

Kinetics of Oxidation of Aldehydes in Absence and Presence of Surfactants

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The kinetics of oxidation of aldehydes by bromate in the absence of any surfactant has been studied and compared with the kinetic parameters observed in the presence of anionic surfactant of sodium dodecylsulphate (SDS) and 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 hydrogen ion concentration and surfactant concentration.

Key Words: Kinetics, Aldehydes, Surfactants.

INTRODUCTION

The kinetics of oxidation of aldehydes has attracted interest of several research groups. A number of inorganic and organic oxidants have been used to investigate the kinetics of these reactions. Ramachandram *et al.*¹ studied the kinetics of oxidation of acetaldehyde, propionaldehyde and butyraldehyde by peroxomonosulphate (PMS) in acid medium and proposed alternate routes for oxidation of aldehydes. Amalendu *et al.*² studied the kinetics of oxidation of benzaldehyde by acid bromate. The author has proposed the mechanism involving formation of an unstable bromate ester subsequently decomposing to products. Banerji and co-workers³⁻⁹ carried out a detailed investigation on the kinetics of oxidation of aliphatic aldehydes by different oxidants like pyridinium hypobromide perbromide, pyridinium bromochromate, pyridinium fluorochromate, N-bromoacetamide, N-bromobenzamide, N-chloroaryl sulfonamide and N-bromoaryl sulfonamide.

In view of the great similarity with enzyme catalyzed reactions¹⁰⁻¹³, the 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 close proximity (generally 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 very limited cases, whereas the micelle 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 anionic and cationic

surfactants on the kinetic parameters and mechanism of oxidation of formaldehyde and chloral hydrate by sodium bromate in acid medium.

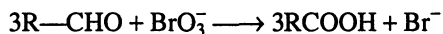
EXPERIMENTAL

Formaldehyde (E. Merck), chloral hydrate (G.S. Chemical), sodium bromate (Fluka), sodium dodecyl sulphate (Fluka), cetylpyridinium chloride (Loba Chemie), sodium thiosulphate (Loba Chemie), H_2SO_4 (Galaxo) were used without further purification.

For the preparation of stock solutions double distilled water was used as solvent. Bromate was measured iodometrically against standardized thiosulphate. The calculated amount of solid sodium dodecylsulphate (SDS) was added directly to the substrate solution. Stock solution of 0.01 mol dm^{-3} cetylpyridinium chloride (CPC) was prepared and its required volume was used in particular run. The concentration of oxidant was kept constant at $0.004 \text{ mol dm}^{-3}$ throughout kinetic experiments, as the variation in [oxidant] itself had no effect on the observed rate constant.

For the identification of the products, the calculated amount of bromate and acidified solution of aldehyde were mixed together under the reaction conditions identical to those of the kinetic experiment. The reaction mixture was kept overnight at 30°C . The presence of corresponding acid was identified by their characteristic colour reaction¹⁴. No gas was evolved during the oxidation of aldehyde in the absence and in the presence of surfactants.

Varying ratios of aldehyde and bromate were mixed in H_2SO_4 medium at 30°C and kept for 24 h. Estimation of unreacted bromate (as determined iodometrically) showed that one mole of aldehyde consumed three moles of bromate under experimental conditions as reported by Samaddar and Sondu^{2, 15}



All the reactions were carried out in a glass stoppered conical flask at the required temperature. The temperature was maintained in a thermostated water bath at $\pm 0.1^\circ\text{C}$ of desired 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 rates were reproducible to within $\pm 5\%$. The *pseudo*-first order rate constant, k_{obs} (s^{-1}), was completed by least squares method for $\log R$ vs. time (where R is the microburette reading). Requisite amount of aldehyde, sulphuric acid was taken in a conical flask and measured amount of bromate solution was taken in another flask. The two flasks were thermally equilibrated for 15 min in the thermostated water bath. The 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 (iodometrically) in a measured aliquot (5 mL) of the reaction mixture at various time intervals. The reaction was studied up to 80% consumption of bromate.

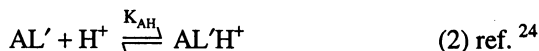
RESULTS AND DISCUSSION

Ahmad *et al.*¹⁶⁻²² studied the oxidative decarboxylation of amino acids by

different oxidants both in absence and in presence of SDS and CPC. However, bromate, which can be used under physiological condition to bring about decarboxylation of amino acid, has not been fully investigated in the presence of cationic and anionic surfactant.

Kinetics of Oxidation of Formaldehyde in the Absence of Surfactant

It appears that the oxidation of formaldehyde involves two different routes. One of these routes is independent of hydrogen ion concentration and the other route is acid catalyzed. In the acid medium aldehyde (AL) is present in three different forms involving the following equilibria:

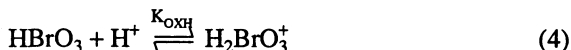
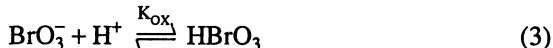


where AL' represents the hydrated and AL'H⁺ its protonated form. K_A and K_{AH} may be defined as

$$K_A = \frac{[AL']}{[AL]} \quad \text{and} \quad K_{AH} = \frac{[AL'H^+]}{[AL'][H^+]}$$

In case of formaldehyde and chloral hydrate K_A is too large⁶, therefore, it may be assumed that aldehyde is present only as AL(OH)₂, represented as AL'.

On the other hand the bromate as oxidant is also involved in the following equilibria²⁵:

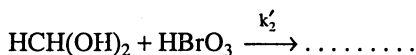


K_{OX} and K_{OXH} may be defined as

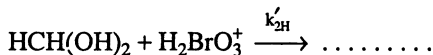
$$K_{OX} = \frac{[HBrO_3]}{[BrO_3^-][H^+]} \quad \text{and} \quad K_{OXH} = \frac{[H_2BrO_3^+]}{[HBrO_3][H^+]}$$

The above equilibria show that in the acid medium the active oxidising species with Br(V) oxidation state are BrO₃⁻, HBrO₃, H₂BrO₃⁺.

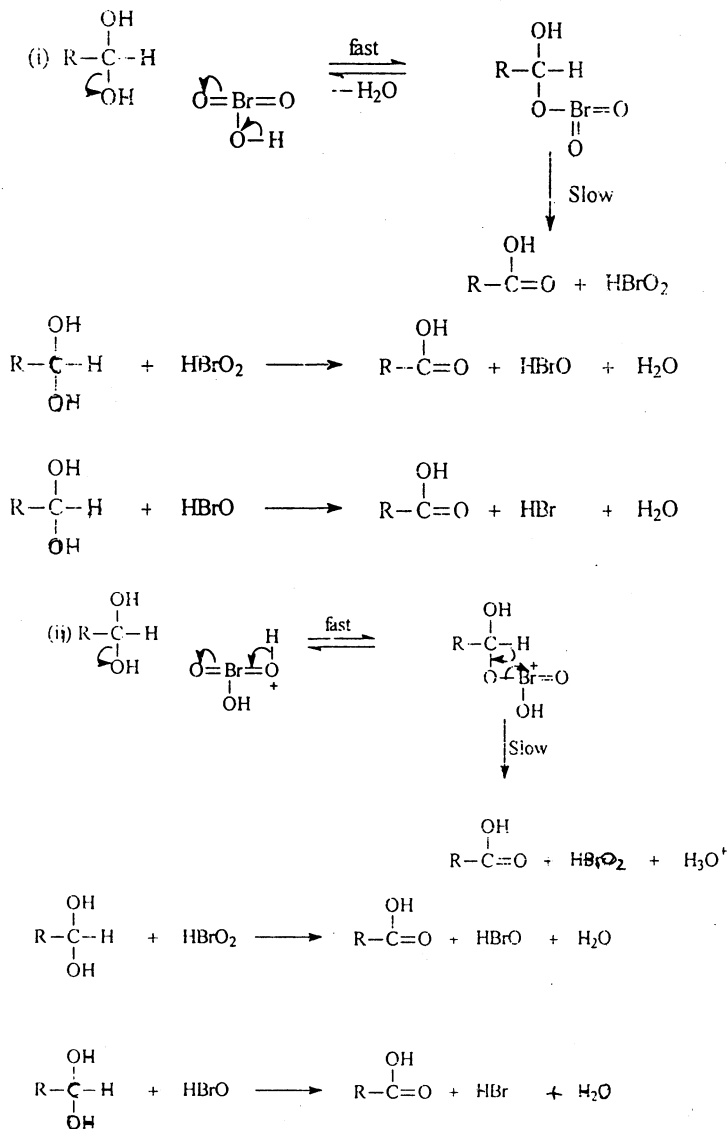
The fact that one of the kinetic route does not depend upon hydrogen ion concentration suggests that the unprotonated aldehyde HCH(OH)₂ is interacting with HBrO₃. In the process of electron transfer the unprotonated aldehyde may release its electron more easily as compared to protonated aldehyde. By the same argument the oxidising species HBrO₃ will accept the electrons more readily as compared to BrO₃⁻. It is therefore suggested that route one which is not affected by hydrogen ion is a bimolecular process.



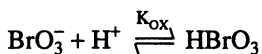
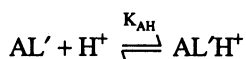
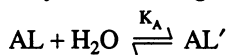
On the other hand, it is proposed that the second path which is hydrogen ion catalyzed involves bimolecular interaction between HCH(OH)₂ and H₂BrO₃⁺.

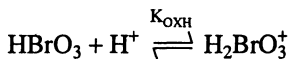


Most of the authors working with this system have proposed a similar mechanism^{2, 26}.



On the basis of above discussion the complete mechanism for the oxidation of formaldehyde in the absence of any surfactant is given as under.





On the basis of the above scheme the following rate expression may be obtained.

