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Kinetics of Oxidation of L - Menthol by Hypervalent Manganese in Aqueous Bisulfate and Micellar Media

J. Prasad[1], A. Ramakrishna Reddy[2], T. Venugopal Rao[3], K. C. Rajanna4

[1, 3]Department of Chemistry, Rayalaseema University, Kurnool- 518 007(A.P.) India

[4]Department of Chemistry, Osmania University, Hyderabad- 500007(T.S.) India

[2] M V S R Engineering College, Hyderabad - 501510(T.S.) India

Abstract: Present study authors have taken up the kinetics of oxidation of L- Menthol by hypervalent manganese (Mn(VII) or MnO_4^-) in aqueous acid and cationic micelle (cetyltrimethylammonium bromide (CTAB)) media. Reaction obeyed second order kinetics with first order dependence on [Menthol] and [Mn(VII)], and afforded menthone as product of oxidation. Addition of cationic (CTAB) micelle decreased the rate of oxidation. The mechanism in CTAB medium was explained by the stabilization of $(CTAMnO_4)$ due to the electrostatic interactions operating between anionic or (MnO_4^-) species and cetyltrimethyl ammonium cation $[(CH_3(CH_2)_{15}N(CH_3)_3)^+$ or $(CTA)^+]$ moiety. This species is more selective than strongly oxidizing $HMnO_4$ reagent, and could be useful to control over oxidation caused by $HMnO_4$. Mechanism of CTAB catalysed reaction could be explained by Menger – Portnoy's enzymatic model.

Keywords: Kinetics; Oxidation; Menthol, Mn(VII); CTAB micelles; rate enhancements;

I.   INTRODUCTION

Menthol (I) is a monocyclic terpene alcohol that occurs naturally in more than 100 essential oils, including spearmint and peppermint. The characteristic minty aroma and cooling qualities of synthetic *d, l*-menthol and the natural *l*-menthol isomer have resulted in its use in a variety of commercial products such as toothpaste, mouthwash, foods, cigarettes, and oral pharmaceutical preparations. Menthol is widely used in a variety of commercial products and foods. It is oxidized to menthone by oxidizing agents such as chromic acid or dichromate, though under some conditions the oxidation can go further and break open the ring. Kinetics of oxidation of menthol (I) has been taken up several groups workers in recent past [1-7].

(I) Menthol   (II) Menthone
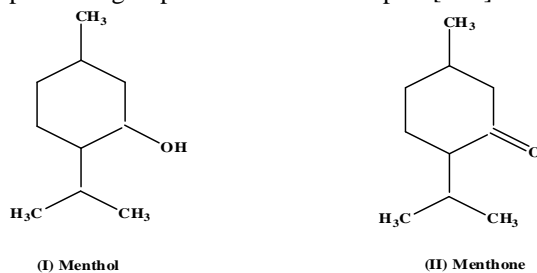
In many ways menthol (I) reacts like a secondary alcohol and oxidized by acid dichromate to corresponding ketone (menthone(II)). However, under   Menthol reacts in many ways like a normal secondary alcohol.

Potassium permanganate ($KMnO_4$) is a novel and eco-friendly hypervalent manganese reagent, which finds its use as an economically cheap and easily available laboratory desk-top reagent. Because of these reasons, $KMnO_4$ has received the attention of chemists all over the world almost since one century [8, 9]. Oxidation of several organic compounds with different functional groups by Mn(VII) has been reported by several research groups [10-18].

Surfactants are amphipathic molecules having both hydrophobic and hydrophilic properties, which have attracted growing attention of chemists, biologists, and biochemists to explore their use in chemical, biochemical, and biological research applications. In many cases their research findings revealed several analogies prevail between micellar and enzyme catalysis [19-30]. The salient properties of the surfactants that affect electron transfer reactions are localization and compartmentalization effect, pre-orientational polarity and counter-ion effect and the effect of charged interfaces [24–28].   The present paper deals with the micellar effects on $KMnO_4$ oxidation of menthol in the presence of bisulfate medium.

