Kinetics and Mechanism of SDS Catalyzed Reaction between Ethanol and N-bromobenzamide

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A reaction between ethanol and N-bromobenzamide (NBB) in acidic medium has been found to be catalyzed by an anionic surfactant SDS. The log $(a - x)$ *vs.* t curve displays an inflection, *i.e.*, slow first stage followed by relatively faster second stage. In both the stages the reaction follows first order behaviour with respect to substrate and N-bromobenzamide. The cause of autocatalysis has been attributed to Br⁻ ions, which was further substantiated by the removal of first stage on initial addition of potassium bromide. The pre-micellar kinetics has been rationalised in the light of pseudo-phase model. The positive cooperativity index has been computed $(n = 1.47)$. The solvent composition variation and addition of benzamide have also been studied. On the basis of the various observations and product characterization, most plausible mechanisms have been envisaged.

Key Words: N-Bromobenzamide, Inflection, Micellar, Autocatalysis.

INTRODUCTION

A considerable amount of work has been done by various workers on oxidation of primary alcohols by N-halo compounds in general and N-bromobenzamide in particular[1-5] but no information is available on the oxidation of ethanol by N-bromobenzamide (NBB) in micellar system. Therefore, the present study of oxidation of ethanol by NBB in presence of sodium dodecyl sulfate, an anionic surfactant, is undertaken.

EXPERIMENTAL

All chemicals used were of BDH/Fluka/Merck or AnalaR. Stock solution of ethanol was prepared by dissolving it in distilled water while the progress of the reaction was monitored by iodometric estimations of the reaction mixture at various time intervals. To avoid photochemical effect the reaction bottle was painted black.

RESULTS AND DISCUSSION

This has been observed that for the micellar catalyzed oxidation of ethanol,

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the plot of log (a - x) *vs.* time exhibits two stages, slow initial stage followed by relatively faster second step (Fig. 1). Linearity of both the stages indicates unit order with respect to the oxidant in both the stages for each substrate. The variation of initial concentration of NBB has practically no effect on the reaction rate and the values of pseudo first order constants k_1 (for the first stage) and k_1' (for the second stage) for all the substrates are found to be fairly constant. The
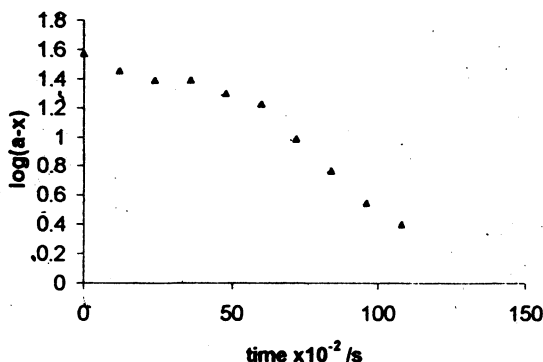

Fig. 1

order with respect to oxidant is thus confirmed to be one.

Dependence of rate on [Ethanol]:   With the increase in the concentration of substrate the pseudo first order rate constants $k_1(k_1')$ are found to be increased. Plot of log k_1 (log k_1') *vs.* log [ethanol] give straight lines with slopes equal to 0.93 ($r^2 = 0.997$) and 0.94 ($r^2 = 0.986$) for the first and second stages respectively. These values confirm that the order of reaction with respect to each substrate is one.

Dependence of rate on surfactant concentration: The reaction rate increases with the increase in concentration of sodium dodecyl sulphate (NaDS) from 2.0×10^{-3} to 2.0×10^{-2} M [Table-1]. The reported cmc of sodium dodecyl sulfate is 8.1×10^{-3} M. The catalysis below cmc, *i.e.*, premicellar catalysis is not unusual[6]. The rate of reactions gets enhanced due to the fact that small aggregates of the detergent molecules exist below the cmc and that they catalyse the reaction. The mathematical justification of premicellar catalysis by sodium dodecyl sulfate has therefore been treated by a scheme proposed by Piszpiwicz[7].

$$\log [(k_{obs} - k_0)/(k_m - k_{obs})] = n \log [D] - \log K_D \qquad (1)$$

From eq. (1) the plot of log $[(k_{obs} - k_0)/(k_m - k_{obs})]$ *vs.* log [D] should be linear with a slope = n, called the index of co-operativity whose values ranges from 1 to 6. In the present case the value of n for ethanol has been found to be 1.47 indicating a positive cooperativity, *i.e.*, induced interaction of the additional substrate molecule due to the interaction of the micelle with the first substrate molecule.

