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Oxidation ofPropionaldehyde by Potassium Permanganate in Micellar Medium: A Kinetic Study

Sarika Goyal*, Dr. Geetha Sarasan*
**Department of Chemistry, Govt. Holkar Science College, Indore-452001, M.P., India*

Abstract: *The kinetics of oxidation of propionaldehyde by potassium permanganate in acidic medium and in presence of cationic surfactant, cetyl pyridinium bromide (CPB) has been studied in pseudo first order reaction condition by UV-Visible spectrophotometer. In this paper,the effect of [propionaldehyde], [potassium permanganate], [sulphuric acid], [CPB] and temperature on oxidation of propionaldehydehave been reported. The Rate of reaction increase with increase in concentration of propionaldehyde and acid. Rate of reaction remains almost constantwith increase in concentration of potassium permanganateat pseudo first order conditions.The reaction is first order with respect to oxidant and fractional order with respect to substrate. The effect of surfactant is found to be rate enhancing. The positive value of co-oprativity obtained from piszkiewicz model shows premicellar catalysis in this case. The salt effect has been studied and it is found that in the absence of surfactant the salts studied have no effect on the rate of the reaction but in the presence of surfactant, the rate of reaction increases with the increasing concentration of salts. From the study of effect of temperature on the reaction, various kinetic and thermodynamic parameters are calculated and summarised. From the results obtained, a plausible mechanism is proposed.*

Keywords: *cetyl pyridinium bromide, kinetic study, $KMnO_4$, propionaldehyde.*

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I. Introduction

Various researchers have studied biologically important oxidation-reduction reaction in the absence and presence of micellar medium. Now-a-days surfactant has become a very interesting subject for investigation due to their catalytic efficiency at a certain concentration in solution. Monomers of surfactants aggregates to form micelle and one of the most important property of micelle is their ability to effect the rate of reaction. The kinetics of oxidation of aldehydes by various oxidants like oxone[1], potassium permanganate[2,3], chloramine-T[4], BIDC[5], BTMACB[6], hexacyanoferrate (III)[7], H_2O_2[8], quinolinium dichromate (QDC)[9], Cr (IV), V(V), Co (III)[10], 1-bromobenzimidazole[11] etc. have been reported by many researchers. But there are only a few in the presence of surfactant[12-14]. So the present effort is to study the kinetics of oxidation of propionaldehyde by $KMnO_4$in presence and absence of cetyl pyridinium bromide (CPB).

II. Experimental

All chemicals used in this experiment were AR Grade. The stock solutionsof propionaldehyde, $KMnO_4$, sulphuric acid and surfactant (CPB) were prepared in double distilled water. Solution of $KMnO_4$ was stored in brown bottle and covered with black paper to avoid any photochemical decomposition. The reaction was started with the addition of oxidant ($KMnO_4$) in reaction mixture and the unreacted $KMnO_4$ was estimated spectrophotometrically at various intervals of time. Ostwald's isolation method was used to study the reaction. The effect of a particular reactant was studied by varying its concentration keeping constant concentration of all other reactants.

III. Results and Discussion

Effect of [$KMnO_4$] on the reaction rate:

To study the effect of $KMnO_4$ concentration on the reaction rate, the reaction was conducted at different initial concentration of $KMnO_4$keeping the concentration of all other reactants constant in presence and absence of the surfactant, CPB. The k values obtained are almost constant (Table 1) and the plot of k vs. [$KMnO_4$] is linear which shows the order of reaction is first withrespect to $KMnO_4$both in the presence and absence of the surfactant (Fig.1).