Using the mass-balanced equation for the aldehyde, the concentration of different species may be obtained in terms of total aldehyde concentration, $[\text{AL}]_{\text{T}}$:

$$\begin{aligned} [\text{AL}]_{\text{T}} &= [\text{AL}'] + [\text{AL}'\text{H}^+] \\ &= [\text{AL}'] + K_{\text{AH}}[\text{H}^+][\text{AL}'] \\ [\text{AL}]_{\text{T}} &= (1 + K_{\text{AH}}[\text{H}^+])[\text{AL}'] \\ [\text{AL}'] &= [\text{AL}]_{\text{T}} \cdot \frac{1}{(1 + K_{\text{AH}}[\text{H}^+])} \end{aligned} \tag{7}$$

$$[\text{AL}'\text{H}^+] = [\text{AL}]_{\text{T}} \cdot \frac{K_{\text{AH}}\text{H}^+}{(1 + K_{\text{AH}}[\text{H}^+])} \tag{8}$$

Similarly using the mass-balanced equation for Br(V) species, the concentration of different species may be obtained in terms of total bromate concentration.

$$\begin{aligned} [\text{BrO}_3^-]_{\text{T}} &= [\text{BrO}_3^-] + [\text{HBrO}_3] + [\text{H}_2\text{BrO}_3^+] \\ &= \frac{[\text{HBrO}_3]}{K_{\text{OX}}[\text{H}^+]} + [\text{HBrO}_3] + K_{\text{OXH}}[\text{H}^+] \cdot [\text{HBrO}_3] \end{aligned} \tag{9}$$

$$[\text{HBrO}_3] = [\text{BrO}_3^-]_{\text{T}} \cdot \frac{K_{\text{OX}}[\text{H}^+]}{(1 + K_{\text{OX}}[\text{H}^+] + K_{\text{OX}} \cdot K_{\text{OXH}}[\text{H}^+]^2)} \tag{10}$$

$$[\text{BrO}_3^-] = [\text{BrO}_3^-]_{\text{T}} \cdot \frac{1}{(1 + K_{\text{OX}}[\text{H}^+] + K_{\text{OXH}} \cdot K_{\text{OX}}[\text{H}^+]^2)} \tag{11}$$

$$[\text{H}_2\text{BrO}_3^+] = [\text{BrO}_3^-]_{\text{T}} \cdot \frac{K_{\text{OX}}K_{\text{OXH}}[\text{H}^+]^2}{(1 + K_{\text{OX}}[\text{H}^+] + K_{\text{OX}} \cdot K_{\text{OXH}}[\text{H}^+]^2)} \tag{12}$$

The kinetic expression for route one may be obtained as under.

$$r_1 = k'_2[\text{AL}'][\text{HBrO}_3] \tag{13}$$

$$r_1 = \frac{k'_2[\text{AL}]_{\text{T}}[\text{BrO}_3^-]_{\text{T}}K_{\text{OX}}[\text{H}^+]}{(1 + K_{\text{AH}}[\text{H}^+])(1 + K_{\text{OX}}[\text{H}^+] + K_{\text{OX}} \cdot K_{\text{OXH}}[\text{H}^+]^2)}$$

$$r_1 = \frac{k'_2[\text{AL}]_{\text{T}}[\text{BrO}_3^-]_{\text{T}}K_{\text{OX}}[\text{H}^+]}{1 + (K_{\text{AH}} + K_{\text{OX}})[\text{H}^+]}$$

If $(K_{\text{AH}} + K_{\text{OX}}) \gg 1$ and neglecting $[\text{H}^+]^n$ if $n > 1$

$$r_1 = {}^0k_{2F} [AL]_T [BrO_3^-]_T \quad (14)$$

where,

$${}^0k_{2F} = \frac{k_2' K_{OX}}{(K_{AH} + K_{OX})}$$

Similarly the kinetic expressions for route-2 may be obtained as given below:

$$r_2 = k_{2H}' [AL]_T [H_2BrO_3^+] \quad (15)$$

$$= \frac{k_{2H}' [AL]_T [BrO_3^-]_T K_{OX} \cdot K_{OXH} [H^+]^2}{(1 + K_{AH} [H^+])(1 + K_{OX} [H^+] + K_{OX} \cdot K_{OXH} [H^+]^2)}$$

If $(K_{AH} + K_{OX}) \gg 1$ and neglecting $[H^+]^n$ if $n > 1$.

$$r_2 = {}^0k_{2H} [H^+] [AL]_T [BrO_3^-]_T \quad (16)$$

where,

$${}^0k_{2H} = \frac{k_{2H}' K_{OX} \cdot K_{OXH}}{(K_{AH} + K_{OX})}$$

The total rate expression for the oxidation of formaldehyde may, therefore, be given as

$$\begin{aligned} \frac{-d[Br(V)]}{dt} &= r_1 + r_2 \\ &= ({}^0k_{2F} + {}^0k_{2H} [H^+]) [AL]_T [BrO_3^-]_T \\ {}^{01}k_{obs} &= ({}^0k_{2F} + {}^0k_{2H} [H^+]) [AL]_T \\ {}^{02}k_F &= {}^0k_{2F} + {}^0k_{2H} [H^+] \end{aligned} \quad (17)$$

The above expression stands verified by the fact that the plot between pseudo first-order rate constant (k_{obs}) vs. total aldehyde concentration $[AL]_T$ is linear and passes through origin at different $[H^+]$ and temperatures in Fig. 1.

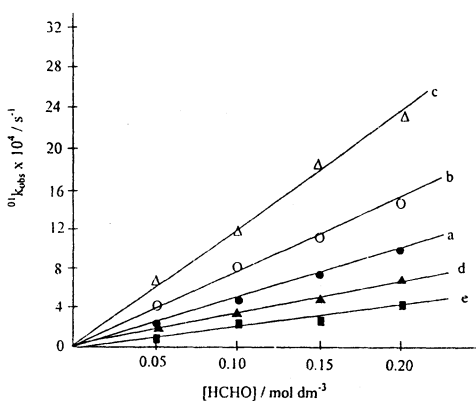


Fig. 1. Showing dependence of k_{obs} on $[HCHO]$ at different temperatures and $[H^+]$ in the absence of surfactant $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$

- a: $[H^+] = 0.20 \text{ mol dm}^{-3}$ at 25°C , b: $[H^+] = 0.20 \text{ mol dm}^{-3}$ at 30°C ,
 c: $[H^+] = 0.20 \text{ mol dm}^{-3}$ at 35°C , d: $[H^+] = 0.10 \text{ mol dm}^{-3}$ at 25°C ,
 e: $[H^+] = 0.05 \text{ mol dm}^{-3}$ at 25°C .

It is further verified that a plot between 0k_F versus $[H^+]$ is linear giving a positive intercept in Fig. 2. The presence of the intercept indicates that the reaction is following two routes, one, which is catalyzed by hydrogen ion concentration and the other route is not affected. The rate constant ${}^0k_{2H}$ and ${}^0k_{2F}$ are associated with these two routes respectively. With the help of these graphs the values of ${}^0k_{2F}$ from the intercept and ${}^0k_{2H}$ from the slope have been determined (Tables 1 and 2).

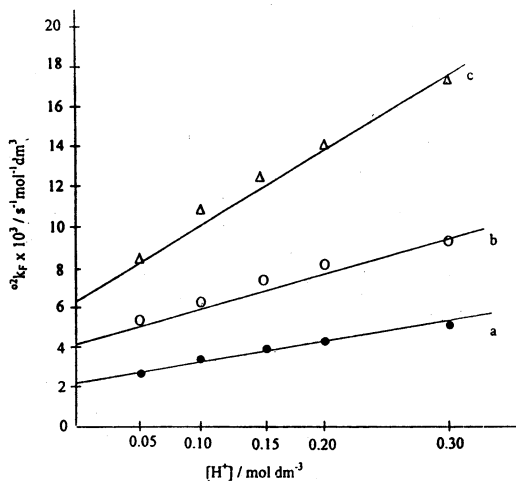
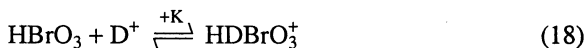


Fig. 2. Showing the variation of 0k_F with $[H^+]$ at different temperatures in the absence of surfactant at $[HCHO] = 0.10 \text{ mol dm}^{-3}$, $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
 a: 25°C, b: 30°C, c: 35°C

Kinetics of Oxidation of Formaldehyde in Presence of CPC

One of the interesting features of oxidation of formaldehyde in the presence of CPC is that the reaction is catalyzed even in the pre-micellar concentration range. There is no change in the catalytic behaviour in the post-cmc region. This fact may be accommodated by introducing the following equilibrium in the mechanism proposed earlier.



${}^+K$ may be defined as

$${}^+K = \frac{[HDBrO_3^+]}{[HBrO_3] \cdot [D^+]}$$

and assuming that $HDBrO_3^+$ is one of the active oxidising species in the presence of CPC. Due to this equilibrium, however, the mass-balanced equation for Br(V) would also include $HDBrO_3^+$. The concentration of active oxidising species may be calculated on the basis of new mass balanced equation as given below:

$$\begin{aligned}
 [\text{BrO}_3^-]_{\text{T}} &= [\text{BrO}_3^-] + [\text{HBrO}_3] + [\text{H}_2\text{BrO}_3^+] + [\text{HDBrO}_3^+] \\
 &= \frac{[\text{HBrO}_3]}{K_{\text{OX}}\text{H}^+} + [\text{HBrO}_3] + [\text{HBrO}_3] \cdot K_{\text{OXH}}[\text{H}^+] + [\text{HDBrO}_3^+] \\
 &\hspace{15em} \text{neglecting } [\text{H}^+]^n \text{ if } n > 1 \\
 &= \left(\frac{1 + K_{\text{OX}}[\text{H}^+] + K_{\text{OX}}^+K[\text{D}^+][\text{H}^+]}{K_{\text{OX}}K[\text{D}^+][\text{H}^+]} \right) [\text{HDBrO}_3^+] \quad (19)
 \end{aligned}$$

$$[\text{HDBrO}_3^+] = \frac{[\text{BrO}_3^-]_{\text{T}} \cdot K_{\text{OX}}^+ K[\text{D}^+][\text{H}^+]}{(1 + K_{\text{OX}}[\text{H}^+] + K_{\text{OX}}^+[\text{H}^+]^+K[\text{D}^+])} \quad (20)$$

$$[\text{HBrO}_3] = \frac{[\text{BrO}_3^-]_{\text{T}} \cdot K_{\text{OX}}[\text{H}^+]}{(1 + K_{\text{OX}}[\text{H}^+] + K_{\text{OX}}^+[\text{H}^+]^+K[\text{D}^+])} \quad (21)$$

$$[\text{H}_2\text{BrO}_3^+] = \frac{[\text{BrO}_3^-]_{\text{T}} \cdot K_{\text{OX}} \cdot K_{\text{OXH}}[\text{H}^+]^2}{(1 + K_{\text{OX}}[\text{H}^+] + K_{\text{OX}}^+[\text{H}^+]^+K[\text{D}^+])} \quad (22)$$

It is further assumed that route-1 and route-2 envisaged earlier remain unaffected by the presence of the surfactant but a new reaction path comes into play in which HDBrO_3^+ is the active oxidising species. Since the mass-balanced equation for Br(V) has changed, the kinetic expressions for route-1 and route-2 have also been modified as discussed below:

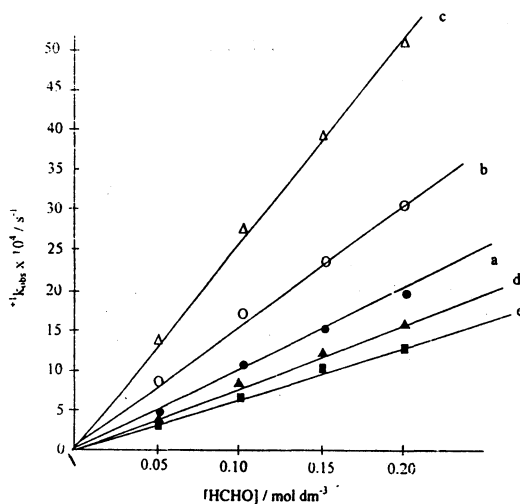


Fig. 3. Showing dependence of k_{obs} with $[\text{HCHO}]$ at different temperatures in the presence of CPC at $[\text{H}^+] = 0.20 \text{ mol dm}^{-3}$, $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$;
 a: $[\text{CPC}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ at 25°C , b: $[\text{CPC}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ at 30°C ,
 c: $[\text{CPC}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ at 35°C , d: $[\text{CPC}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ at 25°C ,
 e: $[\text{CPC}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ at 25°C .

