

Kinetic and Mechanistic Investigation of Oxidation of Butan-2-ol by N-Bromosaccharin in Aqueous Acetic Acid Medium in the Presence and Absence of Surfactants

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Abstract

The oxidation of butan-2-ol by N-bromosaccharin in aqueous acetic acid medium and in the presence of Hg(II) acetate was investigated in presence and absence of both cationic and anionic surfactant. The reaction between alcohol and NBSA in aqueous acetic acid medium exhibits 1:1 stoichiometry. The reaction is first order in NBSA both in presence and absence of micelles. The kinetic results indicate that the first order kinetics in butan-2-ol at lower concentration tends towards a zero order at its higher concentration. Both type of micelles catalyze the oxidation reaction. Binding parameters have been analyzed by the data using the Piszewicz model. A suitable mechanism was proposed on the basis of experimental results. The activation parameters were calculated.

Keywords: Oxidation, Butan-2-ol, N-Bromosaccharin, Cetyltrimethyl Ammonium Bromide (CTAB), Sodium Lauryl Sulphate (NaLS).

studies of cyclic and secondary alcohols in the presence[1] and absence[2] of added saccharin, primary alcohol[3], ketones [4], α -hydroxy acids[5], α - amino acids[6] etc. have been investigated by N-bromosaccharin.

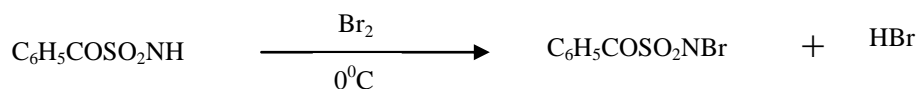
Alcohols are most exhaustively explored for oxidative kinetic investigation. The oxidative kinetics of primary and secondary alcohols by different oxidants like N-bromosuccinimide (NBS)[7], pyridinium chlorochromate (PCC)[8], bromine-T[9], potassium bromate[10-13], cerium (IV)[14,15], thallium (III) acetate[16], peroxy disulphate[17] etc. have been reported. The literature survey reveals that there is no report on the mechanistic studies on catalytic effect of both cationic (CTAB) and anionic (NaLS) surfactant on the N-bromosaccharin oxidation of butan-2-ol.

1. Introduction

N-bromosaccharin is a stable compound and moderately strong oxidizing agent. Kinetic oxidation

2. Experimental

N-Bromosaccharin was prepared by the bromination of alkaline solution of saccharin at 0°C .



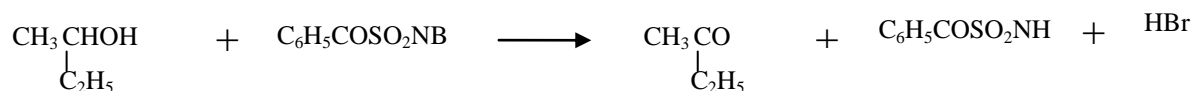
It is insoluble in water hence aqueous acetic acid solution is used. The strength of the solution is estimated iodometrically [18].The solution of butan-2-ol, CTAB , NaLS ,sodium perchlorate ,potassium dichromate and saccharin were prepared by dissolving their appropriate amount in distilled water

3. Kinetic studies

Kinetic studies of reactions were carried out using Ostwald's isolation method. Mercuric acetate used traps bromine by forming unionized HgBr_2 and HgBr_4^- . The rate of reaction was followed by estimating the unreacted N-bromosaccharin iodometrically.

4. Stoichiometry and Product Analysis

Stoichiometric studies were carried out under condition $[\text{NBSA}] \gg \gg [\text{butan-2-ol}]$ in the presence and absence of micelles. The reaction mixture containing $[\text{NBSA}] = 2.0 \times 10^{-2}\text{M}$, $[\text{butan-2-ol}] = 2.0 \times 10^{-3}\text{M}$, $[\text{Hg}(\text{OAc})_2] = 1.0 \times 10^{-2}\text{M}$, $[\text{CTAB}] = 5.0 \times 10^{-6}\text{M}$, $[\text{NaLS}] = 5.0 \times 10^{-5}\text{M}$, $\text{AcOH-H}_2\text{O} = 40\%$ (v/v) was kept for 36 h at 40°C temperature. The concentration of NBSA was estimated at regular interval of time iodometrically. It has been observed that one mol alcohol consumed one mol of oxidant yielding corresponding ketone as oxidation product. Stoichiometric equation may be represented as:



The oxidation product of methyl ethyl ketone was confirmed by forming its 2,4-dinitrophenylhydrozone derivative(m.p.= 115°) .