Table 1

Effect of [$KMnO_4$]		
[C_2H_5CHO] = 0.001 N, [H_2SO_4] = 0.5 N, [CPB] = 0.0001 N at Temperature = 298 K		
[KMnO4]	**k value (without CPB)**	**k value (with CPB)**
0.0001	0.024	0.026
0.0002	0.020	0.022
0.0003	0.016	0.022
0.0004	0.015	0.019
0.0005	0.012	0.018

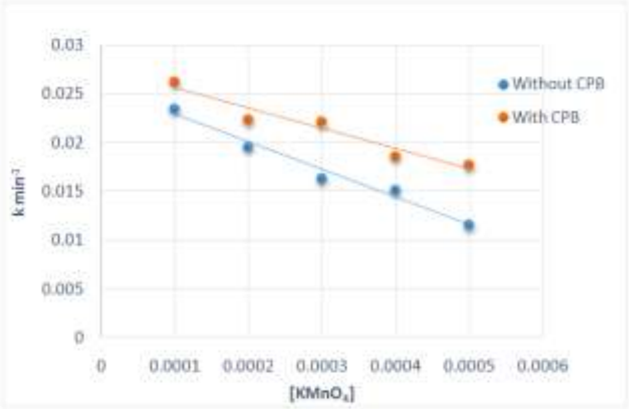

Fig. 1Effect of [$KMnO_4$]

Effect of [C_2H_5CHO]on the reaction rate:

The oxidation of propionaldehyde by $KMnO_4$ in acidic medium has been investigated and the effect of [propionaldehyde] on the reaction rate was studied byvarying the initial concentration of propionaldehyde with constant concentration of $KMnO_4$ and sulphuric acid in the presence and absence of CPB.The rate of reaction increases with increase in concentration of propionaldehyde in both cases (i.e. in the presence and absence of the surfactant).At lower concentrations of aldehyde, the rate is almost same in both the cases studied but at higher concentrations, eventhough the rate increases with increase in aldehyde concentration, the rate in the presence of CPB is less than that in the absence of CPB (Table 2). The plot of log k vs.log [C_2H_5CHO] isa straight line(Fig.2). From the graph it is clear that the order of the reaction with respectto propionaldehyde is fractional in both the conditions. Michaelis-Menten plot 1/k vs. 1/[C_2H_5CHO] gives straight line with an intercept (Fig.3), which shows the formation of an intermediate complex[15].

Table 2

Effect of [propionaldehyde]		
[H_2SO_4] = 0.5 N, [$KMnO_4$] = 0.0001 N, [CPB] = 0.0001 N at Temperature = 298 K		
3 + log [C_2H_5CHO]	**2 + log k (without CPB)**	**2 + log k (with CPB)**
0.00	0.37	0.42
0.30	0.57	0.50
0.48	0.64	0.67
0.60	0.81	0.68
0.70	0.93	0.71

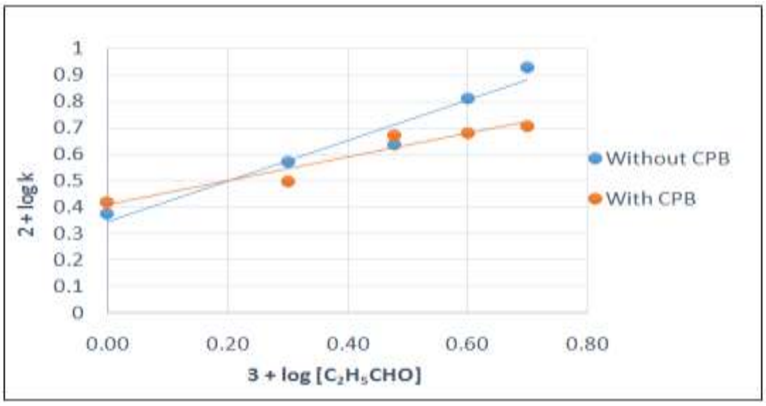

Fig. 2 Effect of [Propionaldehyde]

