MnO_4^-$ were determined in presence of varying sodium lauryl sulphate [SLS] concentration in the acidity range 0.05 to 0.25 (M). The kinetic data are reported in Table- 3 and plot of $k_\psi$ against [SLS] are given in Fig.1. Examination of data in the table as well as the plots obtained at different acidity definitely proves catalysis of the oxidation process by SLS at lower surfactant concentration which however decreases at higher [SLS].

**Table-3**

Pseudo first order rate constants for the oxidation of HMBA by permanganate with different concentration of SLS.

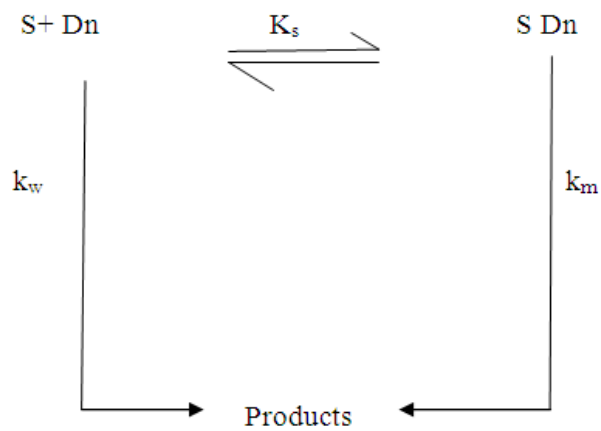
$10^3[MnO_4]$ = mol.dm$^{-3}$,$10^2$[HMBA] = 1.0 mol.dm$^{-3}$, Temperature =35$^0$C, Solvent = Aq.medium.

| $10^3$[SLS] Mol.dm$^{-3}$ | $10^2K\psi$ $min^{-1}$ | | |
|---|---|---|---|
| | $10^2[H^+]$ =5.0 mol.dm$^{-3}$ | $10^2[H^+]$=15.0 mol.dm$^{-3}$ | $10^2[H^+]$ =25.0 mol.dm$^{-3}$ |
| --- | 0.8 | 3.51 | 7.01 |
| 2.0 | 1.62 | 4.44 | 7.72 |
| 4.0 | 2.51 | 4.89 | 8.51 |
| 6.0 | 3.42 | 5.34 | 9.42 |
| 8.0 | 4.31 | 6.23 | 10.21 |
| 10.0 | 5.01 | 7.51 | 11.01 |
| 12.0 | 5.62 | 8.22 | 11.67 |
| 14.0 | 6.21 | 9.12 | 12.41 |
| 16.0 | 6.57 | 9.86 | 13.01 |
| 20.0 | 7.31 | 10.51 | 13.51 |
| 25.0 | 8.12 | 10.93 | 13.81 |
| 30.0 | 7.49 | 9.98 | 13.01 |
| 40.0 | 5.90 | 7.41 | 10.91 |
| 50.0 | 2.43 | 4.53 | 7.01 |




*Graph -1, In X- AXIS $10^3$[SLS] and in Y- AXIS $10^3k_\psi$*

The kinetic data can be explained by means of micellar pseudophase kinetic model given by Menger and Portnoy[8] which however is applicable to inhibition by micelles. This model considers the micelle to be separate from the aqueous phase and the observed rate is equal to sum of rates in the aqueous and micellar phase which is explained by the following scheme.




SCHEME-A

Where Ks is the binding constant of the substrate and Dn is the micellized surfactant. $k_w$ and $k_m$ are the rate constants in absence and presence of the surfactant respectively. The above scheme leads to the observed rate constant ( $k_\psi$ ) given by the equation.

$$k_\psi = \frac{k_w + k_m K_s \{[D]-cmc\}}{1+ K_s \{[D]-cmc\}} \quad \ldots\ldots\ldots\ldots\ldots 7$$

Rearrangement of the eq.7 gives the reciprocal form (eq.8)

$$\frac{1}{(k_w-k_\psi)} = \frac{1}{(k_m-k_w)} + \frac{1}{((k_m-k_w)K_s\{[D]-cmc\}} \quad \ldots\ldots\ldots\ldots\ldots 8$$

Eq.8 can modify to accommodate the catalysed reactions and takes the form.

$$\frac{1}{(k_\psi-k_w)} = \frac{1}{(k_m-k_w)} + \frac{1}{((k_m-k_w)K_s\{[D]-cmc\}} \quad \ldots\ldots\ldots\ldots\ldots 9$$

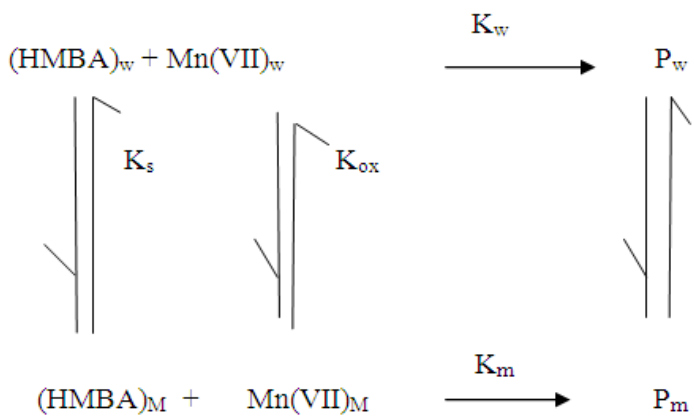
Validity of the eq.9 can be established if the plot of $(k_\psi-k_w)^{-1}$ against $\{[D]-cmc\}^{-1}$ is linear. But the plots exhibited poor linearity when the experimental data were used. However plot of $(k_\psi-k_w)^{-1}$ against $[D]^{-1}$ i.e. analytical surfactant concentration is fairly linear (Fig. 2) suggesting cmc values either have not significance or are negligible under the reaction conditions.

