



Effect of Cationic Surfactant on the Kinetics of Oxidation of Propionaldehyde

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(Received: 1 January 2010;

Accepted: 3 June 2011)

AJC-10019

The kinetics of oxidation of propionaldehyde by bromate in the absence of any surfactant has been studied and compared with the kinetic parameters observed in the presence of cationic surfactant of cetylpyridinium chloride (CPC). The observed rate law is:

$$-d[\text{BrO}_3^-] / dt = k'[\text{Aldehyde}][\text{BrO}_3^-]$$

where k' is a complex function of $[\text{H}^+]$ and $[\text{CPC}]$.

Key Words: Cetylpyridinium chloride, Kinetic, Propionaldehyde, Oxidation.

INTRODUCTION

The kinetics of oxidation of aldehydes has attracted interest of several research groups. The number of oxidants has been used to investigate the kinetics of these reactions. Rao *et al.*¹ studied the kinetics and mechanism of oxidation of aliphatic aldehydes by quinolinium bromochromate. The kinetics of oxidation of acetaldehyde, propionaldehyde and butyraldehyde by peroxomonosulphate in acid medium has been studied² and proposed the alternate routes for oxidation of aldehydes. Banerji and coworkers³⁻⁹ carried out a detail investigation on the kinetics of oxidation of aliphatic aldehydes by different oxidant. Sundaram¹⁰ studied the kinetics of oxidation of substituted benzaldehyde by acid bromate. The author has proposed the mechanism involving formation of an unstable bromate ester subsequently decomposing to products.

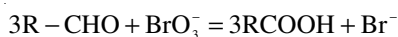
Due to great similarity with enzyme catalyzed reaction¹¹⁻¹⁵, surfactant catalyzed reactions have attracted interest of a number of researchers. The similarity of two reactions are based on both having similar structure containing hydrophobic core and polar group. The catalytic effect of micelles has been attributed to the fact that micelles bring the reacting molecule in the stern layer. On the other hand the inhibition may be observed due to adsorption of one reactant and repelling the other by the polar micellar surface. However, the role of micelles in the kinetics of oxidation of carbonyl compound has been studied in limited cases, whereas the micelles catalyzed hydrolysis of a large number of substrates has been fully investigated. The work in this paper was carried out to study the impact of cationic surfactant *i.e.*, cetylpyridinium chloride

(CPC) on the kinetic parameters and mechanism of oxidation of propionaldehyde by sodium bromate in acid medium.

EXPERIMENTAL

Sodium bromate (Fluka) cetylpyridinium chloride (Loba Chemie), sodium thiosulphate (Loba Chemie), H_2SO_4 (Galaxo) was used without further purification.

Double distilled water was used as solvent for the preparation of stock solutions. Bromate was measured iodometrically against standardized thiosulphate. Stock solution of CPC [0.01 mol dm^{-3}] was prepared and its required volume was used in a particular run. Kinetic experiments were performed under the varying conditions of [substrate] $[\text{H}^+]$, [CPC] and temperature. The concentration of oxidant was kept constant at $0.004 \text{ mol dm}^{-3}$ through out the kinetics experiments as variation in the concentration of oxidant has no effect on the observed rate constant. For the identification of products the calculated amount of bromate and acidified solution of propionaldehyde were mixed together under the reaction conditions identical to those of the kinetic experiment. The reaction mixture was kept over night at $35 \text{ }^\circ\text{C}$. The presence of corresponding acid was identified by their characteristic colour reaction¹⁶. No gas evolved during the oxidation of propionaldehyde in absence and presence of cetyl pyridinium chloride. Different ratio of propionaldehyde and sodium bromate were mixed in sulphuric acid medium at $35 \text{ }^\circ\text{C}$ and kept for 24 h. Estimation of unreacted bromate (as determined iodometrically) showed that one mole of aldehyde consume three moles of bromate under the experimental conditions as reported^{17,18}.