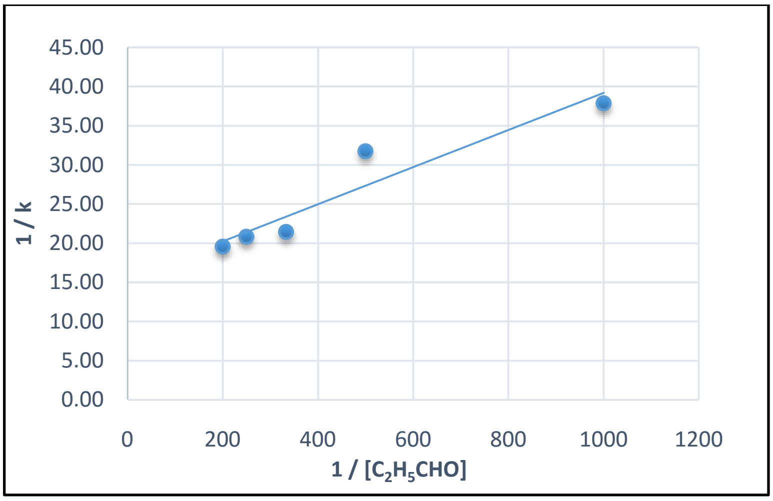

Fig. 3 Michaelis-Menten plot

Effect of [H_2SO_4] on the reaction rate:

Effect of variation of sulphuric acid was studied on the oxidation of propionaldehyde at constant substrate and oxidant concentrations. The rate of reaction increases with increasing concentration of sulphuric acid in both cases (Table 3). A plot oflog k vs. log [H^+] is a straight line (Fig.4).

Table 3

Effect of [H_2SO_4]		
[C_2H_5CHO] = 0.001 N, [$KMnO_4$] = 0.0001 N, [CPB] = 0.0001 N at Temperature = 298 K		
1+log [Acid]	2 + log k (without CPB)	2 + log k (with CPB)
0.70	0.37	0.42
1.00	0.49	0.50
1.18	0.63	0.62
1.30	0.71	0.79
1.40	0.75	0.87

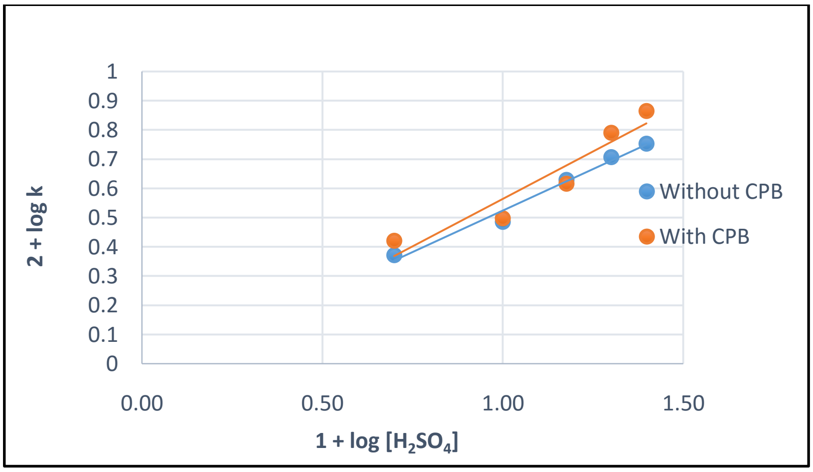

Fig. 4Effect of [H_2SO_4]

Effect of [CPB] on the reaction rate:

Effect of CPB concentration on the oxidation of propionaldehyde at constant concentration of other reactants has been studied. A plot oflog k vs.log [CPB] is straight line with positive slope indicates the catalytic activity of CPB in the present case (Fig.5). It is observed that the reaction rate increases even below the CMC value of the surfactant. The concentration of CPB was varied from 1×10^{-4} N to 5×10^{-4} N. its maximum concentration used is 5×10^{-4} N. this value is below the CMC of CPB which is reported in the literature as 9×10^{-4} mol/dm^{-3}. This may be due to the catalysis by premicellar aggregates. This premicellar catalytic effect is verified with the help of Piszkiewicz model[16]. According to this model, the plot of log(k_{obs}-k_o)/k_m-k_{obs} vs. log [CPB] is a straight line with positive slope (n = 2.5065) shows positive co-operativity (Fig.6). Thevalue of 'n' for premicellar catalysis is inbetween 1 and 6. In case of micellar catalysis this value should be more than 20.The positive co-operativity obtained also supports the substrate promoted micellization which is analogous to positive co-operativity in case of enzymatic reactions[17].