The reason may be due to the presence of large $[H^+]$ and organic molecules for which cmc values are significantly decreased. Perez Benito and Rodenas have ignored the cmc while calculating micelle concentration for the reasons mentioned above in their study of oxidation of primary alcohols by Cr(VI) in SLS medium

From the intercepts and ratio of intercepts to slope values show that the value gradually increases with increase of acid concentration. This can be attributed to the formation of $HMnO_4$ with ease due to reaction between $MnO_4^-$ and $H^+$ with increasing acidity. Thus our earlier postulation that the reaction taking

place between the reactant and $HMnO_4$ appears to be in conformity with the increasing association constant.

The plot of k against [SLS] (Fig.2) showed the reaction rate to increase up to a certain micelle concentration above the cmc and then decreases. Hence it is likely that both the reactants are partitioned between the bulk aqueous phase and the micellar pseudo phase, since both hydrophobic and electrostatic interaction may be operative. So a second rationale to explain the observed catalysis is provided by Berezin[10] who proposed the scheme- B for the above catalysed reaction.




The observed rate constant $k_\psi$ may be given by the equation.

$$k_\psi = \frac{k_w + k_m K_s K_{ox} \overline{C}}{(1+K_sC)(1+K_{ox}C)} \quad \text{.....10}$$

Where $k_w$ is the first order rate constant in absence of the micelle, $K_s$ and $K_{ox}$ are the binding constants of HMBA and Mn(VII) with the SLS micelle respectively and 'C' is the analytical concentration of SLS. The rate in the aqueous medium '$k_w$' can be neglected compared to the other them i.e. $K_mK_sK_{ox}C$ and rearranged the above equation changes to eq.11

$$\frac{1}{k_\psi} = \frac{1}{k_mK_{ox}K_sC} + \frac{K_s + K_{ox}}{k_m K_s K_{ox}} + \frac{C}{k_m} \quad \text{.....11}$$

According to the eq. 11 the plot of $1/k_\psi$ against C i.e. [SLS] would show a minimum at the value $C_{min}$= 1($K_sK_o$)1/2 and $1/k_\psi$ would be linearly dependent on C for values of C greater than $C_{min}$. in fact the plot of $1/k_\psi$ against $C>C_{min}$ shows that a linear dependence exists between $1/k_\psi$ and C (Fig.3). The Slope of the plot used to compute $k_m$ and the intercept is equal to $K_s+K_o/K_sK_o$ using the slope and intercept values and the relationship Cmin= $1/(K_sK_o)^{1/2}$, K and $K_{ox}$ value. Large value of the binding constant of the HMBA can be explained by the penetration of the HMBA species into the hydrophobic core of the micelle. Whereas the smaller binding constant of the oxidant i.e. Mn (VII) may be due to binding at the surface of the micelle due to the hydrophilic forces as already mentioned. In addition to the low binding constant of the oxidant is due to the reduced interaction between the same charged species of the oxidant as well as anionic micelle at the surface. These observations are quite interesting because the binding constant for the oxidant calculated by Berezin model broadly remains same as that calculated by the modified Menger and Portnoy mode. The binding constant values and used to calculate the transfer free energy from water to micelle from the relation.

$(\mu^0_m - \mu^0_w) = -\Delta\mu^0 = RTIn(55.5K)$ .....12

Where K is the bonding constant

**Table-4**

Binding constant ($K_{ox}$) and $K_m$ in the micellar media for the oxidation of HMBA by $MnO_4^-$ in presence of SLS at different acidities.

$10^3[MnO_4^-]$= 1.0 mol.dm$^{-3}$, $10^2$[HMBA] = 1.0 mol.dm$^{-3}$, Temperature= 35$^0$C, Solvent= Aq.medium.

| $10^2[H^+]$ mol.dm$^{-3}$ | $K_{ox}$ | $10^2K_m$ |
|---|---|---|
| 5.0 | 9.54 | 9.23 |
| 15.0 | 3.55 | 13.70 |
| 25. | 4.28 | 16.64 |

$\Delta\mu^o$ for both HMBA and Mn(VII) have been computed and recorded in Table- 4. Small values of $\Delta\mu^o_{ox}$ are interpreted as surface interaction of the Solute[11-13] and the larger value of $\Delta\mu^o$s are taken to be indication of hydrophobic interaction[14-15] of the molecule in the core of the micelle. Hence HMBA appears bound to the micelle by hydrophobic interaction whereas Mn(VII) may be bound to the micelle by hydrophilic forces in the ionic region of the micelle. Inspection of the $k_m$ from modified Menger and Portnoy model.

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