The experiments were carried out in glass stoppered coming conical flask at the required temperature. The temperature was maintained in a thermostatic water bath at $\pm 0.1^\circ\text{C}$ of the required value. Kinetic experiments were performed under pseudo-first order conditions employing 10-fold (or greater) excess of aldehyde over bromate. Duplicate kinetic runs showed that the rate was reproducible within $\pm 5\%$. The pseudo-first order rate constants, k_{obs} (s^{-1}) was computed from the linear least squares method of $\log R$ versus time (where R is the micro burette reading). Requisite amount of aldehyde and sulfuric acid were taken in a conical flask and measured amount of sodium bromate solution was taken in another flask. The two flasks were thermally equilibrated for 15 min in a thermostated water bath. Then sodium bromate solution was added to the flask containing aldehyde solution and was mixed thoroughly by shaking. The progress of the reaction was followed by measuring the unreacted bromate (by iodometric titration) in a measured aliquot (5 mL) of the reaction mixture at various time intervals. The reaction was studied up to 80% consumption of bromate.

RESULTS AND DISCUSSION

Ahmad *et al.*¹⁹ studied the kinetics of oxidation of formaldehyde and chloralhydrate by acid bromate both in absence and presence of sodium dodecyl sulfate (SDS) and cetylpyridinium chloride (CPC). Ahmad *et al.*²⁰⁻²⁷ also studied the oxidative decarboxylation of amino acid and oxidation of toluidines by different oxidants both in absence and presence of anionic, cationic and neutral surfactants. However, bromate, which can be used under the physiological condition to bring about oxidation of other aldehydes, toluidines and decarboxylation of amino acid has not been fully investigated in presence of anionic, cationic and neutral surfactants.

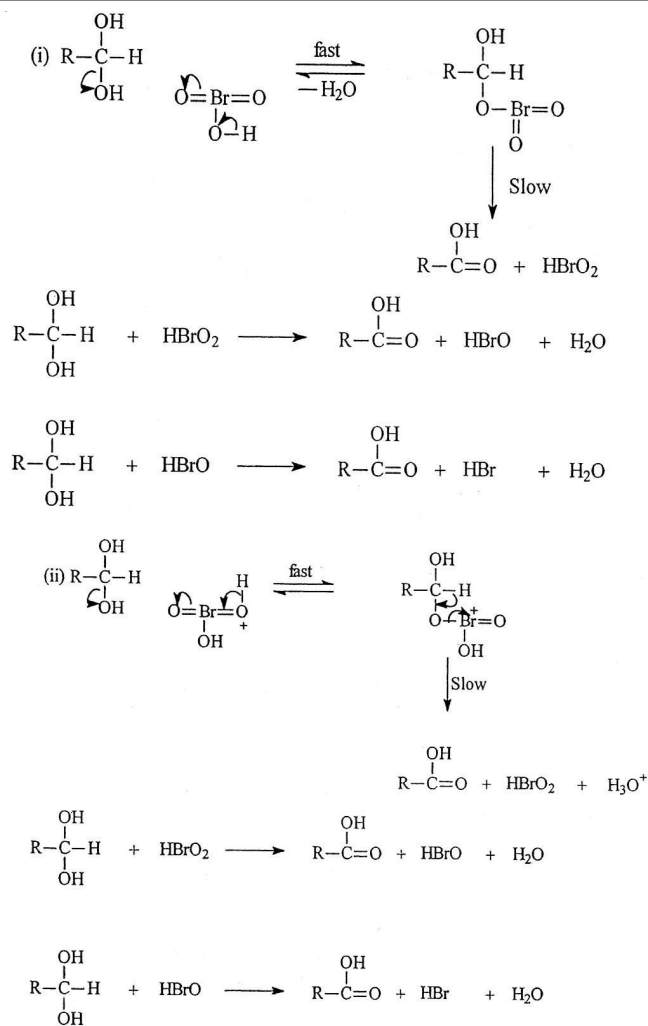
Kinetics of oxidation of propionaldehyde: In absence of any surfactant the kinetic features of the oxidation of propionaldehyde are found to be similar to those observed in the case of formaldehyde and chloral hydrate. However, in presence of CPC, it is observed that in the pre-micellar concentration region the oxidation rate remains unaffected. The reaction follows Menger's²⁸ equation in the post CMC region. It is further observed that SDS has no effect on the oxidation rate of propionaldehyde.