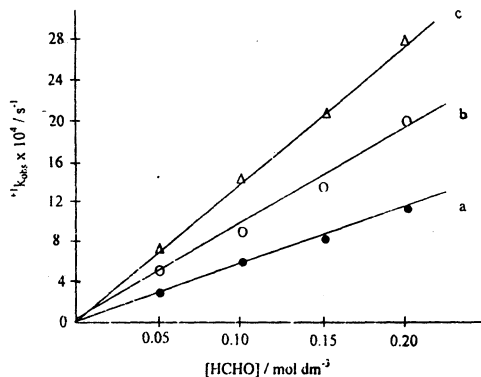
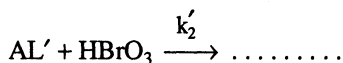


Fig. 4. Showing dependence of k_{obs} with $[HCHO]$ at different temperatures in the presence of CPC at $[H^+] = 0.10 \text{ mol dm}^{-3}$; $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$; $[CPC] = 1 \times 10^{-3} \text{ mol dm}^{-3}$
 a: 25°C, b: 30°C, c: 35°C

Route-1



$$r_1 = k_2'[AL'] [HBrO_3]$$

$$= \frac{k_2'[AL]_T [BrO_3^-]_T K_{OX} [H^+]}{(1 + K_{AH} [H^+]) (1 + K_{OX} [H^+] + K_{OX} [H^+] K [D^+])}$$

neglecting $[H^+]^n$ if $n > 1$ and $(K_{OX} + K_{AH}) \gg 1$

$$r_1 = \frac{k_2' K_{OX} [H^+] [AL]_T [BrO_3^-]_T}{1 + K_{OX} [H^+] + K_{AH} [H^+] + K_{OX} K [H^+] [D^+]}$$

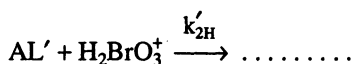
$$r_1 = \frac{k_2' K_{OX} [AL]_T [BrO_3^-]_T}{{}^+K_F + {}^+K'_F [D^+]}$$
(23)

where ${}^+K_F = K_{AH} + K_{OX}$ and ${}^+K'_F = K_{OX} + K$

$$r_1 = {}^+k_{2F} [AL]_T [BrO_3^-]_T$$
(24)

where ${}^+k_{2F} = \frac{k_2' K_{OX}}{{}^+K_F + {}^+K'_F [D^]}$

Route-2

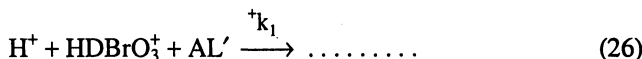


$$r_2 = k_{2H}' [AL'] [H_2BrO_3^+]$$

$$\begin{aligned}
 &= \frac{k'_{2H}[AL]_T[BrO_3^-]_T K_{OX} \cdot K_{OXH} [H^+]^2}{(1 + K_{AH} [H^+])(1 + K_{OX} [H^+] + K_{OX} {}^+K [H^+][D^+])} \\
 &= \frac{k'_{2H} K_{OX} K_{OXH} [H^+][AL]_T [BrO_3^-]_T}{{}^+K_F + {}^+K'_F [D^+]} \\
 &= {}^+k_{2H} [H^+][AL]_T [BrO_3^-]_T \tag{25}
 \end{aligned}$$

where ${}^+k_{2H} = \frac{k'_{2H} K_{OX} K_{OXH}}{{}^+K_F + {}^+K'_F [D^+]}$

Route-3



$$\begin{aligned}
 r_3 &= {}^+k_1 [H^+][HDBrO_3^+][AL'] \\
 &= \frac{{}^+k_1 [H^+][AL]_T [BrO_3^-]_T (K_{OX} \cdot {}^+K [D^+][H^+])}{(1 + K_{AH} [H^+])(1 + K_{OX} [H^+] + K_{OX} {}^+K [H^+][D^+])} \\
 &= \left(\frac{{}^+k_1 K_{OX} {}^+K}{{}^+K_F + {}^+K'_F [D^+]} \right) [D^+][H^+][AL]_T [BrO_3^-]_T \\
 &= \frac{{}^+k_{HD} [D^+][H^+][AL]_T [BrO_3^-]_T}{({}^+K_F + {}^+K'_F [D^+])} \tag{27}
 \end{aligned}$$

where ${}^+k_{HD} = {}^+k_1 K_{OX} {}^+K$

Total reaction rate is thus given as

$$\frac{-d[Br(V)]}{dt} = r_1 + r_2 + r_3$$

$$r = \frac{(k'_2 K_{OX} + K'_{2H}) K_{OX} K_{OXH} [H^+] + {}^+k_{HD} [D^+][H^+]}{({}^+K_F + {}^+K'_F [D^+])} [AL]_T [BrO_3^-]_T \tag{28}$$

Dividing by ${}^+K_F$ both numerator as well as denominator,

$$\frac{{}^+k_{obs}}{[AL]_T} = {}^+2k_F = \frac{{}^0k_{2F} + {}^0k_{2H} [H^+] + {}^+k'_{HD} [H^+][D^+]}{(1 + {}^+K''_F [D^+])}$$

where ${}^+K''_F = ({}^+K'_F / {}^+K_F)$ and ${}^+k'_{HD} = ({}^+k_{HD} / {}^+K_F)$

$${}^+2k_F = \frac{{}^0k_{2F}}{(1 + {}^+K''_F [D^+])} + \frac{({}^0k_{2H} + {}^+k'_{HD} [D^+])[H^+]}{(1 + {}^+K''_F [D^+])} \tag{29x}$$

$${}^+2k_F = I_{XF} + S_{XF} [H^+] \quad \text{at constant } [D^+]$$

where $I_{XF} = \frac{{}^0k_{2F}}{(1 + {}^+K''_F [D^+])}$ and $S_{XF} = \frac{{}^0k_{2H} + {}^+k'_{HD} [D^+][H^+]}{(1 + {}^+K''_F [D^+])}$

$$\frac{1}{I_{XF}} = \frac{1}{{}^0k_{2F}} + \frac{{}^+K_F''[D^+]}{{}^0k_{2F}} \quad (30a)$$

The above equation is verified at different hydrogen ion concentrations, CPC concentrations and temperatures. It is observed that at a fixed concentration of CPC the plot between ${}^+k_F$ versus $[H^+]$ is linear giving a positive intercept in Fig. 6. The intercept decreases with increasing concentration of CPC. The dependence

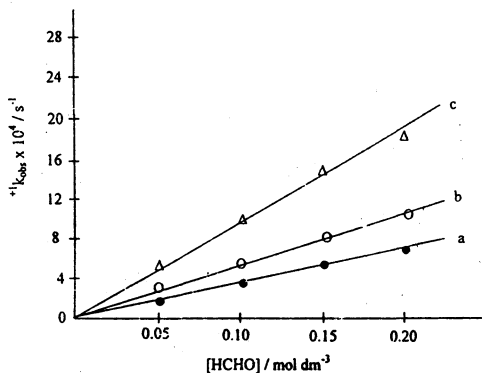


Fig. 5. Showing dependence of k_{obs} with $[HCHO]$ at different temperatures in the presence of CPC at $[H^+] = 0.05\ mol\ dm^{-3}$; $[NaBrO_3] = 4 \times 10^{-3}\ mol\ dm^{-3}$; $[CPC] = 1 \times 10^{-3}\ mol\ dm^{-3}$.
a: 25°C, b: 30°C, c: 35°C

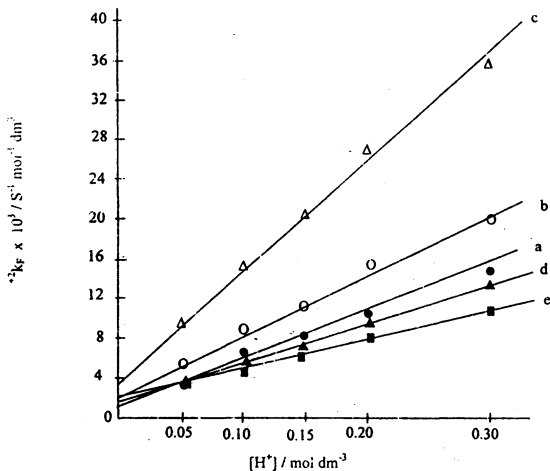


Fig. 6. Showing the variation of ${}^+k_F$ with $[H^+]$ at different temperatures in the presence of CPC at $[HCHO] = 0.10\ mol\ dm^{-3}$; $[NaBrO_3] = 4 \times 10^{-3}\ mol\ dm^{-3}$
a: $[CPC] = 2 \times 10^{-3}\ mol\ dm^{-3}$ at 25°C, b: $[CPC] = 2 \times 10^{-3}\ mol\ dm^{-3}$ at 30°C,
c: $[CPC] = 2 \times 10^{-3}\ mol\ dm^{-3}$ at 35°C, d: $[CPC] = 1 \times 10^{-3}\ mol\ dm^{-3}$ at 25°C,
e: $[CPC] = 5 \times 10^{-4}\ mol\ dm^{-3}$ at 25°C.

of the intercept of equation (29x) has been further investigated by making the plot between the reciprocal of intercept versus $[CPC]$. It is found to be linear (Fig. 7) and from the intercept and slope of these lines, values of ${}^0k_{2F}$, ${}^+K_F''$ were evaluated at different temperatures and compared with those obtained in the absence of surfactant. These data have been presented in Table-1