5. Results and discussion

N-bromosaccharin oxidation of butan-2-ol in the presence and absence of cetyltrimethylammonium bromide (CTAB)- cationic surfactant and sodium laurylsulphate (NaLS) – anionic surfactant was carried out under the condition $[\text{butan-2-ol}]$ and $[\text{Hg}(\text{II})] \gg \gg [\text{NBSA}]$.The reaction follows first order kinetics uniformly. The pseudo-first order rate constant decreases with increase in initial concentration of oxidant(Table-1).

Table-1 Dependence of rate on the concentration of reactants

[NBSA] 10 ³ M	[Butan-2-ol] 10 ² M	[HClO ₄] M	10 ³ k ₁ min ⁻¹		
			Without Micelles	With CTAB	With NaLS
2.00	2.0	0.0	46.47	50.33	44.18
2.50	2.0	0.0	42.38	38.25	40.23
3.33	2.0	0.0	41.13	33.80	38.28
5.00	2.0	0.0	35.31	27.18	30.95
10.0	2.0	0.0	22.11	15.60	23.35
2.0	1.25	0.0	36.25	37.00	35.25
2.0	1.43	0.0	39.15	40.46	38.15
2.0	1.66	0.0	42.23	44.18	41.44
2.0	2.50	0.0	48.72	53.35	47.18
2.0	3.33	0.0	52.42	59.44	51.97
2.0	2.0	0.10	51.17	55.63	49.17
2.0	2.0	0.20	53.87	58.12	51.81
2.0	2.0	0.30	55.91	59.86	53.81
2.0	2.0	0.40	58.72	62.25	56.61
2.0	2.0	0.50	61.19	64.55	59.2

[Hg(OAc)₂] = 1.0 x 10⁻²M, [CTAB] = 5.0 x 10⁻⁶M, [NaLS] = 6.66 x 10⁻⁵M, HOAc – H₂O = 40% (v/v), Temp = 30⁰C

The decrease in rate constant with increase in the concentration of oxidant suggests that N-bromosaccharin is involved in a pre-equilibrium with some nucleophile (probably H₂O) to form some intermediate with lower reactivity. Similar retardation in pseudo first order rate constant value was reported in N-bromosaccharin oxidation of benzhydrol[19], benzyl alcohol[20] and primary aliphatic alcohol[3]. The dependence of rate on the concentration of butan-2-ol was studied at different concentrations of alcohol and constant concentration of other reactants both in the presence and absence of micelles. The first order rate constant increases with increase in the concentration of butan-2-ol in each case (Table 1). For alcohol-NBSA-surfactant system the plot between k₁ and [butan-2-ol] is initially linear passing through origin and then bends towards X-axis at higher concentration of butan-2-ol. The double reciprocal plot between k₁ and [butan-2-ol] is linear with positive intercept on Y-axis (Fig-1) which provides a kinetic evidence for intermediate complex formation between oxidant and substrate species in pre- equilibrium step.