Kinetics of oxidation of propionaldehyde in absence of surfactant: As discussed earlier the oxidation of aldehydes by Br(V) in acid medium have two routes. One of these reaction paths is affected by $[\text{H}^+]$ whereas the other reaction path shows no dependence on $[\text{H}^+]$. In an earlier publication we have already described the mechanism oxidation of propionaldehyde of these two routes and their kinetic expressions¹⁹. The rate law for the oxidation of propionaldehyde in absence of any surfactant is given below:

$$\text{Reaction rate} = ({}^0k_{2p} + {}^0k_{2H}[\text{H}^+])[\text{AL}]_T[\text{BrO}_3^-]_T$$

From above the pseudo-first order rate constant ${}^{01}k_{\text{obs}}$ may be defined as,

$$\begin{aligned} {}^{01}k_{\text{obs}} &= ({}^0k_{2p} + {}^0k_{2H}[\text{H}^+])[\text{AL}]_T \\ \frac{{}^{01}k_{\text{obs}}}{[\text{AL}]_T} &= {}^0k_p = {}^0k_{2p} + {}^0k_{2H}[\text{H}^+] \end{aligned} \quad (1)$$



It is found that the plot between ${}^{01}k_{\text{obs}}$ and $[\text{AL}]_T$ at different temperatures are linear (Fig. 1). The dependence of ${}^{02}k_p$ on $[\text{H}^+]$ is also found to be linear (Fig. 2) and from the intercepts of these plots the values of ${}^0k_{2p}$ (rate constant associated with the reaction path which is unaffected by $[\text{H}^+]$) were determined and also from slopes the values of ${}^0k_{2H}$ (the rate constant associated with reaction path which is $[\text{H}^+]$ catalyzed) are obtained and presented in Tables 2 and 3. Mechanism is similar as reported in earlier publication¹⁹.

Kinetics of oxidation of propionaldehyde in presence of cetylpyridinium chloride: In presence of CPC, as discussed earlier, the oxidation rate remains unaffected in the pre-micellar concentration region. The catalytic effect is observed only in the post CMC region.

The observed kinetic features of the reaction in presence of CPC are fully justified by the mechanism given below. It is assumed that the reaction occurs in two phases. In the bulk the two routes mentioned earlier remain unaffected. On the other hand at the surface of the positively charged micelle of cetyl pyridinium chloride (CPC), the oxidation of propionaldehyde takes place. It is further assumed that the distribution of propionaldehyde between the micellar phase and aqueous phase is fast and at constant $[\text{H}^+]$, the reaction follows Menger's equation, which is derived as below:



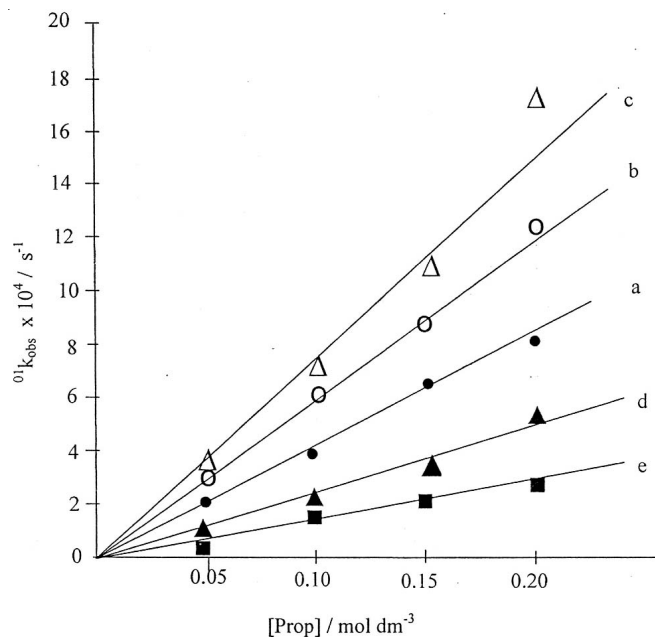


Fig. 1. Showing dependence of k_{obs} on $[Prop]$ at different temperatures and $[H^+]$ in absence of surfactant; $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$ (a) $[H^+] = 0.20 \text{ mol dm}^{-3}$ at 35 °C; (b) $[H^+] = 0.20 \text{ mol dm}^{-3}$ at 40 °C; (c) $[H^+] = 0.20 \text{ mol dm}^{-3}$ at 45 °C; (d) $[H^+] = 0.10 \text{ mol dm}^{-3}$ at 35 °C; (e) $[H^+] = 0.05 \text{ mol dm}^{-3}$ at 35 °C