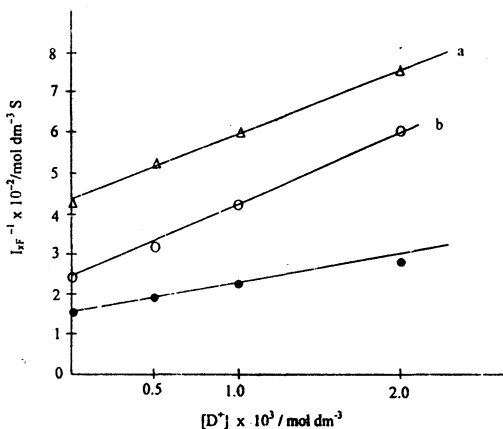


Fig. 7. Showing dependence of I_{XF}^{-1} (intercept from Fig. 2, 6, eqn. 30a) on $[D^+]$ at different temperatures; $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
a: 25°C, b: 30°C, c: 35°C

Furthermore, knowing the value of ${}^+K_F''$ the slopes of the plots of the above equation have been used for evaluating the rate constants ${}^0k_{2H}$ and ${}^+k'_{HD}$ as have been given below.

$$S_{XF} = \frac{{}^0k_{2H} + {}^+k'_{HD}[D^+]}{(1 + {}^+K_F''[D^+])}$$

$$(1 + {}^+K_F''[D^+])S_{XF} = {}^0k_{2H} + {}^+k'_{HD}[D^+] \quad (30b)$$

From the above equation it is evident that the plot between the left hand side $(1 + {}^+K_F''[D^+]) S_{XF}$ versus $[D^+]$ should be linear at different temperatures and should give a positive intercept in Fig. 8. It may also be remembered that ${}^0k_{2H}$ must be similar to the value obtained in the absence of surfactant as presented in Table-2. These values are quite comparable, justifying our assumption that the reaction path which is hydrogen catalyzed in the absence of surfactant remains unaffected. The value of ${}^+k'_{HD}$, the rate constant associated with the process which is acid catalyzed as well as CPC catalyzed-at different temperatures have been presented in Table-3.

Kinetics of Oxidation of Formaldehyde in Presence of SDS

The kinetic features for the oxidation of formaldehyde in the presence of SDS are found to be similar to those exhibited in the presence of CPC. However, overall catalytic effect of SDS on the reaction rate is much less than that of CPC. The dependence of the reaction rate on hydrogen ion concentration remains

unchanged. It is further observed that the reaction is catalyzed in the pre-micellar concentration as well as in post-cmc region. These kinetic features have been explained by introducing slight modification in the reaction scheme discussed earlier. It is assumed that route-1 and route-2, which are major reaction paths in the absence of any surfactant, remain unaffected in the presence of SDS. However, the mass balanced equation for Br(V) changes due to the presence of the following equilibrium:

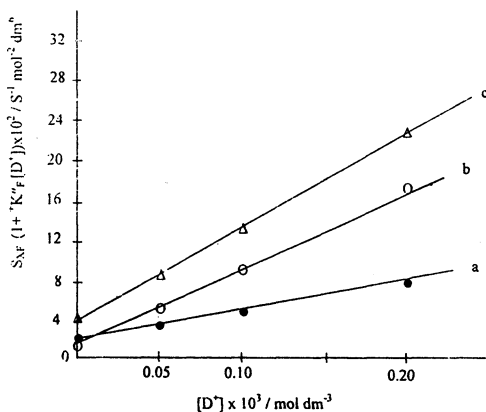
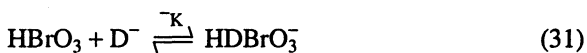


Fig. 8. Showing dependence of $S_{XF}(1 + K_F''[D^+])$ on $[D^+]$ at different temperatures (where S_{XF} is slope from Figs. 2, 6, eqn. 30b); $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
 a: 25°C, b: 30°C, c: 35°C



K may be defined as

$$K = \frac{[HDBrO_3^-]}{[HBrO_3][D^-]}$$

The concentration of different active Br(V) species is calculated on the basis of new mass balanced equation as given below:

$$\begin{aligned} [BrO_3^-]_T &= [BrO_3^-] + [HBrO_3] + [H_2BrO_3^+] + [HDBrO_3^-] \\ &= \frac{[HBrO_3]}{K_{OX}[H^+]} + [HBrO_3] + [HBrO_3] \cdot K_{OX}[H^+] + [HDBrO_3^-] \end{aligned}$$

neglecting $[H^+]^n$ if $n > 1$

$$[BrO_3^-]_T = \left(\frac{1 + K_{OX}[H^+] + K_{OX}K[D^-][H^+]}{K_{OX}K[D^-][H^+]} \right) [HDBrO_3^-] \tag{32}$$

$$[HDBrO_3^-] = \frac{[BrO_3^-]_T K_{OX}K[D^-][H^+]}{(1 + K_{OX}[H^+] + K_{OX}K[H^+][D^-])} \tag{33}$$

$$[\text{HBrO}_3] = \frac{[\text{BrO}_3^-]_T K_{\text{OX}}[\text{H}^+]}{(1 + K_{\text{OX}}[\text{H}^+] + K_{\text{OX}}^- K[\text{H}^+][\text{D}^-])} \quad (34)$$

$$[\text{H}_2\text{BrO}_3^+] = \frac{[\text{BrO}_3^-]_T K_{\text{OX}} K_{\text{OXH}}[\text{H}^+]^2}{(1 + K_{\text{OX}}[\text{H}^+] + K_{\text{OX}}[\text{H}^+] K[\text{D}^-])} \quad (35)$$

The kinetics expressions for route-1 and route-2 are slightly modified because of the new mass balanced equation. The rate expression for the different routes is obtained as:

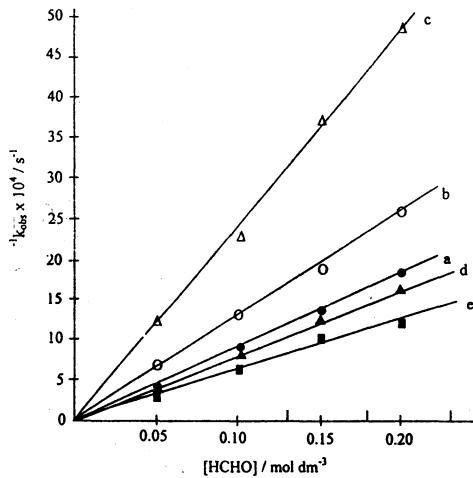


Fig. 9. Showing dependence of k_{obs} on $[\text{HCHO}]$ at different temperatures in presence of SDS at $[\text{H}^+] = 0.20 \text{ mol dm}^{-3}$; $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$;
 a: $[\text{SDS}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ at 25°C , b: $[\text{SDS}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ at 30°C ,
 c: $[\text{SDS}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ at 35°C ; d: $[\text{SDS}] = 1 \times 10^{-2} \text{ mol dm}^{-3}$ at 25°C ,
 e: $[\text{SDS}] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ at 25°C .

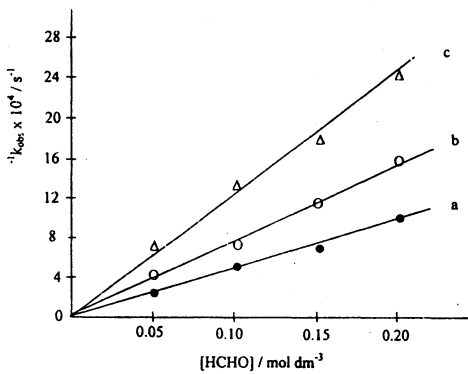


Fig. 10. Showing dependence of k_{obs} on $[\text{HCHO}]$ at different temperatures in presence of SDS at $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$; $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{SDS}] = 1 \times 10^{-2} \text{ mol dm}^{-3}$
 a: 25°C , b: 30°C , c: 35°C

Route-1

$$\begin{aligned}
 & \text{AL}' + \text{HBrO}_3 \xrightarrow{k'_2} \dots\dots\dots \\
 r_1 &= k'_2[\text{AL}'][\text{HBrO}_3] \\
 &= \frac{k'_2[\text{AL}]_T}{(1 + K_{\text{AH}}[\text{H}^+])} \cdot \frac{[\text{BrO}_3^-]_T K_{\text{OX}}[\text{H}^+]}{(1 + K_{\text{OXH}}[\text{H}^+] + K_{\text{OX}}^{-} K[\text{H}^+][\text{D}^-])} \\
 & \hspace{15em} \text{neglecting } [\text{H}^+]^n \text{ if } n > 1
 \end{aligned}$$

$$\begin{aligned}
 r_1 &= \frac{k'_2 K_{\text{OX}}[\text{H}^+][\text{AL}]_T[\text{BrO}_3^-]_T}{1 + K_{\text{OX}} + K_{\text{AH}} + K_{\text{OX}}^{-} K[\text{D}^-]} \\
 r_1 &= \frac{k'_2 K_{\text{OX}}[\text{AL}]_T[\text{BrO}_3^-]_T}{\bar{K}_F + \bar{K}'_F[\text{D}^-]} \tag{36}
 \end{aligned}$$

where

$$\bar{K}_F = K_{\text{AH}} + K_{\text{OX}} \quad \text{and} \quad \bar{K}'_F = K_{\text{OX}}^{-} K$$

$$\begin{aligned}
 r_1 &= \left(\frac{k'_2 K_{\text{OX}}}{\bar{K}_F + \bar{K}'_F[\text{D}^-]} \right) [\text{AL}]_T [\text{BrO}_3^-]_T \\
 r_1 &= \bar{k}_{2F} [\text{AL}]_T [\text{BrO}_3^-]_T \tag{37}
 \end{aligned}$$

where

$$\bar{k}_{2F} = \left(\frac{k'_2 K_{\text{OX}}}{\bar{K}_F + \bar{K}'_F[\text{D}^-]} \right)$$

Route-2

$$\begin{aligned}
 & \text{AL}' + \text{H}_2\text{BrO}_3^+ \xrightarrow{k'_{2H}} \dots\dots\dots \\
 r_2 &= k'_{2H}[\text{AL}'][\text{H}_2\text{BrO}_3^+] \\
 &= \frac{k'_{2H} K_{\text{OX}} K_{\text{OXH}}[\text{H}^+][\text{AL}]_T[\text{BrO}_3^-]_T}{\bar{K}_F + \bar{K}'_F[\text{D}^-]} \tag{38}
 \end{aligned}$$

$$r_2 = \bar{k}_{2H}[\text{H}^+][\text{AL}]_T[\text{BrO}_3^-]_T \tag{39}$$

where

$$\bar{k}_{2H} = \left(\frac{k'_{2H} K_{\text{OX}} K_{\text{OXH}}}{\bar{K}_F + \bar{K}'_F[\text{D}^-]} \right)$$

In the presence of sodium dodecylsulphate the reaction path which is acid catalyzed as well as surfactant catalyzed is given as route-3. The kinetic expression for this reaction path is given below.