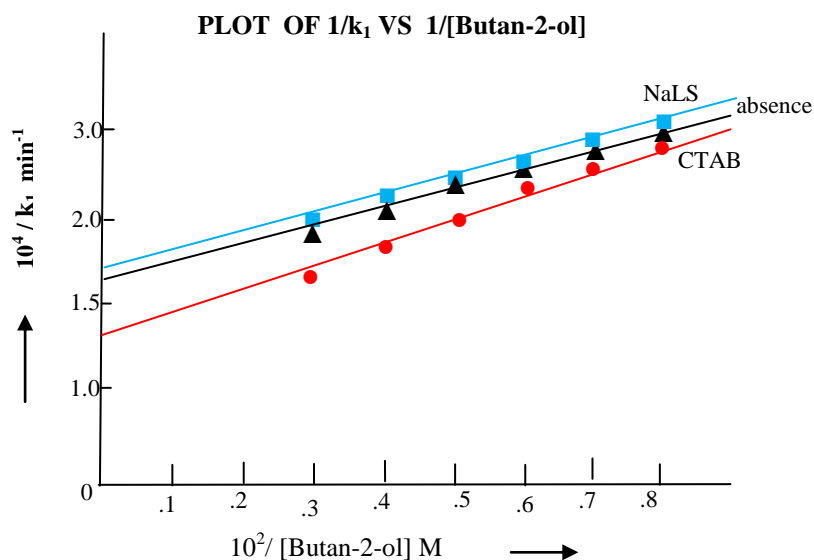


Fig. 1 : [NBSA] = 2.0 x 10⁻³M, [Hg (OAc)₂] = 1.0 x 10⁻²M · [CTAB] = 5.0 x 10⁻⁶M
 [NaLS] = 6.66.0 x 10⁻⁵M, HOAc– H₂O = 40%(v/v), Temp = 30⁰C

Oxidation of butan-2-ol with NBSA was investigated in varying initial concentrations of both CTAB and NaLS. The plot of k_1 versus [surfactant] depicts a curve with a maximum for both micelles i.e. the rate of oxidation increases with increase in [surfactant] before cmc and then after cmc rate is almost constant at higher concentration of surfactant[21]. The nature of plot (Fig. 2) suggest that the reaction is micellar catalyzed and biphasic i.e. the substrate alcohol is partitioned between the micelles and aqueous phase and hence the reaction proceeds in both the phase.

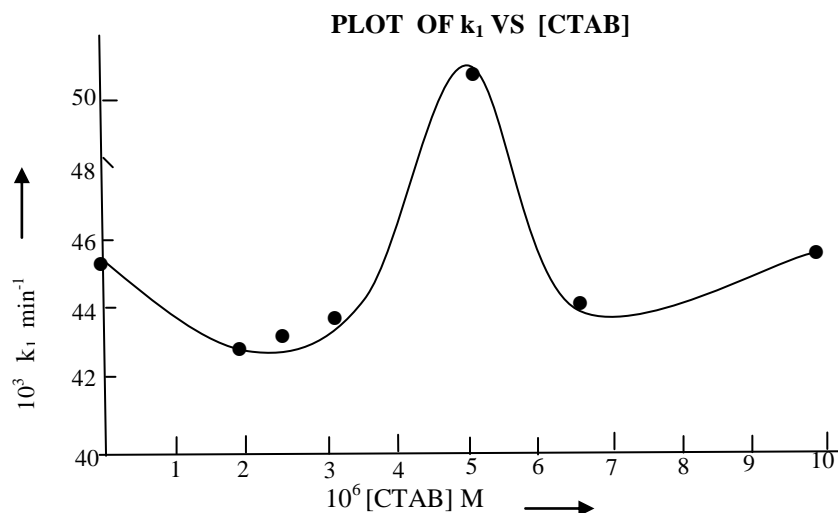


Fig. 2 : [NBSA] = $2.0 \times 10^{-3}M$, [Hg (OAc)₂] = 1.0×10^{-2} , [Butan-2-ol] = $2.0 \times 10^{-2}M$
HOAc – H₂O = 40%(v/v) , Temp = 30⁰ C

The effect of variation in the concentration of perchloric acid on the reaction rate was examined at different initial concentrations of perchloric acid. The pseudo first order rate constant increases with increasing concentration of acid (Table-1) suggesting that reaction is acid catalyzed in both absence and presence of micelles . However, the plots of $\log (k_1- k_0)$ against $\log [HClO_4]$ are linear with slope value nearly one confirming the order in perchloric acid is one.

Saccharin was identified as the reduction product of the oxidant .Hence the effect of addition of saccharin to the reaction mixture was studied at different concentrations of saccharin [Table 2]. From the table it is evident that with increasing concentration of saccharin rate of oxidation decreases. This retarding effect of saccharin may be attributed to its involvement in pre equilibrium hydrolysis of oxidant.