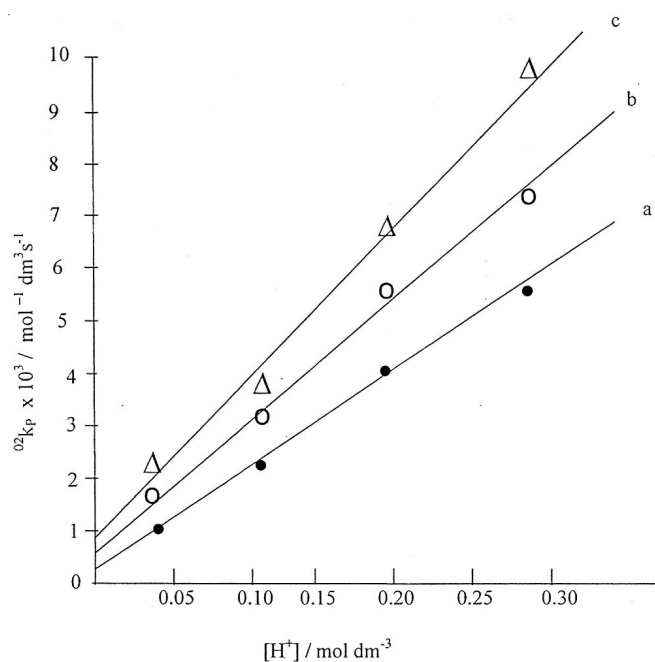


Fig. 2. Showing the variation of ${}^{02}k_p$ with $[H^+]$ at different temperatures in absence of surfactant at $[Prop] = 0.10 \text{ mol dm}^{-3}$; $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$ (a) 35 °C (b) 40 °C (c) 45 °C

K_{AH} defined as:

$$K_{AH} = \frac{[AL'H^+]}{[AL][H^+]}$$



where Cn^+ represents positively charged micelle of cetyl pyridinium chloride.

$$K_c = \frac{[AL'Cn^+]}{[AL'][Cn^+]}$$

Using the mass balanced equation the concentration of reactive species may be represented in terms of $[AL]_T$

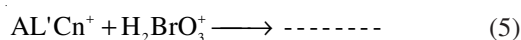
$$\begin{aligned} [AL]_T &= [AL'] + [AL'H^+] + [AL'Cn^+] \\ &= \frac{[AL'Cn^+]}{K_c[Cn^+]} + \frac{K_{AH}[H^+][AL'Cn^+]}{K_c[Cn^+]} + [AL'Cn^+] \\ &= \frac{(1 + K_{AH}[H^+] + K_c[Cn^+])[AL'Cn^+]}{K_c[Cn^+]} \end{aligned}$$

or,

$$[AL'Cn^+] = \frac{[AL]_T K_c [Cn^+]}{(1 + K_{AH}[H^+] + K_c[Cn^+])} \quad (4)$$

The rate expression of route 3 may be obtained as under:

Route-3



$$r_3 = {}^+k'[AL'Cn^+][H_2BrO_3^+]$$

$$\begin{aligned} &= \frac{{}^+k'K_c[Cn^+][AL]_T}{(1 + K_{AH}[H^+] + K_c[Cn^+])} \cdot \frac{K_{OX}K_{OXH}[H^+]^2[BrO_3^-]_T}{(1 + K_{OX}[H^+] + K_{OX}K_{OXH}[H^+]^2)} \\ &= \frac{{}^+k'K_{OX}K_{OXH}K_c[Cn^+][H^+]^2[AL]_T[BrO_3^-]_T}{1 + K_{OX}[H^+] + K_{AH}[H^+] + K_c[Cn^+] + K_{OX}K_c[Cn^+][H^+]} \\ &= \frac{{}^+k'K_{OX}K_{OXH}K_c[Cn^+][AL]_T[BrO_3^-]_T[H^+]}{(K_{OX} + K_{AH} + K_{OX}K_c[Cn^+])} \\ &= \frac{{}^+k'K_{OXH} \left(\frac{K_{OX}K_c}{K_{OX} + K_{AH}} \right) [H^+][Cn^+][AL]_T[BrO_3^-]_T}{1 + \left(\frac{K_{OX}K_c}{K_{OX} + K_{AH}} \right) [Cn^+]} \\ &= \frac{{}^+k'_m {}^+K_p[Cn^+][H^+][AL]_T[BrO_3^-]_T}{1 + {}^+K_p[Cn^+]} \quad (6) \end{aligned}$$

where,

$${}^+K_p = \left(\frac{K_{OX}K_c}{K_{OX} + K_{AH}} \right)$$

and ${}^+k'_m = ({}^+k'K_{OXH})$

Now the overall reaction rate in presence of CPC is given as:

$$\frac{-d[Br(V)]}{dt} = \frac{({}^0k_{2P} + {}^0k_{2H}[H^+] + {}^+k'_m {}^+K_p[H^+][Cn^+])[AL]_T[BrO_3^-]_T}{(1 + {}^+K_p[Cn^+])} \quad (7)$$

$$k_{obs} = \left(\frac{{}^0K_{2P} + {}^0k_{2H}[H^+] + {}^+k'_m {}^+K_p[H^+][Cn^+]}{1 + {}^+K_p[Cn^+]} \right) [AL]_T$$

$$\frac{k_{obs}}{[AL]_T} = \left(\frac{{}^0k_{2P} + {}^0k_{2H}[H^+] + {}^+k'_m {}^+K_p[H^+][Cn^+]}{1 + {}^+K_p[Cn^+]} \right)$$

$${}^{+2}k_p = \frac{{}^0k_{2P} + \{ {}^0k_{2H} + {}^+k'_m {}^+K_p[Cn^+][H^+] \}}{1 + {}^+K_p[Cn^+]}$$

At constant $[H^+]$

$${}^{+2}k_p = \frac{{}^{\circ}k_{2p} + \{{}^{\circ}k_{2H} + {}^+k_m {}^+K_p [Cn^+]\}}{1 + {}^+K_p [Cn^+]}$$

where

$${}^+k_m = {}^+k'_m [H^+]$$

$$({}^+k_p - {}^{\circ2}k_p) = \frac{{}^{\circ2}k_p + {}^+k_m {}^+K_p [Cn^+]}{(1 + {}^+K_p [Cn^+])} - {}^{\circ2}k_p$$

$$= \frac{{}^+k_m {}^+K_p [Cn^+] - {}^{\circ2}k_p {}^+K_p [Cn^+]}{(1 + {}^+K_p [Cn^+])}$$

$$({}^+2k_p - {}^{\circ2}k_p) = \frac{({}^+k_m - {}^{\circ2}k_p) {}^+K_p [Cn^+]}{(1 + {}^+K_p [Cn^+])}$$

$$\frac{1}{({}^+2k_p - {}^{\circ2}k_p)} = \frac{1}{({}^+k_m - {}^{\circ2}k_p)} + \frac{1}{({}^+k_m - {}^{\circ2}k_p)} \cdot \frac{1}{({}^+K_p [Cn^+])} + \frac{1}{({}^+k_m - {}^{\circ2}k_p)}$$

or

$$\frac{1}{({}^+2k_p - {}^{\circ2}k_p)} = \frac{1}{({}^+k_m - {}^{\circ2}k_p)} + \frac{1}{({}^+k_m - {}^{\circ2}k_p)} \cdot \frac{1}{({}^+K_p [Cn^+])}$$

$$\frac{1}{({}^{\circ2}k_p - {}^+2k_p)} = \frac{1}{({}^{\circ2}k_p - {}^+k_m)} + \frac{1}{({}^{\circ2}k_p - {}^+k_m)} \cdot \frac{1}{({}^+K_p [Cn^+])}$$

The concentration of micelles $[Cn^+]$ may be obtained using Shinoda and Hutchinson assumption²⁹.

$$[Cn^+] = \frac{(D_o - CMC)}{N}$$

$$\frac{1}{({}^{\circ2}k_p - {}^+2k_p)} = \frac{1}{({}^{\circ2}k_p - {}^+k_m)} + \frac{1}{({}^{\circ2}k_p - {}^+k_m)} \cdot \frac{N}{({}^+K_p (D_o - CMC))} \quad (8)$$

The above equation has been verified plotting reciprocal of $({}^{\circ2}k_p - {}^+2k_p)^{-1}$ versus $(D_o - CMC)^{-1}$, which is found to be linear giving a positive intercept. The values of ${}^+k_m$ and ${}^+K_p$ have been calculated using the intercept and slope of these plots at different temperatures and assuming further that the aggregate number 95 is not affected by change of temperature³⁰. These values have been presented in Table-1.