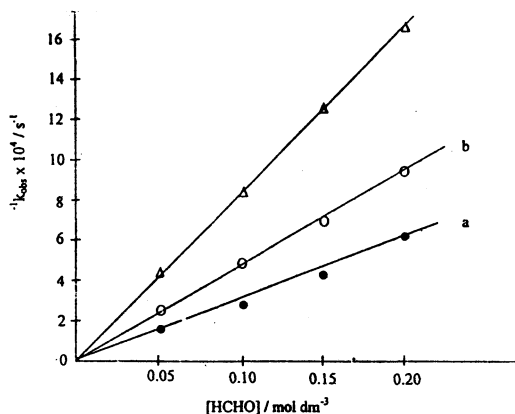


Fig. 11. Showing dependence of k_{obs} on $[\text{HCHO}]$ at different temperatures in presence of SDS at $[\text{H}^+] = 0.05 \text{ mol dm}^{-3}$; $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{SDS}] = 1 \times 10^{-2} \text{ mol dm}^{-3}$
 a: 25°C, b: 30°C, c: 35°C

Route-3



$$\begin{aligned} r_3 &= \bar{k}_1 [\text{HDBrO}_3^-] [\text{AL}/\text{H}^+] \\ &= \frac{\bar{k}_1 [\text{AL}]_{\text{T}} [\text{BrO}_3^-]_{\text{T}} (\bar{K}_{\text{AH}} \bar{K}_{\text{OX}} \bar{K} [\text{D}^-] [\text{H}^+])}{(\bar{K}_{\text{F}} + \bar{K}'_{\text{F}} [\text{D}^-])} \\ r_3 &= \frac{\bar{k}_{\text{HD}} [\text{D}^-] [\text{H}^+] [\text{AL}]_{\text{T}} [\text{BrO}_3^-]_{\text{T}}}{\bar{K}_{\text{F}} + \bar{K}'_{\text{F}} [\text{D}^-]} \quad (41) \end{aligned}$$

where $\bar{k}_{\text{HD}} = (\bar{k}_1 \bar{K}_{\text{AH}} \bar{K}_{\text{OX}} \bar{K})$

Total reaction rate

$$r = r_1 + r_2 + r_3$$

$$\frac{-d[\text{Br(V)}]}{dt} = \frac{(k'_2 \bar{K}_{\text{OX}} + k_{2\text{H}} \bar{K}_{\text{OX}} \bar{K}_{\text{OXH}} [\text{H}^+] + \bar{k}_{\text{HD}} [\text{H}^+] [\text{D}^-])}{\bar{K}_{\text{F}} + \bar{K}'_{\text{F}} [\text{D}^-]} [\text{AL}]_{\text{T}} [\text{BrO}_3^-]_{\text{T}} \quad (42)$$

Dividing by \bar{K}_{F} both in numerator as well as in denominator,

$$\frac{-1 k_{\text{obs}}}{[\text{AL}]_{\text{T}}} = -2 k_{\text{F}} = \frac{{}^0 k_{2\text{F}} + {}^0 k_{2\text{H}} [\text{H}^+] + \bar{k}'_{\text{HD}} [\text{H}^+] [\text{D}^-]}{1 + \bar{K}''_{\text{F}} [\text{D}^-]}$$

where

$$\bar{K}''_{\text{F}} = \bar{K}'_{\text{F}} / \bar{K}_{\text{F}} \quad \text{and} \quad \bar{k}'_{\text{HD}} = (\bar{k}_{\text{HD}} / \bar{K}_{\text{F}})$$

$$-2 k_{\text{F}} = \frac{{}^0 k_{2\text{F}}}{(1 + \bar{K}''_{\text{F}} [\text{D}^-])} + \frac{({}^0 k_{2\text{H}} + \bar{k}'_{\text{HD}} [\text{D}^-])}{(1 + \bar{K}''_{\text{F}} [\text{D}^-])} [\text{H}^+]$$

$$^{-2}k_F = I_{YF} + S_{YF}[H^+] \quad \text{at constant } [D^-] \quad (43Y)$$

where
$$I_{YF} = \frac{{}^0k_{2F}}{(1 + \overline{K}_F''[D^-])} \quad \text{and} \quad S_{YF} = \frac{{}^0k_{2H} + \overline{K}'_{HD}[D^-]}{1 + \overline{K}_F''[D^-]}$$

The above equation has been verified by plotting $^{-2}k_F$ versus $[H^+]$ at constant surfactant concentration, the plot is found to be linear giving a positive intercept in Fig. 12. The dependence of this intercept, I_{YF} on $[\text{surfactant}]$ has been analyzed by using the data available at different concentrations of surfactant and temperatures.

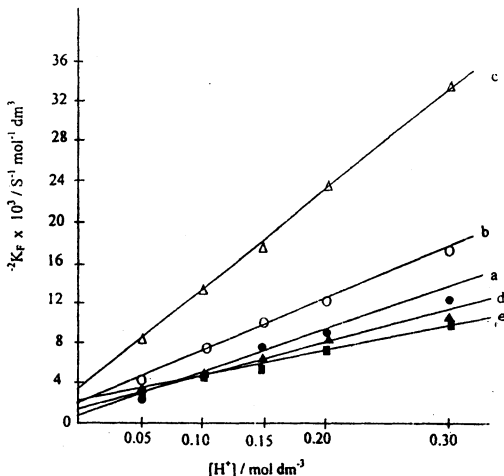


Fig. 12. Showing the variation of $^{-2}k_F$ with $[H^+]$ at different temperatures in presence of SDS at $[\text{HCHO}] = 0.10 \text{ mol dm}^{-3}$; $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$;
 a: $[\text{SDS}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ at 25°C, b: $[\text{SDS}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ at 30°C,
 c: $[\text{SDS}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ at 35°C, d: $[\text{SDS}] = 1 \times 10^{-2} \text{ mol dm}^{-3}$ at 25°C,
 e: $[\text{SDS}] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ at 25°C.

$$I_{YF} = \frac{{}^0k_{2F}}{(1 + \overline{K}_F''[D^-])}$$

$$\frac{1}{I_{YF}} = \frac{1}{{}^0k_{2F}} + \frac{\overline{K}_F''[D^-]}{{}^0k_{2F}} \quad (44a)$$

The equation (44a) shows that the plot between reciprocal of I_{YF} vs. $[D^-]$ should be linear as observed in Fig. 13. The intercept of these plots gives ${}^0k_{2F}$ and slope \overline{K}_F'' at different temperatures. It may be remembered that the rate constant, ${}^0k_{2F}$, represents the reaction path which is unaffected by hydrogen ion concentration and surfactant concentration. If the proposed mechanism is true then the rate constant obtained above should match with those obtained in the absence of CPC/SDS, and also with those obtained in the presence of CPC earlier, ${}^0k_{2F}$.

obtained at different conditions are presented in Table-1. This clearly shows that the values are well within the experimental range of error.

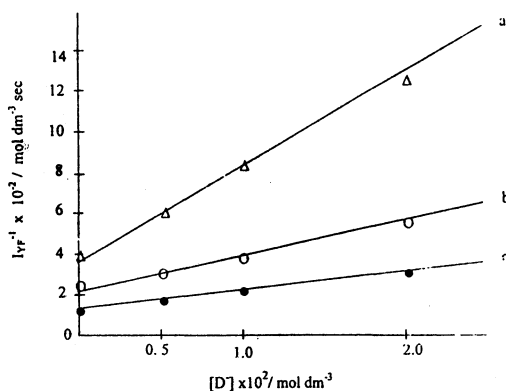


Fig. 13. Showing dependence of $1/v_F^{-1}$ (intercept from Figs. 2, 12, eqn. 44a) on $[D^-]$ at different temperatures; $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
a: 25°C, b: 30°C, c: 35°C

TABLE-1

Temperature (°C)	${}^0k_{2F}^{(*)} \times 10^3$ ($\text{s}^{-1}\text{mol}^{-1}\text{dm}^3$)	${}^0k_{2F}^{(\Delta)} \times 10^3$ ($\text{s}^{-1}\text{mol}^{-1}\text{dm}^3$)	${}^0k_{2F}^{(\#)} \times 10^3$ ($\text{s}^{-1}\text{mol}^{-1}\text{dm}^3$)
25	2.40	2.10	2.78
30	4.02	4.17	4.76
35	6.40	6.67	6.89

${}^0k_{2F}^{(*)}$ obtained using equation (17) in absence of surfactant

${}^0k_{2F}^{(\Delta)}$ obtained using equation (30a) in presence of CPC

${}^0k_{2F}^{(\#)}$ obtained using equation (44a) in presence of SDS

Similarly the slope of equation (43Y) has been put to test knowing the value of \bar{K}_F'' (Table-3) equation (44) can be arranged as:

$$S_{YF} = \frac{{}^0k_{2H} + \bar{k}'_{HD}[D^-]}{(1 + \bar{K}_F''[D^-])}$$

$$(1 + \bar{K}_F''[D^-])S_{YF} = {}^0k_{2H} + \bar{k}'_{HD}[D^-] \quad (44b)$$

The plot between $(1 + \bar{K}_F''[D^-])S_{YF}$ versus $[D^-]$ is linear giving a positive intercept in Fig. 14. The intercept determines ${}^0k_{2H}$, the rate constant associated with reaction path, which is hydrogen ion catalyzed and not affected by the presence of CPC or SDS. These rate constants have been obtained as earlier at different conditions and are given in Table-2.