II.   EXPERIMENTAL DETAILS

Laboratory distilled water was further distilled over alkaline $KMnO_4$ and acidified $K_2Cr_2O_7$ in a sequence.   Menthol was procured from Sigma-Aldrich (India) through a local vendor. All the other chemicals were purchased from Avra or SD-fine chemicals (India).

1) *Kinetic Studies:* All the electronic absorption spectroscopic studies were made on double beam Shimadzu recording type spectrophotometer equipped with externally controlled thermostatic arrangement. Matched quartz cells were used to perform the study. Rate of disappearance of [Mn(VII)] was monitored spectrophotometrically by recording absorbance values as a function of time (A_t) at 530 nm.

2) *Product Analysis:* Product analysis was taken up under kinetic conditions. For this purpose, a mixture of fifty (50) mmol of menthol (dissolved in acetonitrile) and slight excess of KMnO4 (52 mmol dissolved in 10 mmol of $NaHSO_4$) were mixed in a reaction flask at thoroughly and allowed to react at 40^oC, till the reaction is completed, as ascertained by TLC as well constancy in the absorbance of reaction mixture. The contents were then extracted with dichloromethane. The organic layer was separated and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by flash column chromatography (SiO_2, ethyl acetate–hexane 1:2). A portion of the isolated product was dissolved in suitable amount of acetonitrile followed by the addition of excess (200 mL) of a saturated solution of Brady's reagent (2,4-dinitrophenylhydrazine) in 2 mol/ dm^3 acid and kept overnight in a refrigerator. The precipitated 2,4- dinitrophenyl hydrazone (DNP) was filtered, dried, weighed, recrystallized from ethanol. Obtained 2,4-DNP derivative was characterized by recording IR spectrum, which was in agreement with literature reports, indicating that the obtained product is L-menthone.

III.   RESULTS AND DISCUSSION

1) *Kinetic Observations And Order Of The Reaction:* Under pseudo conditions [Menthol] >> [Mn(VII)] in known concentration of KHSO4, the plots of [ln (A_0/A_t)] versus time were linear passing through origin indicating first order kinetics in [Mn(VII)] according to the following first order rate equation:

$$ln\ [(A_0)/\ (A_t)] = (k')\ t \qquad …. (1)$$

In this equation, (A_0) and (A_t) represent the absorbance values of [$KMnO_4$] at the time of initiating the reaction (zero time) and unreacted [$KMnO_4$] at a given instant of time during the reaction respectively (Fig.1). First order rate constants (k') were obtained from the slopes of these plots, which increased proportionately with the first power raised to [Substrate], indicating first order dependence on [Substrate], which could be seen from the linear plot of (k') versus [Substrate] (Figure.2)., which is in accordance with the following equation:

$$(k') = (k'')\ [Menthol] \qquad ….(2)$$

For any given temperature, second order rate constants (k'') at a fixed [$NaHSO_4$] , [NaF] were obtained from the slopes of above plots. Further the pseudo first order rate constants (k') were found to increase with an increase in [$NaHSO_4$], When the kinetics experiments are conducted at fixed concentrations of menthol, Mn(VII), sodium fluoride (NaF) as shown in the linear plot of (k') vs [$NaHSO_4$] (Figure 3). Graph shown in figure-3 is a straight line with positive slope and definite intercept on ordinate, according to the following empirical equation.

$$(k') = (k_0') + (k_b')\ [NaHSO_4] \qquad (3)$$

This observation confirms that in *situ* generated (H^+) due to the dissociation of [$NaHSO_4$] catalyses the rate of oxidation of menthol.