Table-2 Dependence of rate on the concentration of saccharin

SN	[Saccharin] 10 ³ M	10 ³ k ₁ min ⁻¹		
		Without Micelles	With CTAB	With NaLS
1	0.00	46.47	50.33	44.18
2	2.00	29.75	30.33	26.70
3	2.50	26.78	28.18	21.95
4	3.33	21.53	22.54	16.81
5	5.00	17.15	17.80	13.47
6	10.0	15.26	15.70	11.95

[NBSA] = $2.0 \times 10^{-3}M$, [Hg (OAc)₂] = 1.0×10^{-2} , [Butan-2-ol] = $2.0 \times 10^{-2}M$
[CTAB] = $5.0 \times 10^{-6}M$, [NaLS] = $6.66 \times 10^{-5}M$ HOAc – H₂O = 40%(v/v) , Temp = 30⁰ C

The rate constant increases with increase in the concentration of mercuric acetate. The plot of k_1 versus [mercuric acetate](Fig 4) is obtained linear passing through origin and then bends towards x-axis i.e. at higher concentration range of $\text{Hg}(\text{OAc})_2$, the pseudo first order rate constant is almost constant. In the present investigation, the reaction is carried out at a concentration of mercuric acetate, which do not affect the oxidation rate.

PLOT OF k_1 VS. $[\text{Hg}(\text{OAc})_2]\text{M}$

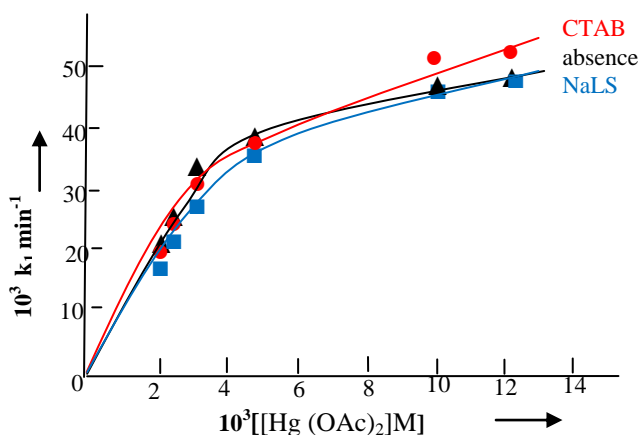


Fig. 3 : $[\text{NBSA}] = 2.0 \times 10^{-3} \text{M}$, $[\text{Butan-2-ol}] = 2.0 \times 10^{-2} \text{M}$, $\text{HOAc-H}_2\text{O} = 40\% (\text{V/V})$, $[\text{CTAB}] = 5.0 \times 10^{-6} \text{M}$, $[\text{NaLS}] = 6.66 \times 10^{-5} \text{M}$, $\text{Temp} = 30^\circ\text{C}$.

The effect of variation in dielectric constant of the medium was investigated with binary mixture of different compositions of acetic acid and water. The value of pseudo first order rate constant increases with increase in concentration of acetic acid in the absence of micelles and in the presence of NaLS but for CTAB- NBSA - alcohol system there is decrease in the value of pseudo first order rate constant beyond 50% acetic acid concentration (Table 3). The nature of the plot suggests interaction between dipole and positive ion in rate determining step.

Table-3 Dependence of rate on dielectric constant of the medium

HOAc-H ₂ O %(V/V)	10 ³ /D	10 ³ k ₁ min ⁻¹		
		Without Micelles	With CTAB	With NaLS
10	15.50	26.50	10.68	15.58
20	17.17	31.20	21.10	24.18
30	19.15	37.58	25.12	29.51
40	21.98	46.47	50.33	44.18
50	25.68	56.13	58.21	49.17
60	30.36	69.75	54.95	54.33
70	38.04	-	43.15	68.39