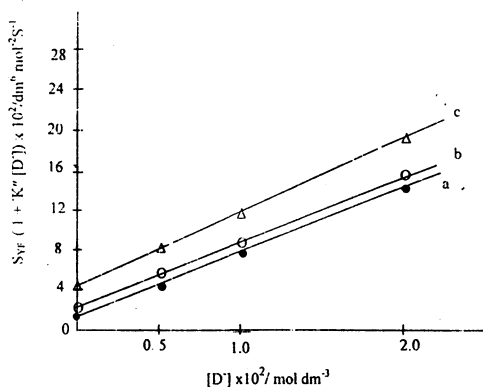


Fig. 14. Showing dependence of $S_{YF}(1 + K''_F [D^-])$ on $[D^-]$ at different temperatures (where S_{YF} is slope from Figs. 2, 12, eqn. 44b); $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
 a: 25°C, b: 30°C, c: 35°C

TABLE-2

Temperature (°C)	${}^0k_{2H}^{(*)} \times 10^2$ ($\text{s}^{-1} \text{mol}^{-2} \text{dm}^6$)	${}^0k_{2H}^{(\Delta)} \times 10^2$ ($\text{s}^{-1} \text{mol}^{-2} \text{dm}^6$)	${}^0k_{2H}^{(\#)} \times 10^2$ ($\text{s}^{-1} \text{mol}^{-2} \text{dm}^6$)
25	1.15	1.75	1.02
30	1.95	1.65	1.60
35	4.15	4.20	4.50

${}^0k_{2H}^{(*)}$ obtained using equation (17) in absence of surfactant

${}^0k_{2H}^{(\Delta)}$ obtained using equation (30b) in presence of CPC

${}^0k_{2H}^{(\#)}$ obtained using equation (44b) in presence of SDS

The above table shows that the values of ${}^0k_{2H}$ obtained using equation (17) are quite in agreement with those obtained by equation (44b) justifying the proposed mechanism. In figure the slope gives K''_{HD} under different conditions which are also tabulated in Table-3.

TABLE-3

Temperature (°C)	${}^+K''_F \times 10^{-2}$ ($\text{mol}^{-1} \text{dm}^3$)	${}^-K''_F \times 10^{-2}$ ($\text{mol}^{-1} \text{dm}^3$)	${}^+k'_{HD}$	${}^-k'_{HD}$
25	2.95	1.23	34.5	34.06
30	7.50	0.86	77.5	68.5
35	5.33	0.52	95.0	79.5

The Kinetics of Oxidation of Chloral hydrate in the Absence of Surfactant

The kinetic features of the oxidation of chloral hydrate are very similar to those observed in the case of formaldehyde in different experimental conditions. The oxidation of chloral hydrate is expected to have slower rate because of electron withdrawing nature of Cl in CCl_3 group which is likely to inhibit the polarization of the carbonyl group, generally, assumed to be first step in the oxidation of aldehyde by Br(V) .

Assuming a similar mass-balanced equation as proposed in the case of formaldehyde to be operating in the case of chloral hydrate, the following rate law has been established in the absence of any surfactant.

$$\begin{aligned} \frac{-d[\text{Br(V)}]}{dt} &= {}^0k_{2C}[\text{AL}]_T[\text{BrO}_3^-]_T + {}^0k_{2H}[\text{H}^+][\text{AL}]_T[\text{BrO}_3^-]_T \\ &= {}^{01}k_{\text{obs}}[\text{BrO}_3^-]_T \end{aligned}$$

where ${}^{01}k_{\text{obs}} = ({}^0k_{2C} + {}^0k_{2H}[\text{H}^+])[\text{AL}]_T$ (45a)

${}^{01}k_{\text{obs}}$ is the observed pseudo first order rate constant and $[\text{AL}]_T$ is total concentration of chloral hydrate.

$$\begin{aligned} \frac{{}^{01}k_{\text{obs}}}{[\text{AL}]_T} &= {}^0k_{2C} + {}^0k_{2H}[\text{H}^+] \\ {}^{02}k_C &= {}^0k_{2C} + {}^0k_{2H}[\text{H}^+] \end{aligned} \quad (45b)$$

where

$${}^0k_{2C} = \frac{k'_{2C}K_{\text{OX}}}{(K_{\text{AH}} + K_{\text{OX}})} \text{ from eqn. (14) and } {}^0k_{2H} = \frac{k'_{2H}K_{\text{OX}} \cdot K_{\text{OXH}}}{(K_{\text{AH}} + K_{\text{OX}})} \text{ from eqn. (16)}$$

The equation (45a) has been verified by plotting ${}^{01}k_{\text{obs}}$ vs. $[\text{AL}]_T$ which is found to be linear passing through origin in Fig. 15. It has also been observed that a plot between ${}^{02}k_C$ vs. $[\text{H}^+]$ is linear (eqn. 45b) giving a positive intercept in Fig. 16. The presence of the intercept indicates that the reaction is following two routes: one, which is catalyzed by hydrogen ion concentration and the other route is not affected. The rate constants ${}^0k_{2H}$ and ${}^0k_{2C}$ are associated with these two routes respectively. With the help of intercept value of ${}^0k_{2C}$ has been determined under different conditions (Table-4).

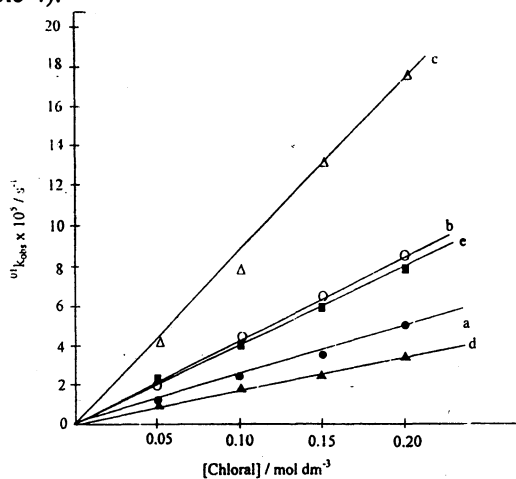


Fig. 15. Showing dependence of k_{obs} on $[\text{Chloral}]$ at different temperatures and $[\text{H}^+]$ in the absence of surfactant; $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$

a: $[\text{H}^+] = 0.20 \text{ mol dm}^{-3}$ at 45°C ,

b: $[\text{H}^+] = 0.20 \text{ mol dm}^{-3}$ at 50°C ,

c: $[\text{H}^+] = 0.20 \text{ mol dm}^{-3}$ at 55°C ,

d: $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$ at 45°C ,

e: $[\text{H}^+] = 0.30 \text{ mol dm}^{-3}$ at 45°C .

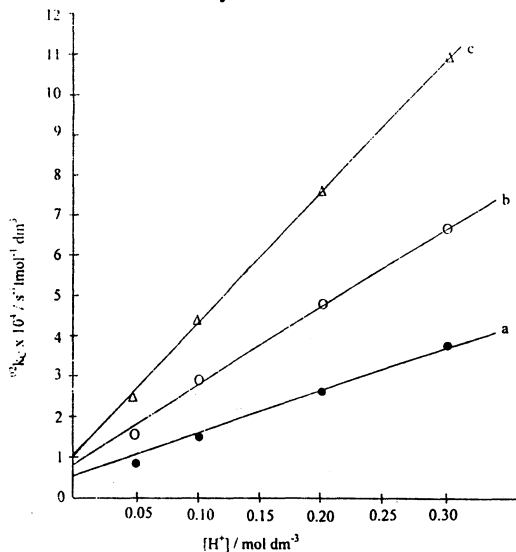


Fig. 16. Showing the variation of ${}^0k_{2C}$ with $[H^+]$ at different temperatures in the absence of surfactant at $[Chloral] = 0.10 \text{ mol dm}^{-3}$; $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
 a: 45°C, b: 50°C, c: 55°C

TABLE-4

Temperature (°C)	${}^0k_{2C}^{(*)} \times 10^4$ ($s^{-1} \text{ mol}^{-1} \text{ dm}^3$)	${}^0k_{2C}^{(\Delta)} \times 10^4$ ($s^{-1} \text{ mol}^{-1} \text{ dm}^3$)	${}^0k_{2C}^{(\#)} \times 10^4$ ($s^{-1} \text{ mol}^{-1} \text{ dm}^3$)
45	0.65	0.65	0.71
50	0.80	0.83	0.95
55	1.00	1.11	1.25

${}^0k_{2C}^{(*)}$ obtained using equation (45b) in absence of surfactant

${}^0k_{2C}^{(\Delta)}$ obtained using equation (49) in presence of CPC

${}^0k_{2C}^{(\#)}$ obtained using equation (53a) in presence of SDS

With the help of slope, the rate constant associated with reaction path, which is hydrogen ion dependent, *i.e.*, ${}^0k_{2H}$ has been determined at different temperatures and are presented the first column in Table-5.

TABLE-5

Temperature (°C)	${}^0k_{2H}^{(*)} \times 10^3$ ($s^{-1} \text{ mol}^{-2} \text{ dm}^6$)	${}^0k_{2H}^{(\Delta)} \times 10^3$ ($s^{-1} \text{ mol}^{-2} \text{ dm}^6$)	${}^0k_{2H}^{(\#)} \times 10^3$ ($s^{-1} \text{ mol}^{-2} \text{ dm}^6$)
45	1.05	1.10	1.06
50	1.95	1.90	1.92
55	3.20	3.42	3.45

${}^0k_{2H}^{(*)}$ obtained using equation (45b) in absence of surfactant

${}^0k_{2H}^{(\Delta)}$ obtained using equation (50) in presence of CPC

${}^0k_{2H}^{(\#)}$ obtained using equation (54) in presence of SDS

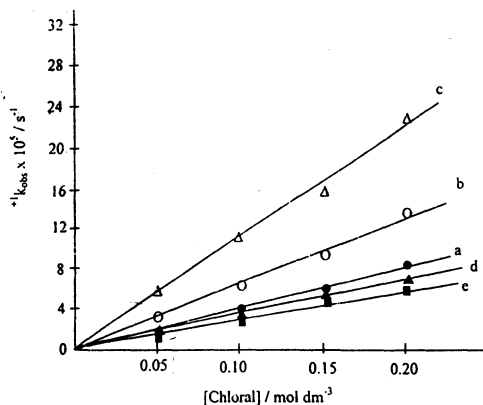


Fig. 17. Showing dependence of k_{obs} on $[\text{Chloral}]$ at different temperatures in the presence of CPC at $[\text{H}^+] = 0.20 \text{ mol dm}^{-3}$; $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$;
 a: $[\text{CPC}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ at 45°C , b: $[\text{CPC}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ at 50°C ,
 c: $[\text{CPC}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ at 55°C , d: $[\text{CPC}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ at 45°C ,
 e: $[\text{CPC}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ at 45°C .

The mechanism proposed for the oxidation of formaldehyde is also applicable in the case of chloral hydrate without requiring any change.

The oxidation of chloral hydrate in the presence of CPC and SDS exhibits same kinetic features as observed in case of formaldehyde. The catalytic effect of surfactant is much less in case of chloral hydrate as compared to the oxidation of formaldehyde. However, in both the cases it is observed that the reaction is catalyzed even in the pre-micellar concentration region obeying similar rate laws.