Fig.1- Plot of ln(A_0/A_t) vs Time in CTAB mediated oxidation of Menthol in HSO_4^- medium by Mn(VII) at 343 K
10^4[KMnO4] = 5.00 mol/dm^3 ; [Menthol] =0.01 mol/dm^3 ; 10^4 [CTAB] =5.00 mol/dm^3
[$NaHSO_4$] = 0.025 mol/dm^3 ; [NaF] = 0.05 mol/dm^3

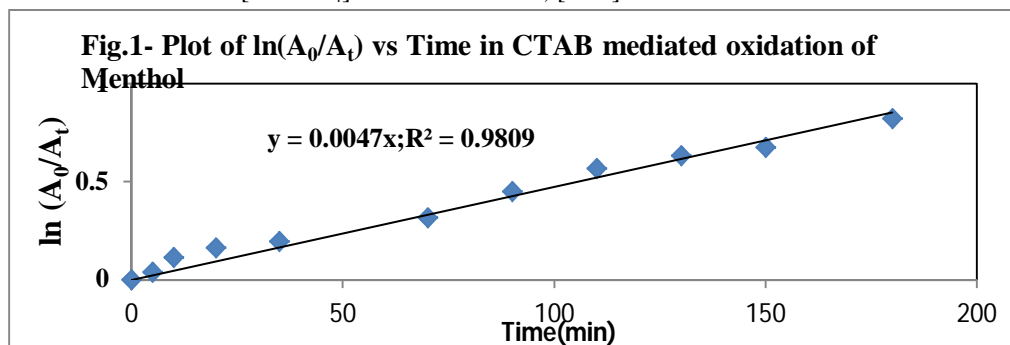Fig.1- Plot of ln(A_0/A_t) vs Time in CTAB mediated oxidation of Menthol

y = 0.0047x; R^2 = 0.9809

Fig.2- Plot of (k') vs [Menthol] in CTAB mediated oxidation of Menthol by Mn(VII) at 313K
10^4[KMnO4] = 5.00 mol/dm^3; [NaHSO$_4$] =0.025 mol/dm^3; 10^4 [CTAB] =5.00 mol/dm^3
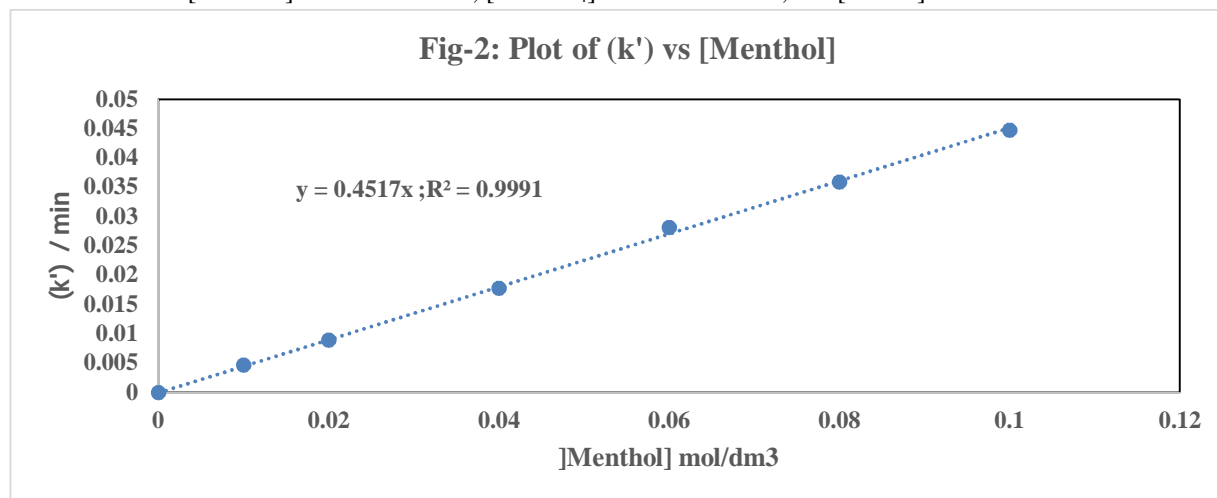

Fig-2: Plot of (k') vs [Menthol]

$y = 0.4517x ; R^2 = 0.9991$

Fig.3- Plot of (k') vs [NaHSO$_4$] in CTAB mediated oxidation of Menthol by Mn(VII)
10^4[KMnO4] = 5.00 mol/dm^3; [Menthol] =0.01 mol/dm^3; 10^4 [CTAB] =5.00 mol/dm^3