$[\text{NBSA}] = 2.0 \times 10^{-3} \text{M}$, $[\text{Hg}(\text{OAc})_2] = 1.0 \times 10^{-2} \text{M}$, $[\text{butan-2-ol}] = 2.0 \times 10^{-2} \text{M}$ $[\text{CTAB}] = 5.0 \times 10^{-6} \text{M}$, $[\text{NaLS}] = 6.66 \times 10^{-5} \text{M}$, $\text{Temp} = 30^\circ\text{C}$

Similar trend was observed by Banerji[22] et. al in N-bromoacetamide oxidation of primary alcohols in acetic acid medium. For CTAB catalysed oxidation, the decrease in rate constant at higher acetic acid concentration (beyond 50%) may be suggesting of HOBr (dipole) as the more reactive oxidant.

Sodium perchlorate (as neutral salt) has no significant effect on oxidation rate in absence as well as presence of micelles.

The reaction was studied at different temperatures and activation parameters were evaluated.

Thermodynamic Parameters

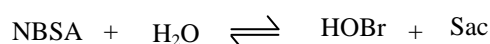
Table - 4

	E_a kJ mol⁻¹	A Sec¹	ΔH* kJ mol⁻¹	ΔG* kJ mol⁻¹	ΔS* JK mol⁻¹
Without Micelles	63.42	5.52 x 10 ⁻⁴	63.27	81.79	62.15
With CTAB	58.10	5.85 x 10 ⁻⁴	54.71	84.18	90.28
With NaLS	38.54	5.54 x 10 ⁻⁴	35.90	81.50	153.02

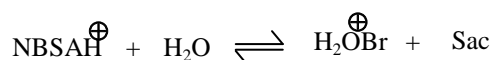
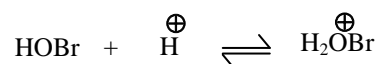
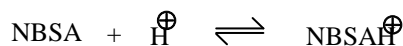
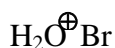
Based on kinetic results stoichiometry and product analysis a probable mechanism for the oxidation of butan-2-ol by N-Bromosaccharin in the presence and absence of micelles has been proposed .

In order to find out the mode of fission during the course of oxidation the effect of added acrylonitrile was investigated. The reaction mixture does not polymerise by added acrylonitrile ruling out the involvement of free radical intermediates.

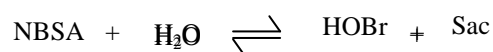
In aqueous medium NBSA hydrolyses according to the following equation



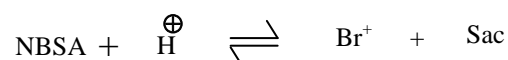
In the presence of mineral acid, the above species get protonated yielding NBSAH⁺ and



In NBSA oxidation of butan-2-ol the retarding effect of added saccharin rules out NBSA or NBSAH⁺ as active oxidant and on the other hand it suggests a pre equilibrium hydrolysis of oxidant.

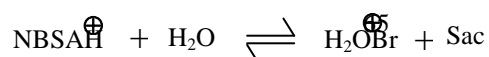
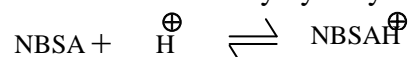


Acid catalysis and retardation of oxidation rate by added saccharin points out Br⁺ or H₂O⁺Br as active oxidant species.

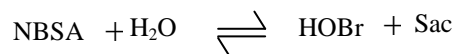


In aqueous solution it is difficult to distinguish between Br⁺ and H₂O⁺Br but since H₂O⁺Br is more electrophilic than Br⁺, it is the preferred species. Formation of hypobromous acidium ion may be formulated in two different ways