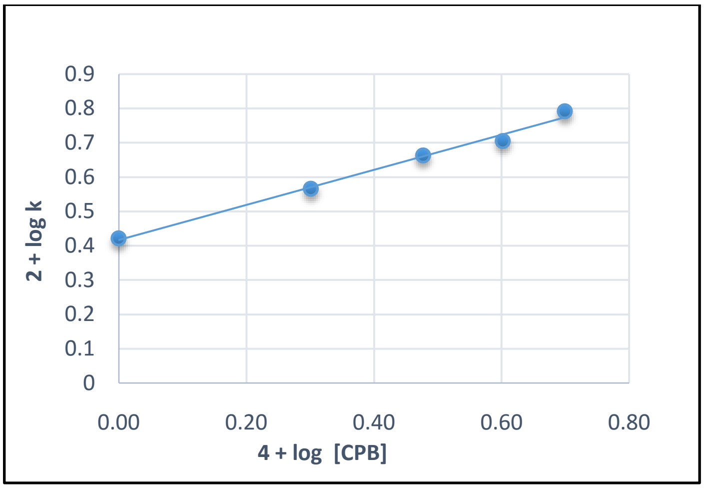

Fig. 5Effect of [CPB]

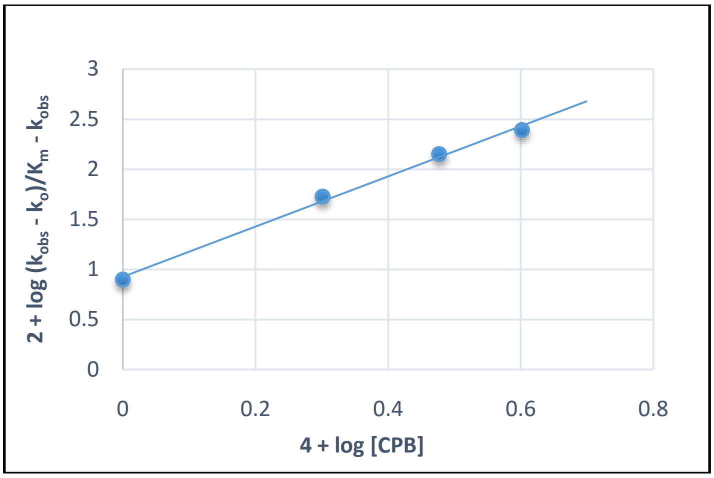

Fig. 6Piszkiewicz plot

Effect of temperature on the reaction rate:

To study the effect of temperature on the reaction rate, experiments were carried out at five different temperatures in presence and absence of CPB keeping the concentration of all other reactants constant. The pseudo first order rate constant values obtained are listed in table 4 and plot ofk vs.temperature (K) in Fig.7. It is clear from table 4 that the rate of reaction increases with increase in temperature in both the cases studied. But it is interesting to note that in the presence of CPB, the increase of reaction rate with respect to increase in temperature is greater than that in absence of the surfactant (CPB). It reveals that the increase in temperature is favouring the formation of premicellar aggregatesand hence enhancing the oxidation process.So the value of energy of activation is greater in the presence of CPB than its absence. Arrhenius equation is verified by plotting log k vs. 1/T (Fig.8).The thermodynamic activation parameters likeEnergy of activation($\Delta Ea^{\#}$), enthalpy of activation($\Delta H^{\#}$), Entropy of activation($\Delta S^{\#}$) and Free Energy of activation($\Delta G^{\#}$)are calculated and shown in Table 5. The negative value of entropy shows that the transition state is highly organised. The value of $\Delta Ea^{\#}$obtained in the presence of CPB supports the increase in the formation of premicellar aggregates and thereby increasing the premicellar catalysis.