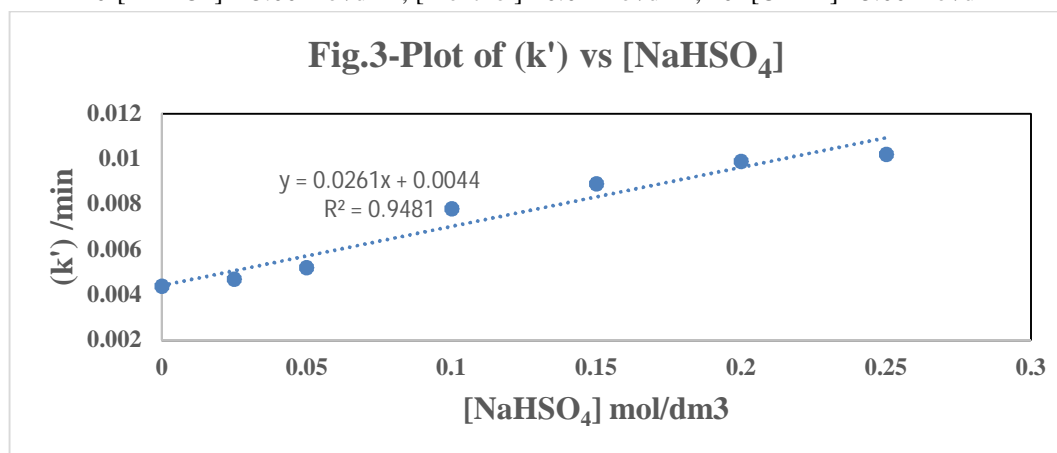**Fig.3-Plot of (k') vs [NaHSO$_4$]**

$y = 0.0261x + 0.0044$
$R^2 = 0.9481$

Fig.4- Plot of (k') vs [CTAB] mediated oxidation of Menthol by Mn(VII) at [NaHSO$_4$] in
Aqueous acetonitrile medium at 313K

**Fig-4: Plot of (k') vs [CTAB] oxidation of Menthol by Mn(VII) in
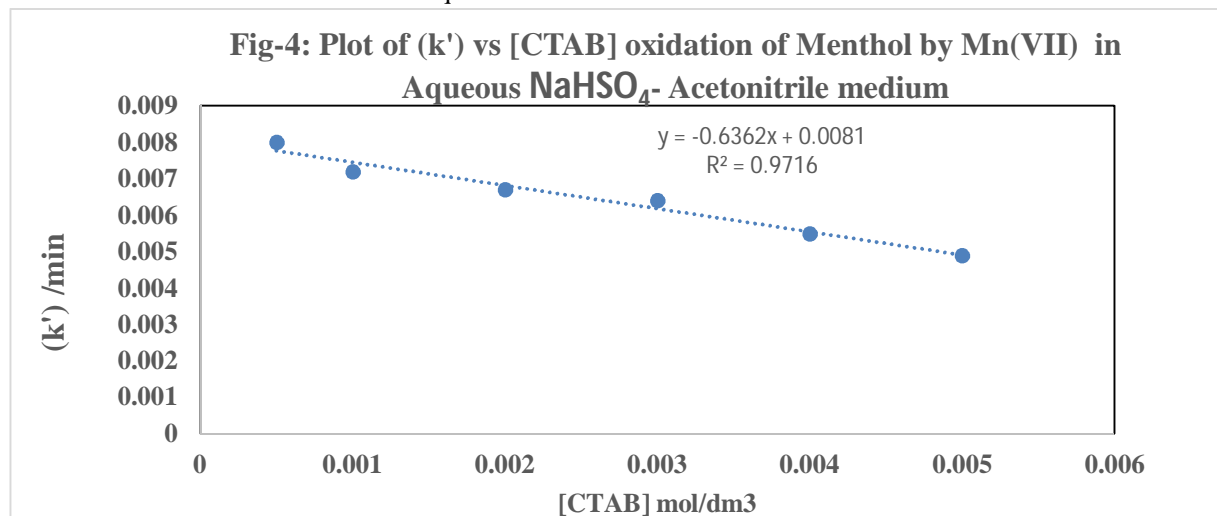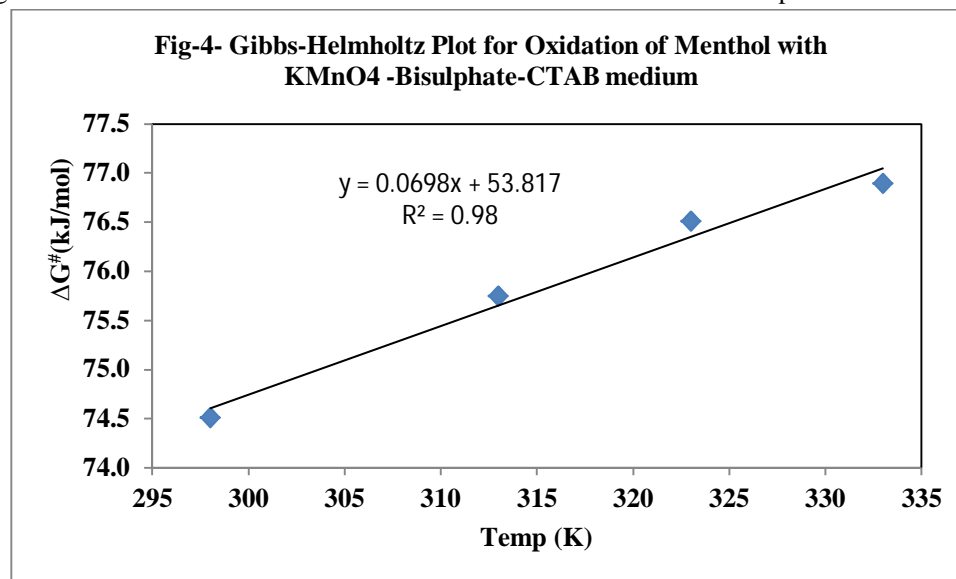Aqueous NaHSO$_4$- Acetonitrile medium**