(a) Protonation of NBSA followed by hydrolysis

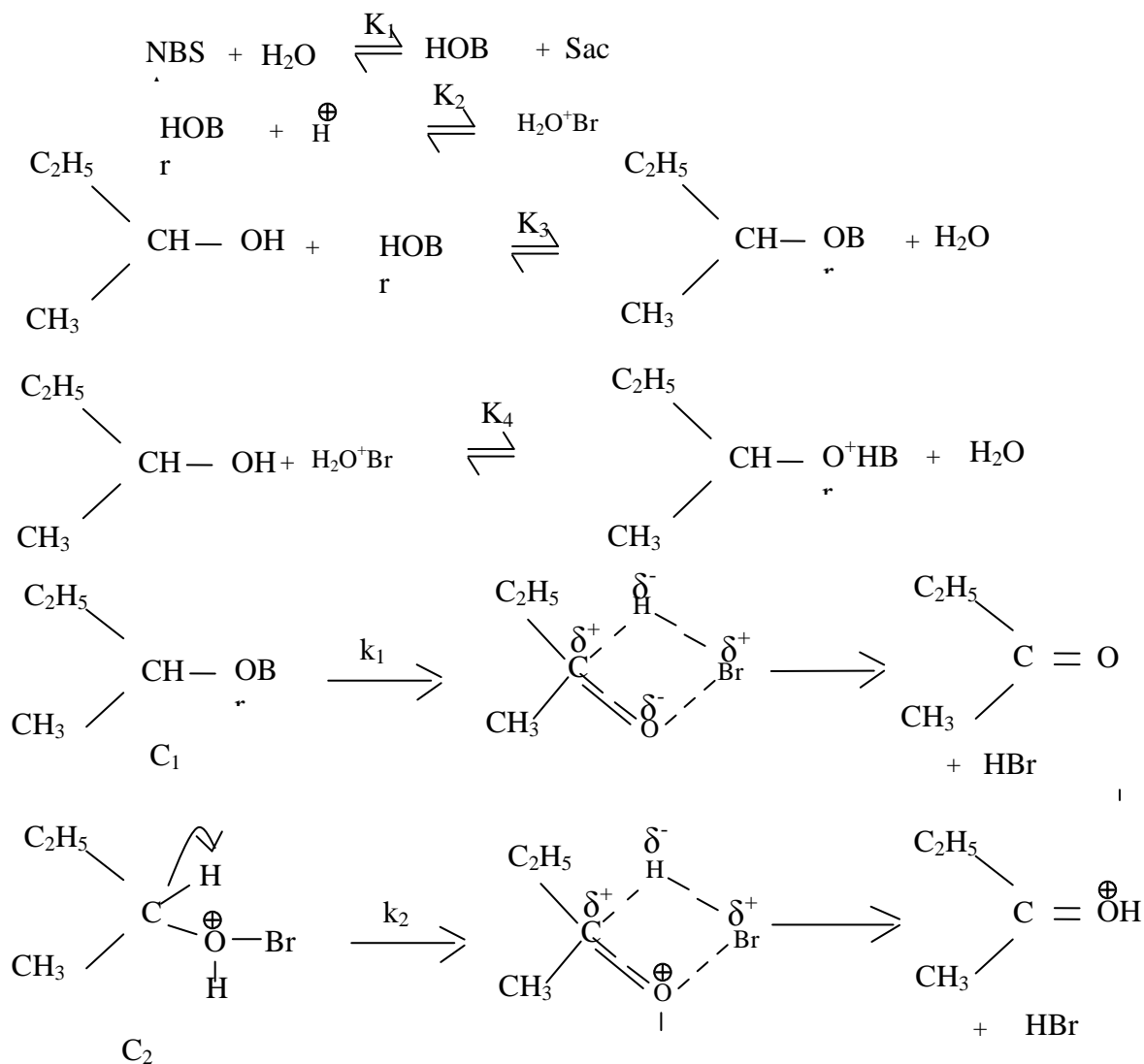


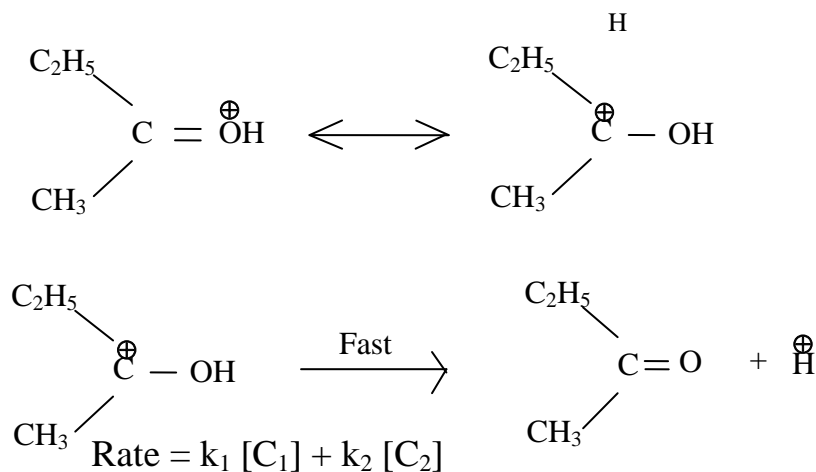
(b) Hydrolysis of NBSA followed by protonation of hydrolytic product



Alcohols are nucleophilic in nature. In present investigation observed acid catalysis suggests the possibility of protonated alcohol as the active reductant species. In such case oxidation of tert-butyl alcohol would have been faster than secondary alcohol under similar experimental conditions. The slow oxidation of tert-butyl alcohol rules out the protonation of alcohol [3]. Hence, the mechanistic step involves interaction between positive oxidant species and neutral alcohol molecule. Medium effect studies also suggest that slow step is positive ion-dipole reaction. In the presence and absence of micelles, Michaelis-Menten kinetics in [alcohol] is observed. This suggests formation of hypobromite ester in pre equilibrium followed by its decomposition in slow step.

Mechanism in the absence of micelles

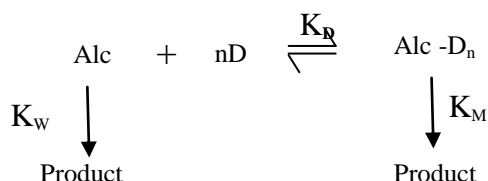




$$\frac{\text{Rate}}{[\text{NBSA}]_T} = k = \frac{K_1 [\text{Butan-2-ol}] (K_3 k_1 + K_2 K_4 k_2 [\text{H}^+])}{[\text{Sac}] + K_1 (1 + K_3 [\text{Butan-2-}]}$$

Oxidation of butan-2-ol in presence of micelles –

Rate enhancement for butan-2-ol-NBSA system in presence of both surfactants suggests that the present investigation is biphasic oxidation i.e. the substrate alcohol is partitioned between the micellar and the aqueous phase and hence the reaction proceed in both the phases. Micellar effects upon oxidation rate of alcohol has been analysed by Pizskiewicz[22] mode