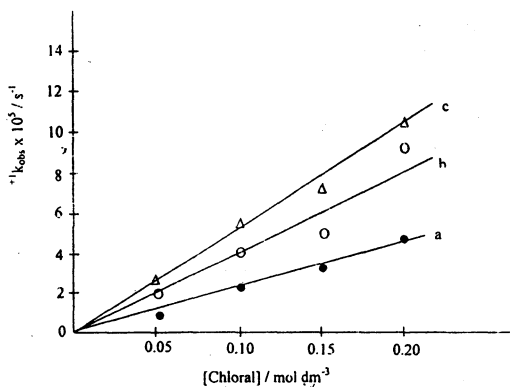


Fig. 18. Showing dependence of k_{obs} on $[\text{Chloral}]$ at different temperatures in the presence of CPC at $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$; $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{CPC}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$
 a: 45°C , b: 50°C , c: 55°C

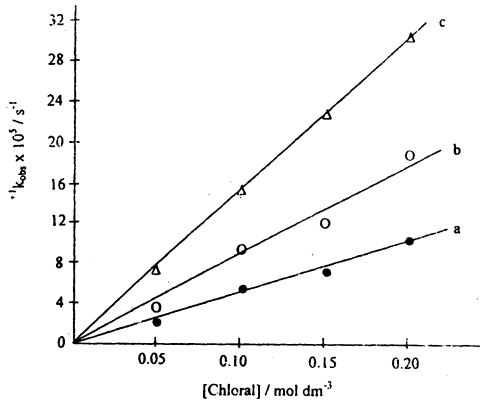


Fig. 19. Showing dependence of k_{obs} on $[Chloral]$ at different temperatures in the presence of CPC at $[H^+] = 0.30 \text{ mol dm}^{-3}$; $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$; $[CPC] = 3 \times 10^{-3} \text{ mol dm}^{-3}$
 a: 45°C, b: 50°C, c: 55°C

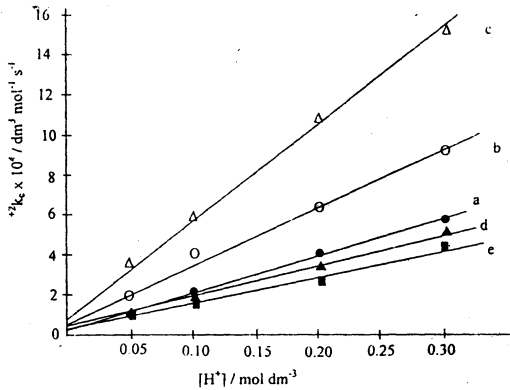


Fig. 20. Showing the variation of ${}^{+2}k_c$ with $[H^+]$ at different temperatures in the presence of CPC at $[Chloral] = 0.10 \text{ mol dm}^{-3}$; $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
 a: $[CPC] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ at 45°C, b: $[CPC] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ at 50°C,
 c: $[CPC] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ at 55°C, d: $[CPC] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ at 45°C,
 e: $[CPC] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ at 45°C.

TABLE-6

Temperature (°C)	${}^{+}K_C'' \times 10^{-2}$ (mol ⁻¹ dm ³)	${}^{-}K_C'' \times 10^{-2}$ (mol ⁻¹ dm ³)	${}^{+}k'_{HD}$	${}^{-}k'_{HD}$
45	8.06	1.35	2.10	0.27
50	6.25	1.22	2.45	0.34
55	3.94	1.20	2.38	0.62

Kinetics of Oxidation of Chloral Hydrate in the Presence of CPC

The oxidation of chloral hydrate follows the reaction rate expression used for the oxidation of formaldehyde.

$$\frac{-d[\text{Br(V)}]}{dt} = \frac{k_2'K_{\text{OX}} + k_2''K_{\text{OX}}K_{\text{OXH}}[\text{H}^+] + {}^+k_{\text{HD}}[\text{H}^+][\text{D}^+]}{{}^+K_{\text{C}} + {}^+K_{\text{C}}'[\text{D}^+]} [\text{AL}]_{\text{T}}[\text{BrO}_3]_{\text{T}} \quad (46)$$

Eqn. (46) is similar to eqn. (28)

where ${}^+K_{\text{C}} = K_{\text{AH}} + K_{\text{OX}}$ and ${}^+K_{\text{C}}' = K_{\text{OX}}{}^+K$

dividing both the numerator as well as denominator by ${}^+K_{\text{C}}$, we get

$$\frac{{}^+k_{\text{obs}}}{[\text{AL}]_{\text{T}}} = {}^+k_{\text{C}} = \frac{{}^0k_{2\text{C}} + {}^0k_{2\text{H}}[\text{H}^+] + {}^+k_{\text{HD}}[\text{H}^+][\text{D}^+]}{1 + {}^+K_{\text{C}}''[\text{D}^+]} \quad (47)$$

where ${}^+K_{\text{C}}'' = ({}^+K_{\text{C}}' / {}^+K_{\text{C}})$

$${}^+k_{\text{C}} = \frac{{}^0k_{2\text{C}}}{(1 + {}^+K_{\text{C}}''[\text{D}^+])} + \frac{({}^0k_{2\text{H}} + {}^+k_{\text{HD}}[\text{D}^+])[\text{H}^+]}{(1 + {}^+K_{\text{C}}''[\text{D}^+])} \quad (47\text{x})$$

$${}^+k_{\text{C}} = I_{\text{XC}} + S_{\text{XC}}[\text{H}^+] \quad \text{at constant } [\text{D}^+] \quad (48)$$

where $I_{\text{XC}} = \frac{{}^0k_{2\text{C}}}{(1 + {}^+K_{\text{C}}''[\text{D}^+])}$ and $S_{\text{XC}} = \frac{({}^0k_{2\text{H}} + {}^+k_{\text{HD}}[\text{D}^+])}{(1 + {}^+K_{\text{C}}''[\text{D}^+])}$

In this case also, the dependence of the intercept on $[\text{D}^+]$ has been verified.

$$\frac{1}{I_{\text{XC}}} = \frac{1}{{}^0k_{2\text{C}}} + \frac{{}^+K_{\text{C}}''[\text{D}^+]}{{}^0k_{2\text{C}}} \quad (49)$$

The plot between I_{XC}^{-1} vs. $[\text{D}^+]$ is linear and the reciprocal of the intercept of this plot gives ${}^0k_{2\text{C}}$, the rate constant associated with the reaction paths, which is not affected by hydrogen ion concentration and the surfactant in Fig. 21. This

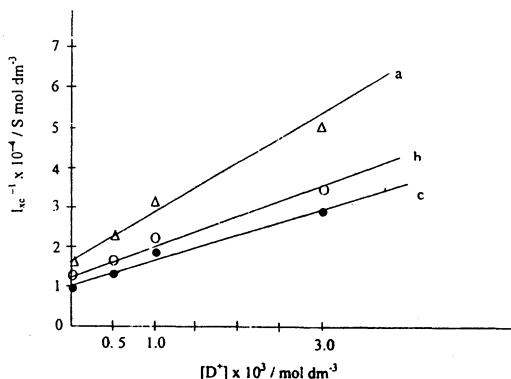


Fig. 21. Showing dependence of I_{XC}^{-1} (intercept from Figs. 16, 36, eqn. 49) on $[\text{D}^+]$ at different temperatures; $[\text{NaBrO}_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
 a: 45°C, b: 50°C, c: 55°C

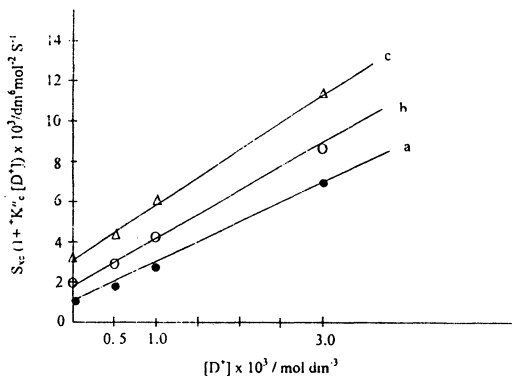


Fig. 22. Showing dependence of $S_{XC}(1 + {}^+K'_C[D^+])$ on $[D^+]$ at different temperatures (Where S_{XC} is slop from Figs. 16, 36, eqs. 50); $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
 a: 45°C, b: 50°C, c: 55°C

value has been obtained earlier using eqn. (45b). Both values are quite in agreement with each other (Table-4). The slopes of these plots are used to determine ${}^+K'_C$.

Using slope of equation (47x),

$$S_{XC} = \frac{{}^0k_{2H} + {}^+k'_{HD}[D^+]}{\{1 + {}^+K'_C[D^+]\}}$$

we can arrange the above equation as

$$S_{XC}\{1 + {}^+K'_C[D^+]\} = {}^0k_{2H} + {}^+k'_{HD}[D^+] \tag{50}$$

The plots between $S_X\{1 + {}^+K'_C[D^+]\}$ vs. $[D^+]$ are also found to be linear at different temperatures in Fig. 22.

Kinetics of Oxidation of Chloral Hydrate in Presence of SDS

As mentioned earlier that the kinetic features of oxidation of chloral hydrate in the presence of SDS follow the same pattern as in the case of formaldehyde, this has been verified by using the rate expression:

$$\frac{-d[Br(V)]}{dt} = \frac{{}^k_2K_{OX} + {}^k_{2H}K_{OX}K_{OXH}[H^+] + {}^k_{HD}[H^+][D^-]}{{}^-K_C + {}^-K'_C[D^-]} [AL]_T [BrO_3^-]_T \tag{51}$$

The dependence of observed pseudo first order rate constant ${}^{-1}k_{obs}$ on $[AL]_T$, $[H^+]$ and $[D^-]$ have been verified using the expression:

$${}^{-1}k_{obs} = \frac{{}^0k_{2C} + {}^0k_{2H}[H^+] + {}^-k'_{HD}[H^+][D^-]}{1 + {}^-K'_C[D^-]} [AL]_T$$

$$\frac{{}^{-1}k_{obs}}{[AL]_T} = {}^{-2}k_C = \frac{{}^0k_{2c} + {}^0k_{2H}[H^+] + {}^-k'_{HD}[H^+][D^-]}{1 + {}^-K'_C[D^-]} \tag{52}$$

where ${}^0k_{2C} = \frac{{}^k_{2C}K_{OX}}{K_{AH} + K_{OX}}$ and ${}^0k_{2H} = \frac{{}^k_{2H}K_{OX}K_{OXH}}{K_{AH} + K_{OX}}$

$$k_{HD} = (k_1 K_{AH} K_{OX} K_C)$$

$$k'_{HD} = \frac{k_{HD}}{K_C} \quad \text{and} \quad K''_C = \frac{K_C}{K_C}$$

The plot between $^{-1}k_{obs}$ versus $[AL]_T$ passes through the origin in Figs. 23–25. Also the plot between $^{-2}k_C$ versus $[H^+]$ at constant $[D^+]$ is found to be linear giving intercept I_{YC} and slope S_{YC} in Fig. 26.