Temperature and solvent composition variation: It has been observed that reactions follow the Arrhenius relationship. All the kinetic and activation

parameters have been calculated. The reactions were studied at different compositions of acetic acid-water mixture (v/v). Examination of the results indicates that the reactions are remarkably affected by the variation in solvent composition. Further Amis plots for all the three substrates, *i.e.*, plots of log k_1 (log k_1') *vs.* 1/D are linear with positive slopes. This indicates the interaction of a positive ion and a dipole in the rate-determining step.

TABLE-1
EFFECT OF VARIATION OF SURFACTANT CONCENTRATION

$[NBB] = 2.5 \times 10^{-3}$ mol dm^{-3}; [ethanol] = $0.5 \times$ mol dm^{-3};
$[H_2SO_4] = 0.5$ mol dm^{-3}; AcOH = 10%;
Temp. 308 K

S.No.	[NaDS] $\times 10^4$ mol dm^{-3}	$k_1 \times 10^4$	$k_1' \times 10^4$
1.	0.0	0.59	3.37
2.	2.0	0.98	3.89
3.	4.0	1.33	4.90
4.	6.0	1.93	6.22
5.	8.0	2.41	7.55
6.	10.0	3.01	8.91
7.	13.0	3.76	9.04
8.	15.0	3.81	9.24

*Mean of duplicate runs.

Effect of addition of bromide ions: In case of reactions oxidized by N-bromobenzamide, the role of bromide ion is vital; therefore, the effects of initially added bromide ions have been studied. As a result of this the slow step is suppressed completely. The reaction becomes simple single step in all the three cases with the magnitude of rate constants found almost same as that of corresponding second stages. Venkatasubramanian *et al.*[8] have made similar observations.

Effect of initially added benzamide: In order to confirm the formation of benzamide in pre-equilibrium state, the effect of initially added benzamide was studied. The reaction rate has been found to be retarded with the incremental addition of benzamide.

Stoichiometry and Product Analysis
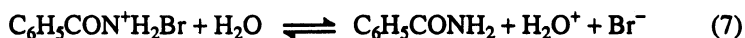
The stoichiometry found to be

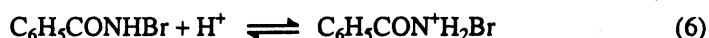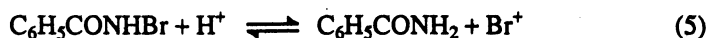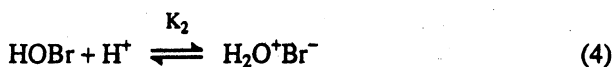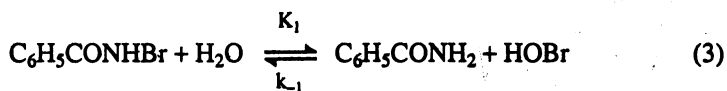$$CH_3CH_2OH + C_6H_5CONHBr \longrightarrow CH_3CHO + C_6H_5CONH_2 + HBr \qquad (2)$$

The product analysis was done under the kinetic conditions. Ethanol (0.05 mol) and NBB (0.01 mol) were made up to 50 mL in H_2SO_4 and kept in dark for 24 h until the completion of the reaction. The solution was then treated overnight with excess (200 mL) saturated solution of 2,4-dinitrophenyl hydrazine (DNP) in 2 mol dm^{-3} hydrochloric acid. The precipitated 2,4-dinitrophenyl hydrazone was

collected by filtration. This was further confirmed by the determination of melting point, TLC and IR with standard.
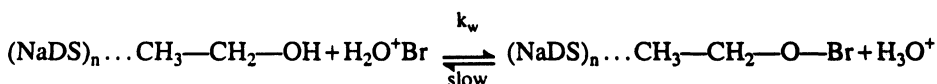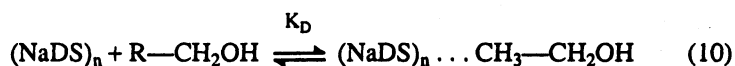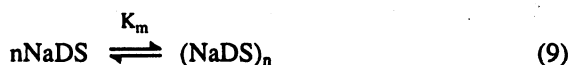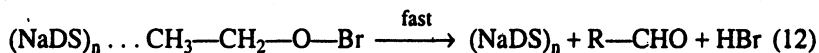
Mechanism