According to kinetic results oxidation of butan-2-ol in presence of NaLS and CTAB is micellar catalyzed however, rate enhancement for NaLS is more pronounced than CTAB. The effective catalysis of oxidation by NaLS may be explained by electrostatic attraction between the protonated oxidant species, H₂O⁺ Br and the anionic micellar which bring both the reactant closer while the repulsive force between cationic micelle surface and H₂O⁺ Br make CTAB less effective.

Table 5 Fitting Parameters : Pizskiewicz Model

Surfactant	n	Log[D] ₅₀	10 ³ K _D
CTAB	0.76	-0.77	31.622
NaLS	0.87	-0.68	15.49

The index of co-operativity (n) is evaluated[23], a value of ‘n’ greater than unity implies positive co-operativity and less than unity implies negative co-operativity.

The value of thermodynamic parameters (table 5) gives additional support to the proposed mechanism. Ea decreases in the presence of

surfactant i.e. alcohol is oxidized at a faster rate in the presence of surfactant. Further the decrease in Ea is more in presence of NaLS than CTAB confirming the rate of micellar catalyzed oxidation is of the order NaLS > CTAB. The value of ΔH*, ΔS* and ΔG* are in favor of a bimolecular mechanism. The value of ΔG is almost equal in

presence and absence of surfactant suggesting that similar mechanism is operating under both conditions.

6. Conclusion

On the basis of kinetic result of the present investigation, among the various active species HOBr and $H_2O^+ Br$ are considered to be active oxidant. The results indicated that NaLS is more effective than CTAB. The oxidation is acid catalyzed. The overall mechanistic sequence described here is consistent with all experimental evidences.

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