TABLE-1					
Temp. (°C)	${}^+K_p \times 10^6$ at $[H^+] = 0.05$ mol dm ⁻³	${}^+K_p \times 10^6$ at $[H^+] = 0.10$ mol dm ⁻³	${}^+K_p \times 10^6$ at $[H^+] = 0.20$ mol dm ⁻³	${}^+K_p \times 10^6$ at $[H^+] = 0.30$ mol dm ⁻³	${}^+k_p \times 10^2$
	35	1.90	1.90	1.80	
40	1.33	1.14	1.19	1.24	1.70
45	0.95	0.89	1.01	0.81	2.40

$$I_M = \frac{1}{({}^{\circ2}k_p - {}^+k_m)}$$

$$I_M = \frac{1}{{}^{\circ2}k_{2p} + {}^{\circ}k_{2H}[H^+] - {}^+k'_m[H^+]}$$

$$I_{M^{-1}} = {}^{\circ}k_{2p} + {}^{\circ}k_{2H}[H^+] - {}^+k'_m[H^+] \quad (8a)$$

where I_M is the intercept of Menger's equation.

$$S_M = \frac{1}{({}^{\circ2}k_p - {}^+k_m)} \cdot \frac{N}{{}^+K_p}$$

$$S_M = \frac{1}{\{{}^{\circ}k_{2p} - {}^{\circ}k_{2H}[H^+] - {}^+k'_m[H^+]\}} \cdot \frac{N}{{}^+K_p}$$

$$S_{M^{-1}} = \frac{{}^{\circ}k_{2p} {}^+K_p}{N} + \frac{\{({}^{\circ}k_{2H} - {}^+k'_m) {}^+K_p\} [H^+]}{N} \quad (8b)$$

where S_M is the slope of Menger's equation.

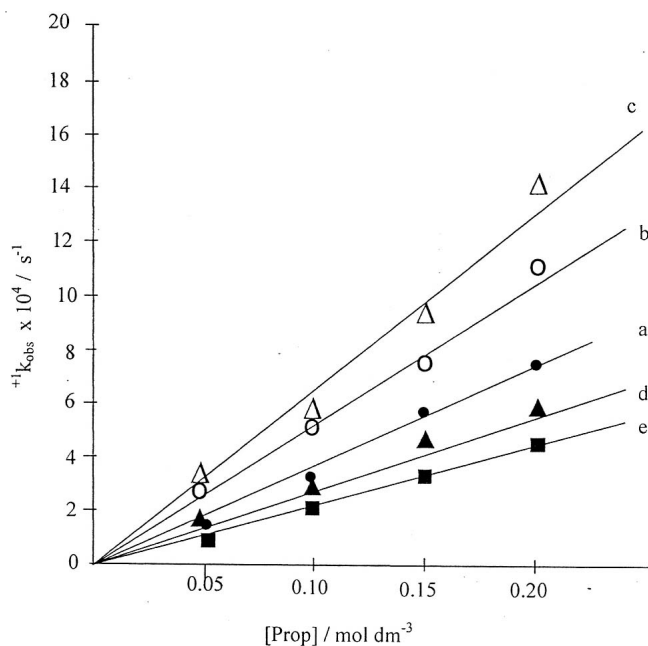


Fig. 3. Showing dependence of k_{obs} on $[Prop]$ at different temperatures in presence of CPC at $[H^+] = 0.20$ mol dm⁻³; $[NaBrO_3] = 4 \times 10^{-3}$ mol dm⁻³ (a) $[CPC] = 1 \times 10^{-3}$ mol dm⁻³ at 35 °C; (b) $[CPC] = 1 \times 10^{-3}$ mol dm⁻³ at 40 °C; (c) $[CPC] = 1 \times 10^{-3}$ mol dm⁻³ at 45 °C; (d) $[CPC] = 2 \times 10^{-3}$ mol dm⁻³ at 35 °C; (e) $[CPC] = 3 \times 10^{-3}$ mol dm⁻³ at 35 °C