$y = -0.6362x + 0.0081$
$R^2 = 0.9716$

Fig-5- Gibbs-Helmholtz Plot for Oxidation of Menthol with KMnO4 -Bisulphate-CTAB medium

Fig-4- Gibbs-Helmholtz Plot for Oxidation of Menthol with KMnO4 -Bisulphate-CTAB medium
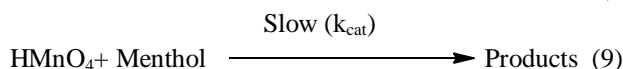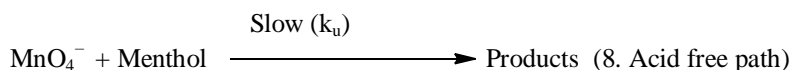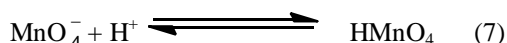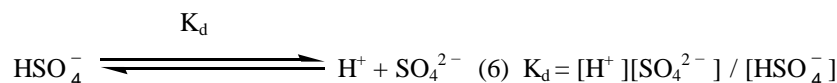
$y = 0.0698x + 53.817$
$R^2 = 0.98$

2) *Reactive Species and Mechanism of Oxidation:* In aqueous medium bisulfate dissociates to release proton (H^+) and (SO_4^{2-}) as shown in the following dissociation step,