Table 4

Effect of Temperature		
$[C_2H_5CHO] = 0.001$ N, $[H_2SO_4] = 0.5$ N, $[KMnO_4] = 0.0001$ N, $[CPB] = 0.0001$ N		
Temperature (K)	**K min^{-1} (without CPB)**	**k min^{-1} (with CPB)**
298	**0.024**	**0.026**
303	**0.036**	**0.045**
308	**0.052**	**0.066**
313	**0.061**	**0.095**
318	**0.075**	**0.106**

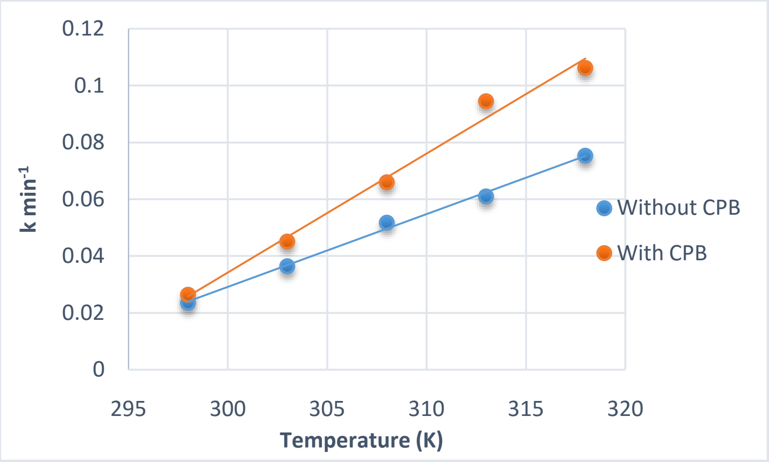

Fig. 7Effect of Temperature

Table 5

Thermodynamic and activation parameters					
[C_2H_5CHO] = 0.001 N, [H_2SO_4] = 0.5 N, [$KMnO_4$] = 0.0001 N, [CPB] = 0.0001 N at Temperature = 298 K					
	$\Delta Ea^{\#}$ KJ Mol^{-1}		**$\Delta H^{\#}$ KJ mol^{-1}**	**$\Delta S^{\#}$ J mol^{-1} K^{-1}**	**$\Delta G^{\#}$ KJ mol^{-1}**
	Calculated	**Graphical**			
Without CPB	**43.47**	**44.95**	**40.99**	**-130**	**79.75**
With CPB	**56.21**	**55.78**	**53.73**	**-86.52**	**79.51**

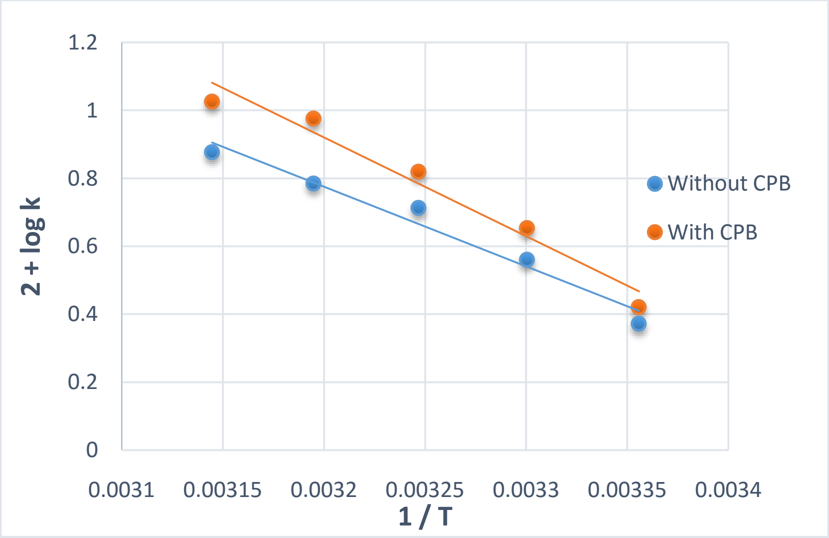

Fig. 8Arrhenius plot

Effect of salt on reaction rate:

The effect of salts likeKCl, KNO_3, $MgCl_2.6H_2O$ and $MgNO_3.6H_2O$ were studied by varying the concentration of salts from 0.02 to 1.0 N keeping constant concentrations of all other reactants(Table 6). In the absence of CPB is no effect of salt on the reaction rate but in the presence of CPC the rate is find to be increasing with the increase of salt. This shows that the salt favours the formation of premicellar aggregates.