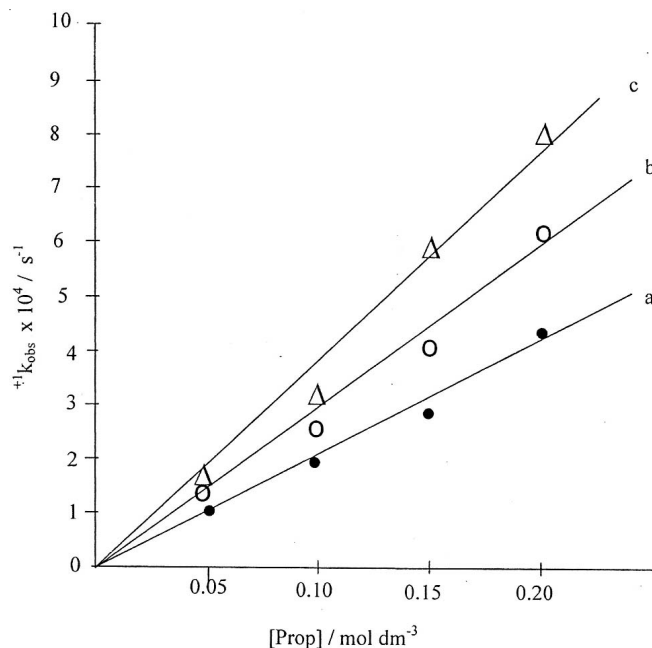


Fig. 4. Showing dependence of k_{obs} on $[Prop]$ at different temperatures in presence of CPC at $[H^+] = 0.10$ mol dm⁻³; $[NaBrO_3] = 4 \times 10^{-3}$ mol dm⁻³; $[CPC] = 1 \times 10^{-3}$ mol dm⁻³; (a) 35 °C (b) 40 °C (c) 45 °C

The eqn. 8 has been used to test the values of ${}^0k_{2P}$ (second order rate constant observed in absence of surfactants associated with reaction path not affected by $[H^+]$ and the value of ${}^0k_{2H}$ observed earlier. The eqn. 8 has been obtained under a constant $[H^+]$. Therefore, both the intercept and slope of the plot shown in Fig. 5 are $[H^+]$ dependent.

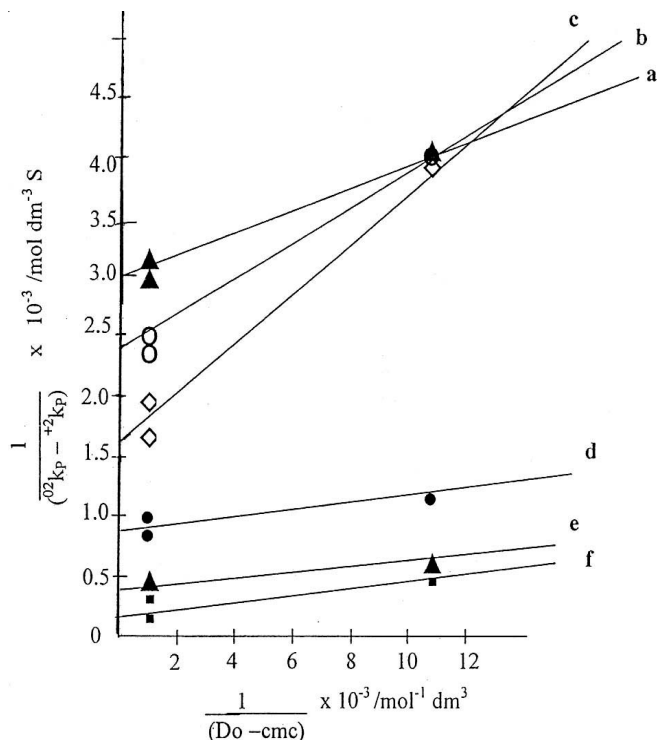


Fig. 5. Plot of $1/(k_p^0 - k_p^+2)$ vs. $1/(D_0 - cmc)$ at different temperatures and at different $[H^+]$; $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$; (a) $[H^+] = 0.05 \text{ mol dm}^{-3}$ at 35 °C; (b) $[H^+] = 0.05 \text{ mol dm}^{-3}$ at 40 °C; (c) $[H^+] = 0.05 \text{ mol dm}^{-3}$ at 45 °C; (d) $[H^+] = 0.10 \text{ mol dm}^{-3}$ at 45 °C; (e) $[H^+] = 0.20 \text{ mol dm}^{-3}$ at 45 °C; (f) $[H^+] = 0.30 \text{ mol dm}^{-3}$ at 45 °C

Using the value of intercept at different $[H^+]$ a plot between I_M^{-1} versus $[H^+]$ Fig. 6 used to calculate the values of rate constant mentioned above and has been presented in Table-2.