$$HSO_4^- \xrightleftharpoons{K_d} H^+ + SO_4^{2-} \quad (4) \quad K_d = [H^+][SO_4^{2-}] / [HSO_4^-]$$
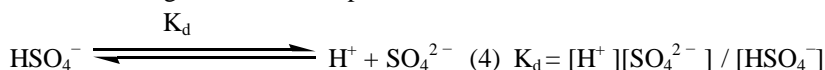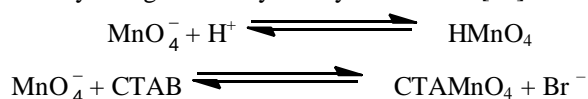
It is well known that potassium permanganate ($KMnO_4$) exists as permanganate anion (MnO_4^-). In the present experimental conditions, permanganate anion (MnO_4^-) could be protonated by abstracting proton released from the dissociation of bisulfate ion. The increase in the pseudo first order rate constant (k') with an increase in [H^+], could be due to the protonation of the oxidant resulting in the formation of a more powerful oxidant (acid permanganate or permanganic acid) $HMnO_4$ due to the protonation of MnO_4^- according to the following equilibrium:
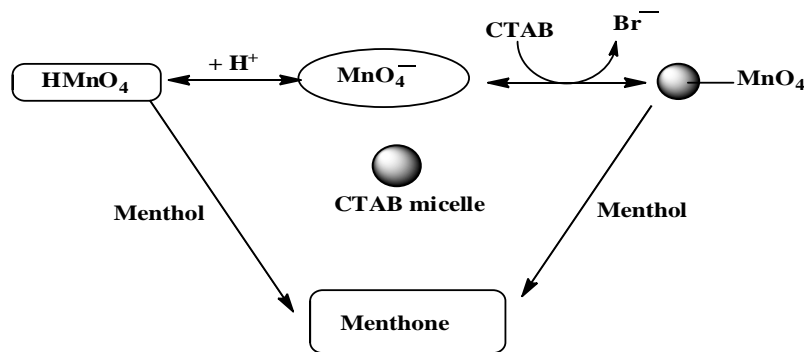
$$H^+ + MnO_4^- \rightleftharpoons HMnO_4 \quad (5)$$
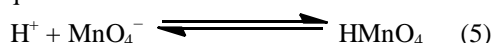
This type of explanation has also been given in the oxidation of several substrates by permanganate (MnO_4^-) in acid media.

$$HSO_4^- \xrightleftharpoons{K_d} H^+ + SO_4^{2-} \quad (6) \quad K_d = [H^+][SO_4^{2-}] / [HSO_4^-]$$

$$MnO_4^- + H^+ \rightleftharpoons HMnO_4 \quad (7)$$

$$MnO_4^- + Menthol \xrightarrow{Slow (k_u)} Products \quad (8. \text{ Acid free path})$$

$$HMnO_4 + Menthol \xrightarrow{Slow (k_{cat})} Products \quad (9)$$

In the above sequence of mechanistic steps, step (8) shows the reaction between (MnO_4^-) i.e., acid-free Mn(VII) and menthol to give products. But, in our experimental studies indicated that the acid –free MnO_4^- reaction menthol (step-8) could not occur even at higher temperatures. Then we have tried the reactions using $NaHSO_4$ as additive. Here also the reactions did not occur smoothly, suggesting that even acidified permanganate ($HMnO_4$) oxidation path (step -9) us not likely. Then we tried with cetyl trimethyl ammonium bromide ($C_{19}H_{42}NBr$ – CTAB) as additive in the presence as well as absence of $NaHSO_4$. The reactions occurred smoothly under these conditions. In view of these observations, we feel that the reaction occurs through the following steps, which could also be further supported by Menger-Portnoy's enzymatic model[29]..

$$MnO_4^- + H^+ \rightleftharpoons HMnO_4$$

$$MnO_4^- + CTAB \rightleftharpoons CTAMnO_4 + Br^-$$

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$HMnO_4$ $\xleftrightarrow{+ H^+}$ MnO_4^- $\xleftrightarrow{CTAB \quad Br^-}$ $\cdot MnO_4$