Table6

Effect of Salt								
[C_2H_5CHO] = 0.001 N, [H_2SO_4] = 0.5 N, [$KMnO_4$] = 0.0001 N, [CPB] = 0.0001 N, Temperature = 298 K								
	k min^{-1} (without CPB)				**k min^{-1} (with CPB)**			
[salt] N	**KCl**	**KNO_3**	**$MgCl_2$**	**$Mg(NO_3)_2$**	**KCl**	**KNO_3**	**$MgCl_2$**	**$Mg(NO_3)_2$**
0.000	**0.024**	**0.024**	**0.024**	**0.026**	**0.026**	**0.026**	**0.026**	**0.026**
0.020	**0.021**	**0.059**	**0.036**	**0.019**	**0.070**	**0.056**	**0.099**	**0.102**

0.040	**0.021**	**0.043**	**0.016**	**0.015**	**0.071**	**0.074**	**0.116**	**0.072**
0.060	**0.022**	**0.031**	**0.018**	**0.016**	**0.080**	**0.079**	**0.129**	**0.062**
0.080	**0.023**	**0.027**	**0.019**	**0.013**	**0.084**	**0.082**	**0.181**	**0.060**
0.100	**0.030**	**0.034**	**0.025**	**0.013**	**0.108**	**0.098**	**0.193**	**0.129**

Reaction mechanism:

$$R-CHO+MnO_4^-+H_3O^+ \underset{k_{-w}}{\overset{k_w}{\leftrightharpoons}} [R-CHOH\ldots OMnO_3]+\ H_2O \text{ (Fast reaction)}$$

$$[R-CHOH\ldots OMnO_3] \overset{k_p}{\rightarrow} R-COOH+H^+ +\ MnO_3^- \text{ (Slow reaction)}$$

Case-I: In the absence of surfactant,

$$\frac{-d\,[oxidant]}{dt}=k_p[R-CHO\ldots OMnO_3]$$

Where, [R-CHO] is concentration of propionaldehyde, oxidant is an MnO_4^-, k_w is the rate constant for the formation of complex, k_{-w} is a dissociation constant for complex and k_p is rate constant for the formation of product. So the rate law of formation of complex as follows,

$$\frac{d\,[R-CHO\ldots OMnO_3]}{dt}=k_w[R-CHO][oxidant]-\ [k_{-w}+k_p][R-CHO\ldots OMnO_3]\ldots\ldots.(1)$$

$$k_w[R-CHO][oxidant]-\left[k_{-w}+k_p\right][R-CHO\ldots OMnO_3]=0$$

$$[R-CHO\ldots OMnO_3]=\frac{k_w[R-CHO][oxidant]}{\left[k_{-w}+k_p\right]}$$

By doing appropriate substitution,

$$\frac{-d\,[oxidant]}{dt}=\frac{k_pk_w[R-CHO][oxidant]_T}{\left\{\left[k_{-w}+k_p\right]+\ k_w[R-CHO]\right\}}$$

Where $[oxidant]_T$ is the total concentration of oxidant.

Case-II:In the presence of surfactant,

$$nD\ \leftrightharpoons\ D_n$$

$$D_n+A\ \leftrightharpoons\ D_n\,A$$

Where D_nA is the micelle associated aldehyde,

$$D_n\,A\ +\ oxidant\ \underset{fast}{\overset{k_c}{\rightarrow}}\ X'$$

$$X'\ \underset{slow}{\overset{k_{p'}}{\longrightarrow}}\ product$$

The total reaction rate can be expressed by,

$$\frac{-d\,[oxidant]}{dt}=\frac{k_pk_w[R-CHO][oxidant]_T}{\left\{\left[k_{-w}+k_p\right]+\ k_w[R-CHO]\right\}}+k_P{}'\,k_c[D_n\,A][oxidant]$$

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