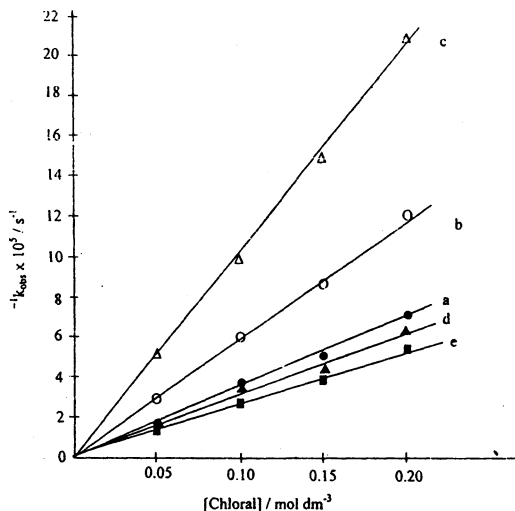


Fig. 23. Showing dependence of k_{obs} on $[Chloral]$ at different temperatures in presence of SDS

at $[H^+] = 0.20 \text{ mol dm}^{-3}$; $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$;

a: $[SDS] = 3 \times 10^{-2} \text{ mol dm}^{-3}$ at 45°C ,

b: $[SDS] = 3 \times 10^{-2} \text{ mol dm}^{-3}$ at 50°C ,

c: $[SDS] = 3 \times 10^{-2} \text{ mol dm}^{-3}$ at 55°C ,

d: $[SDS] = 1 \times 10^{-2} \text{ mol dm}^{-3}$ at 45°C ,

e: $[SDS] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ at 45°C .

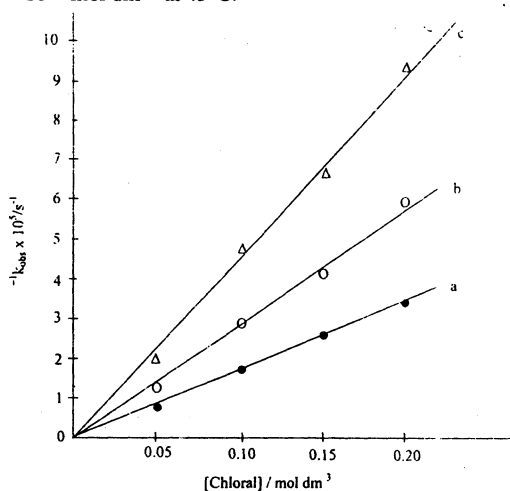


Fig. 24. Showing dependence of k_{obs} on $[Chloral]$ at different temperatures in presence of SDS

at $[H^+] = 0.10 \text{ mol dm}^{-3}$; $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$; $[SDS] = 1 \times 10^{-2} \text{ mol dm}^{-3}$

a: 45°C , b: 50°C , c: 55°C

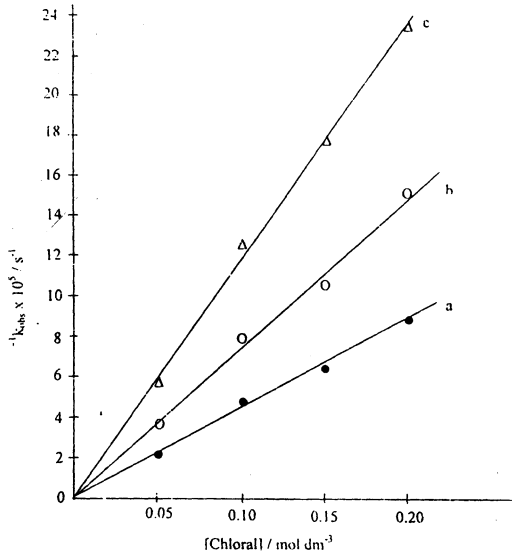


Fig. 25. Showing dependence of k_{obs} on $[Chloral]$ at different temperatures in presence of SDS at $[H^+] = 0.30 \text{ mol dm}^{-3}$, $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, $[SDS] = 1 \times 10^{-2} \text{ mol dm}^{-3}$ a: 45°C, b: 50°C, c: 55°C

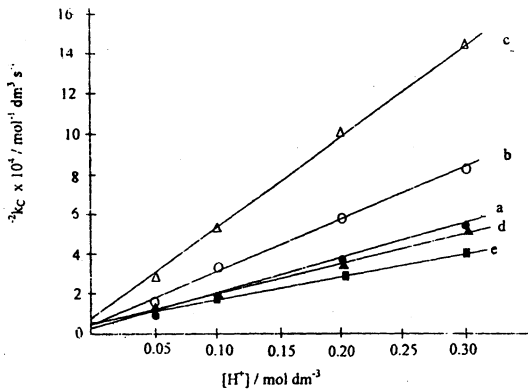


Fig. 26. Showing the variation of $^{-2}k_C$ with $[H^+]$ at different temperatures in presence of SDS at $[Chloral] = 0.10 \text{ mol dm}^{-3}$, $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$; a: $[SDS] = 3 \times 10^{-2} \text{ mol dm}^{-3}$ at 45°C, b: $[SDS] = 3 \times 10^{-2} \text{ mol dm}^{-3}$ at 50°C, c: $[SDS] = 3 \times 10^{-2} \text{ mol dm}^{-3}$ at 55°C, d: $[SDS] = 1 \times 10^{-2} \text{ mol dm}^{-3}$ at 45°C, e: $[SDS] = 5 \times 10^{-3} \text{ mol dm}^{-3}$ at 45°C.

$$^{-2}k_C = \frac{{}^0k_{2C}}{(1 + {}^{-1}K'_c[D^-])} + \frac{({}^0k_{2H} + {}^{-1}k'_{HD}[D^-])}{(1 + {}^{-1}K'_c[D^-])} [H^+] \quad (53)$$

$$^{-2}k_C = I_{YC} + S_{YC}[H^+] \quad \text{at constant } [D^-]$$

where
$$I_{YC} = \frac{{}^0k_{2C}}{1 + {}^-\overline{K}_C''[D^-]} \tag{53a}$$

and
$$S_{YC} = \frac{{}^0k_{2H} + {}^-\overline{K}'_{HD}[D^-]}{1 + {}^-\overline{K}_C''[D^-]} \tag{53b}$$

The dependence of I_{YC} on $[D^-]$ has been tested as discussed earlier. It has been observed that the plot between I_{YC}^{-1} versus $[D^-]$ is linear and giving ${}^0k_{2C}$ and ${}^-\overline{K}_C''$ at different temperatures in Fig. 27. Knowing the value of ${}^-\overline{K}_C''$ the dependence of S_{YC} on $[D^-]$ has also been tested by using the expression in Fig. 28.

$$(1 + {}^-\overline{K}_C''[D^-])S_{YC} = {}^0k_{2H} + {}^-\overline{K}'_{HD}[D^-] \tag{54}$$

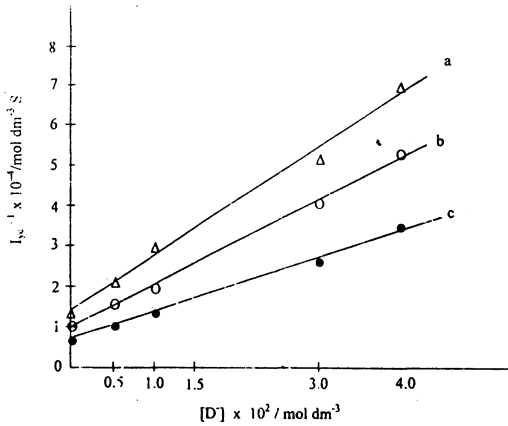


Fig. 27. Showing dependence of I_{YC}^{-1} on $[D^-]$ (intercept from Figs. 16, 26, eqn. 53x) at different temperatures, $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
 a: 45°C, b: 50°C, c: 55°C

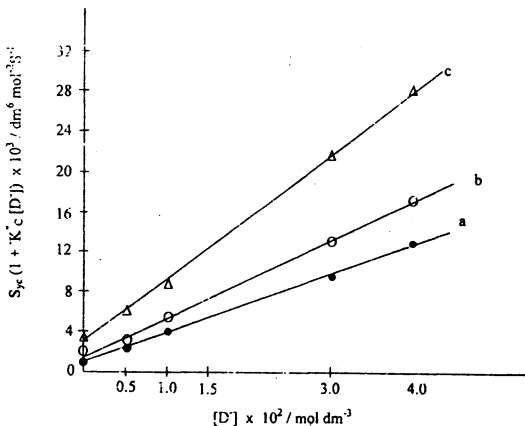


Fig. 28. Showing dependence of $S_{YC}(1 + {}^-\overline{K}_C''[D^-])$ on $[D^-]$ at different temperatures (where S_{YC} is slope from Figs. 16, 26, eqn. 54); $[NaBrO_3] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
 a: 45°C, b: 50°C, c: 55°C

It is observed that ${}^0k_{2H}$ and ${}^0k_{2C}$ obtained earlier in the presence of CPC and also without any surfactant compared well with those obtained in the presence of SDS (Tables 4 and 5) justifying our assumption that the two reaction paths, which operate in the absence of surfactant, remain unaffected by the presence of SDS. It is only the third reaction path in which the oxidising species is HDBrO_3^- , which affects the kinetic parameters. At lower $[\text{H}^+]$ the equation (53) may be modified to

$${}^{-2}k_C = \frac{{}^0k_{2C}}{(1 + {}^{-}K_c''[\text{D}^-])} + \frac{{}^0k_{2H}[\text{H}^+]}{(1 + {}^{-}K_c''[\text{D}^-])}$$

neglecting the ${}^{-}k_{HD}'[\text{D}^-][\text{H}^+]$ in view of the fact that ${}^{-}k_{HD}'$ is much smaller as compared to ${}^{+}k_{HD}'$ appearing in eq. (47). It is observed that at very low $[\text{H}^+]$ the rate of reaction slows down with increase in the concentration of SDS. This pattern remains unchanged at different temperatures. It is also observed that at high concentration of chloral hydrate the effect of concentration of SDS remains marginal on k_{obs} . This suggests that SDS catalyzed reaction path is marginal and overall reaction proceeds in bulk.

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