On the basis of various experimental results and literature following reaction mechanisms have been envisioned for the first and subsequently second stage. N-bromobenzamide like other similar N-haloamides may exist in various forms in the acid medium, *viz.*, free NBB, protonated NBB, Br^+, molecular bromine and $HOBr/H_2O^+Br$. The different forms of reactive species for oxidant can be represented by the following equillibria:

$$C_6H_5CONHBr + H_2O \underset{k_{-1}}{\overset{K_1}{\rightleftharpoons}} C_6H_5CONH_2 + HOBr \qquad (3)$$

$$HOBr + H^+ \overset{K_2}{\rightleftharpoons} H_2O^+Br^- \qquad (4)$$

$$C_6H_5CONHBr + H^+ \rightleftharpoons C_6H_5CONH_2 + Br^+ \qquad (5)$$

$$C_6H_5CONHBr + H^+ \rightleftharpoons C_6H_5CON^+H_2Br \qquad (6)$$

$$C_6H_5CON^+H_2Br + H_2O \rightleftharpoons C_6H_5CONH_2 + H_2O^+ + Br^- \qquad (7)$$

$$C_6H_5CON^+H_2Br + Br^- \rightleftharpoons C_6H_5CONH_2 + Br_2 \qquad (8)$$

If free NBB were the active species in the rate determining step, addition of benzamide would have increased the reaction rate; however, addition of benzamide in the reaction system decreases the reaction rate. This can be easily explained in the light of the equilibrium (1) where benzamide and HOBr are produced. Addition of benzamide shifts the equilibrium to the left thereby reducing the concentration of $HOBr/H_2O^+$ Br, which is the main oxidising species, resulting in the retardation of the reaction rates. Amis plot, *i.e.*, plot of $\log k_1(\log k_1')$ *vs.* $1/D$ is a straight line with a positive slope, suggests that the reaction is between an ion and a dipole.
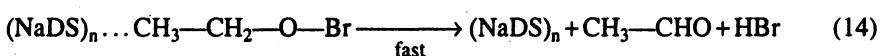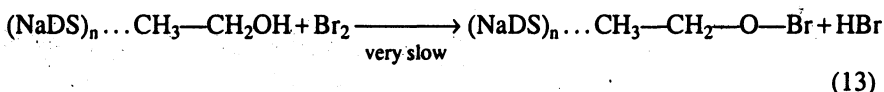
Micellar catalysed mechanism for first stage: In micellar catalysed reactions the first step is the formation of micelle due to aggregation of detergent molecules. Then micelle-substrate interaction takes place. This is followed by the slowest step in which H_2O^+Br oxidizes the substrate followed by the subsequent fast steps.

$$nNaDS \overset{K_m}{\rightleftharpoons} (NaDS)_n \qquad (9)$$

$$(NaDS)_n + R—CH_2OH \overset{K_D}{\rightleftharpoons} (NaDS)_n \dots CH_3—CH_2OH \qquad (10)$$

$$(NaDS)_n \dots CH_3—CH_2—OH + H_2O^+Br \underset{slow}{\overset{k_w}{\rightleftharpoons}} (NaDS)_n \dots CH_3—CH_2—O—Br + H_3O^+$$

$$(11)$$

$$\text{(NaDS)}_n \dots CH_3—CH_2—O—Br \xrightarrow{\text{fast}} \text{(NaDS)}_n + R—CHO + HBr \quad (12)$$

Mechanism for second stage

It has been observed that after about 20% completion of the reaction the solution becomes yellowish. This is obviously due to the liberation of bromine. It is formed due to the interaction between the unreacted NBB and bromide ion, one of the products of the reaction. Bromide ions come into the system as a result of eq. (7). The removal of first stage on addition of potassium bromide supports this. The production of bromine by an autocatalytic reaction was further confirmed by the addition of mercury(II)—a bromocomplexing agent, as it forms unionised mercury-bromo-complexes and removes the first stage[9]. Bromine formed as a result of eq. (8) will simultaneously start oxidizing the micelle-substrate moiety as:

$$\text{(NaDS)}_n \dots CH_3—CH_2OH + Br_2 \longrightarrow \text{(NaDS)}_n \dots CH_3—CH_2—O—\overset{\cdot}{Br} + HBr$$
$$\text{very slow}$$
$$(13)$$

$$\text{(NaDS)}_n \dots CH_3—CH_2—O—Br \xrightarrow{\text{fast}} \text{(NaDS)}_n + CH_3—CHO + HBr \quad (14)$$

The above mechanism leads us to give the rate expression as follows for the first stage:

$$-d[\text{NBB}]/dt = K[n\text{NaDS}][C_6H_5CONHBr][CH_3—CH_2OH]/C_6H_5CONH_2$$

$$\text{where } K = \frac{k_w K_m K_D K_1 K_2 [H^+]}{(K_{-1} + K_J [H^+])}$$

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