CTAB micelle

Menthol   Menthol

Menthone

Scheme-1: [CTAB] mediated oxidation of Menthol by Mn(VII) in presence of NaHSO₄

Thus the foregoing discussions point out that the oxidation of menthol proceeds through the synergistic effect of both CTAB and NaHSO₄. This point could also be supported from two important observations: (1) Liner plot of (k') vs [NaHSO₄] in known CTAB concentration (Figure-3), which revealed a straight line with positive slope and intercept on ordinate. (2) Liner plot of (k') vs [CTAB] in known NaHSO₄ concentration (Figure-4), which revealed a straight line with negative slope and intercept on ordinate. Further the negative slope in figure-4 may also indicate that an increase in [CTAB] stabilizes (CTA-MnO₄) species which enhances the selectivity of Mn(VII) over strong oxidizing (HMnO₄) species. It is also interesting to mention that the plot of (k') vs [Menthol] afforded a straight line passing through origin (as shown in figure-2) under fixed concentrations   of [NaHSO₄] and [CTAB]. This shows that at fixed concentrations   of [NaHSO₄], [CTAB] and temperature reaction followed second order kinetics with first order dependence on [Menthol] and [Mn(VII)]. Second order rate constants (k) were determined at different temperatures, which increased with temperature as suggested by Arrhenius theory of temperature effect on reaction rates. Eyring's theory of reaction rates [31-33] is used for the computation of free energy of activation ($\Delta G^{\#}$) at any specific temperature (T),

$$k = (k_t)\,(RT/Nh)\,\exp\,(-\Delta G^{\#}/RT) \quad \text{……..} \quad (10)$$

(Where the transmission coefficient (k_t) is generally equal to unity). Taking natural logarithms of equation (6), ($\Delta G^{\#}$) equation could be rearranged as,

$$\Delta G^{\#} = RT\ln\,(RT/Nhk) \qquad \text{.......} \quad (11)$$

Substitution of proper values of R, N, and h values (SI units) into equation (7), $\Delta G^{\#}$ could be again simplified to equation (8),

$$\Delta G^{\#} = 8.314 \times T[23.7641 + \ln(T/k)] \quad \text{……} \quad (12)$$

Second order rate constants (k) and computed ($\Delta G^{\#}$) values at various temperatures are compiled in Table-1.

Table 1: Temperature dependant rate constants and activation parameters
10^4[KMnO4] = 5.00 mol/dm^3 ; [Menthol] = 0.01 mol/dm^3 ; [NaHSO₄] =0.125 mol/dm^3 ;
10^4 [CTAB] =5.00 mol/dm^3

Temp (K)	(k) (dm³/mol/min)	$\Delta G^{\#}$ (kJ/mol)	GH Eq.	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/K/mol)
298	0.54	74.5			
313	1.49	75.7	y = 0.0698x +	53.8	- 69.8
323	2.85	76.5	53.817		
323	6.01	76.9			

At this stage enthalpy and entropies of activation ($\Delta H^{\#}$ and $\Delta S^{\#}$) values could be obtained from the Gibbs – Helmholtz plot of ($\Delta G^{\#}$) versus temperature (T) according to equation (13).

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad \text{… (13)}$$

Accordingly, the plot of ($\Delta G^{\#}$) versus (T) should give a straight line with negative slope ($\Delta S^{\#}$) and intercept ($\Delta H^{\#}$) on ordinate. But in practice, either positive or negative slope may be obtained depending on the nature of the transition state.   If the slope is negative, magnitude of entropy of activation ($\Delta S^{\#}$) is positive and *vice-versa*. Positive ($\Delta S^{\#}$) shows a dissociative mechanism, and a

non-rigid or loosely bound transition state in which reactant molecules move randomly by making it unstable. On the contrary, negative magnitude of $(\Delta S^{\#})$ generally suggests greater solvation of the transition state, followed by an associative mechanism in which two reaction partners form a single activated complex [31-33].

IV. CONCLUSIONS

In summary, we have studied the kinetics of Mn(VII) triggered oxidation of menthol in aqueous bisulfate and organized CTAB micelles. Reaction followed second order kinetics with first order dependence on [Menthol] and [Mn(VII)] at fixed concentrations of [NaHSO$_4$], [CTAB]. Reaction did not occur smoothly in the absence of either [NaHSO$_4$] or [CTAB]. Mechanism of oxidation is explained in the lines of Menger-Portnoy's enzymatic model.