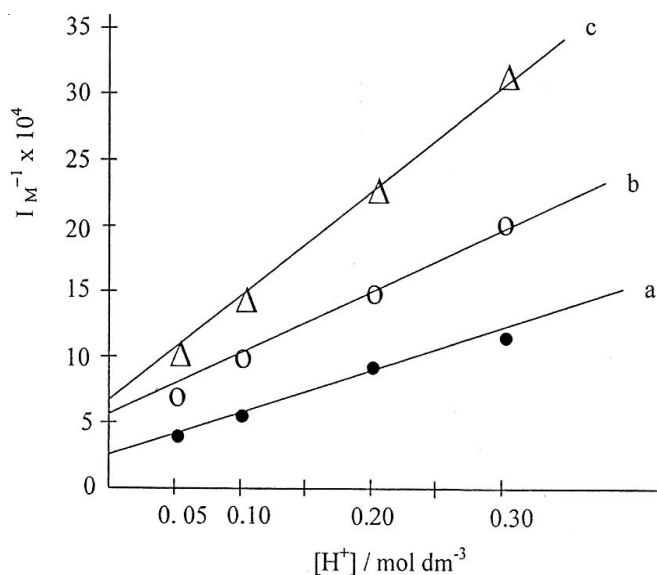


Fig. 6. Plot of I_M^{-1} vs. $[H^+]$ at different temperature (a) 35 °C (b) 40 °C (c) 45 °C

TABLE-2

Temp. (°C)	${}^0k_{2P}^* \times 10^4 \text{ S}^{-1} \text{ mol}^{-1} \text{ dm}^3$	${}^0k_{2P}^{**} \times 10^4 \text{ S}^{-1} \text{ mol}^{-1} \text{ dm}^3$
35	2.85	2.50
40	6.90	6.05
45	7.95	7.00

*Obtained using eqn. 1 in absence of CPC.

**Obtained using eqn. 8a in presence of CPC.

Similarly, from the eqn. 8b, the values of ${}^0k_{2H}$ have been obtained at different temperatures and presented in Table-3.

TABLE-3

Temp. (°C)	${}^0k_{2H}^* \times 10^4 \text{ S}^{-1} \text{ mol}^{-2} \text{ dm}^6$	${}^0k_{2H}^{**} \times 10^4 \text{ S}^{-1} \text{ mol}^{-2} \text{ dm}^6$
35	1.95	1.97
40	2.15	2.20
45	3.06	3.26

*Obtained using eqn. 1 in absence of CPC.

**Obtained using eqn. 8a in presence of CPC.

It appears that the oxidation rate of propionaldehyde in the presence of CPC is retarded due to the fact that propionaldehyde forms a complex with micellar aggregates (CMC³¹ of CPC is $9.0 \times 10^{-4} \text{ mol dm}^{-3}$ at 20 °C) and positively charged oxidizing species such as $H_2BrO_3^+$ is excluded from the micellar phase. It is appears that since the propionaldehyde is not attracted by negatively charged micelles of SDS of (CMC³² of SDS is $8.2 \times 10^{-3} \text{ mol dm}^{-3}$ at 25 °C) the reaction remains unaffected by the presence of sodium dodecyl sulfate. It is further assumed that the oxidizing species $HDBrO_3^-$ does not interact with propionaldehyde due to strong repulsion between carbonyl group of propionaldehyde and the negatively charged oxidizing species, $HDBrO_3^-$.

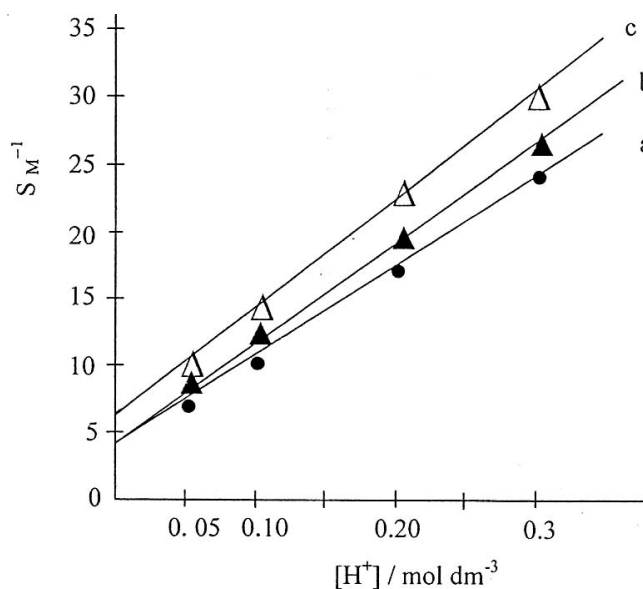


Fig. 7. Plot of S_M^{-1} vs. $[H^+]$ at different temperature (a) 35 °C (b) 40 °C (c) 45 °C

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