V. ACKNOWLEDGMENTS

A. Statement For Conflict Interest
Authors declare that they do not have any conflict of interest.

REFERENCES

[1] Sandborn, L. T. "l-Menthone". Org. Synth. 1929, 9, 52, DOI: 10.15227/orgsyn.009.0052
[2] Brown, H. C.; Garg, C. P.; Liu, K.-T. J. Org. Chem., 1971, 36, 387–390. doi:10.1021/jo00802a005
[3] Pecar, D.; Goresk, A. Chem. Eng. Comm., 2014, 201,1548–1554, 2014
[4] Read, J. Chem. Rev., 1930, 7, 1–50. doi:10.1021/cr60025a001
[5] Cristina Geiger, H.; James S. Donohoe, J. H. J. Chem. Educ. 2012, 89, 1572-1574
[6] Haut, S. H. J. Agric. Food Chem. 1985, 33, 278-280
[7] Prabhu, D. V.; Tandel, M.A.; Parbat, H.A; Gupta, H.; Uchil, M.H. Asian J. Chem., 2014, 26, S6-S8
[8] Stewart, R. "Oxidations in Organic Chemistry," K. B. Wiberg, (Ed.), 1965, Academic Press, London
[9] Dash, S.; Patel, S.; Mishra, B. K. Tetrahedron., 2009, 65, 707–739
[10] Senguptha., K. K.; Khamurain, D. K.; Mukherjee, D. C. Indian J. Chem. 1975, 13, 348
[11] Verma, R. S.; Reddy, M. J.; Shastry, V. R. J. Chem. Soc. Perkin Trans. 2, 1976, 469.
[12] Banerji, K. K. J. Chem. Soc. Perkin Trans. 2, 1973, 435
[13] Banerji, K. K. Bull. Chem. Soc. Jpn. 1973, 46, 3623
[14] Lee, D.G.; Chen, T. J. Org. Chem. 1991, 56, 5341-5345
[15] Hassan, R. M.; Mousa, M. A.; Wahdan, M. H. J. Chem. Soc. Dalton Trans. 1988, 605
[16] Surender Rao V.; Sethuram, B.; Navaneeth. Rao, T. Int. J. Chem. Kinet. 1979, 11, 165.
[17] Subba Rao, P. V. Z. Phys. Chem. (Leipzig), 1971, 246, 352.
[18] Hassan, R. M. Can. J. Chem. 1991, 69, 2018.
[19] Attwood, D.; Florence, A. T. Surfactant Systems their Chemistry Pharmacy and Biological Properties, Chapman and Hall, NY, 1983.
[20] Fendler, J. H. Membrane Mimetic Chemistry, Characterization and Applications of Micelles, Microemulsions, Monolayers, Bilayers, Vescicles, Host-guest Systems and Polyions, Wiley, NY, 1982.
[21] Bunton, C. A. Catal. Rev. Sci. Eng. 1979, 20, 1.
[22] Richmond, W.; Tondre, C.; Krzyzanowska, E.; Szymanowski, J. J. Chem. Soc. Faraday Trans. 1995, 91, 657.
[23] Bunton, C. A. J. Mol. Liq. 1997, 72, 231.
[24] Das, A. K.; Roy, A.; Saha, B. Trans. Met. Chem. 2001, 26, 630–637
[25] Malik, M. A.; Khan, Z. Colloids. Surfaces B: Biointerfaces 2008, 64, 42–48
[26] Bunton, C. A.; Savelli, G. Adv. Phys. Org. Chem. 1987, 22, 213–309.
[27] Mukherjee, K.; Ghosh, S. K.; Ghosh, A.; Saha, R.; Bhattacharya, S. S.; Laskar, S.; Saha, B. Int. J. Chem. Kinet. 2013, 45, 175–186
[28] Nandi, R.; Laskar, S.; Saha, B. Res Chem Intermed. 2017, 43, 1619.
[29] Menger, F. M.; Portony, C. E. J. Am. Chem. Soc. 1967, 89, 4698.
[30] Piszkiewicz, D. J. Am. Chem. Soc. 1977, 99, 7695.
[31] Glasstone, S, Laidler, K. J. , Eyring, H. Theory of Rate Processes. McGraw Hill & Co., New York, 1961.
[32] Laidler, K. J. Chemical Kinetics. Pearson Education, Singapore, 2004.
[33] Espenson, J. H. Chemical Kinetics and Reaction Mechanisms, McGraw-Hill, (2002), p.156-160

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