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Research Article

Oxidative Kinetics of 2- Propanol by N-Bromosaccharin in Aqueous Acetic Acid Medium in the Presence and Absence of Micelles

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Abstract

Kinetic study of N-bromosaccharin oxidation of 2-propanol in aqueous acetic acid medium in the presence and absence of micelles CTAB and NaLS has been investigated. The reaction follows first order kinetics in oxidant both in the presence and absence of CTAB and NaLS. The oxidation exhibits first order dependency at lower concentration of substrate while at higher concentration the reaction follows zero order kinetics. Binding parameters have been calculated by analyzing the data using the model suggested by Piszkiewicz. The effect of temperature on the reaction has been investigated in the temperature range 25^0C to 40^0C. Mechanism proposed and derived rate law is in agreement with the observe kinetics.

Keywords: Oxidation, 2-Proponol, N-Bromo saccharin, Cetytrimethyl Ammonium Bromide (CTAB), Sodium Lauryl Sulphate(NaLS).

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Introduction

The aim of the work is to probe the unreported results on the mechanistic rate of N-bromosaccharin oxidation of 2-propanol in the presence and absence of micelles. N-bromosaccharin oxidation of cyclic and secondary alcohols in the presence [1] and absence [2] of added saccharin, primary alcohol [3], benzyl alcohol [4], secondary aromatic alcohol [5], and cyclohexanol and its derivative [6] has been reported by different workers. The oxidative kinetics of alcohol and secondary alcohol by different oxidants like bromine [7-9], chlorine [10-12], N-bromosuccinimide[13,14], potassium bromate [15, 16], hexavalent chromium compound [17], manganese compound [18], cerium (IV) [19], thallium (III) perchlorate [20] etc. have been reported. The literature survey reveals that there is no report on the mechanistic studies to investigate the catalytic effect of both cationic and anionic surfactant on the N-bromosaccharin oxidation of 2-propanol in aqueous acetic acid medium in the presence of Hg(II) acetate as scavenger for Br^-.

Experimental

N-Bromosaccharin was prepared by the method suggested by Bacchawat and Mathur [21] and the purity of product was standardized by iodometric method Solution of CTAB and NaLS were prepared by dissolving their appropriate amount in distilled water.

$$C_6H_5COSO_2N \xrightarrow[0^0C]{Br_2} C_6H_5COSO_2NB + HBr$$

Reactions were carried out under pseudo first order condition by maintaining large range excess of hydroxy acid and Hg(II) acetate over NBSA in acetic acid -water solvent medium. Mercuric acetate used, traps bromine by forming unionized $HgBr_2$ and $HgBr_4^-$. The rate of reaction was followed by estimating the un-reacted N-bromosaccharin iodometrically.

Stoichiometry and Product Analysis

The stoichiometric studies of alcohol- oxidant system revealed that one mol of alcohol consumed one mol of oxidant. After completion of the reaction, the reaction mixture was extracted with ether and was separated. Acetone as the oxidation product of 2-propanol was identified by forming phenylhydrazone derivative (m.p. of 2:4 dinitrophenylhydrazone of acetone -128$^{0)}$

$$(CH_3)_2\ CHOH + C_6H_5COSO_2NBr \longrightarrow (CH_3)_2\ CO + C_6H_5COSO_2NH + HBr$$

Results

The kinetics of 2- propanol oxidation by N-bromosaccharin in the presence and absence of cetyltrimethylammonium bromide (CTAB)- cationic surfactant and sodium laurylsulphate (NaLS) – anionic surfactant was carried out under the condition [2-propanol] and [Hg(II)] >>> [NBSA]

Dependence of rate on initial concentration of oxidant

Table 1 reveales that in each case the disappearance of the oxidant obeys first order kinetics. Further the rate constant decreases with increase in the concentration of oxidant suggesting that N- bromosaccharin is involved in a pre equilibrium with some nucleophile (probably H_2O) to form some intermediate with lower reactivity. Similar retardation in pseudo first order rate constant value was reported in N-bromosaccharin oxidation of benzlhydrol [5], benzyl alcohol [4] and primary aliphatic alcohol [3].

Table 1 Dependence of rate on the concentration of reactants

[NBSA] 10^3M	**[2-Propanol] 10^2M**	**10^3k_1 min^{-1}**		
		Without Micelles	**With CTAB**	**With NaLS**
2.00	2.0	14.65	22.18	31.85
2.50	2.0	14.15	19.16	31.13
3.33	2.0	12.56	17.86	24.98
5.00	2.0	9.62	13.28	23.98
10.0	2.0	6.55	6.30	10.46
2.0	1.25	9.70	18.10	21.00
2.0	1.43	10.80	19.05	23.40
2.0	1.66	12.43	20.80	26.86
2.0	2.50	18.46	24.64	36.42
2.0	3.33	22.72	26.34	42.85

$[Hg(OAc)_2] = 1.0 \times 10^{-2}$M, [CTAB] = 5.0×10^{-6}M, [NaLS] = 5.0×10^{-5}M, HOAc – H_2O = 40% (v/v), Temp = 30^0C

Dependence of rate on the concentration of alcohol

The first order rate constant increases with increase in the concentration of 2-propanol in each case (Table 1). For each alcohol-NBSA System the plot between k_1 and [2-Propanol] is initially linear passing through origin and then bends towards X-axis at higher concentration of 2-propanol. The double reciprocal plot between k_1 and [2-Propanol] is linear with positive intercept on Y-axis (**Figure 1**) provides a kinetic evidence for intermediate complex formation between oxidant and substrate species in pre- equilibrium step.

Dependence of rate on surfactant concentration

Oxidation of 2-Propanol with NBSA was investigated in varying initial concentrations of both CTAB and NaLS. The nature of plot (**Figure 2**) suggest that the reaction is biphasic micellar catalyzed.

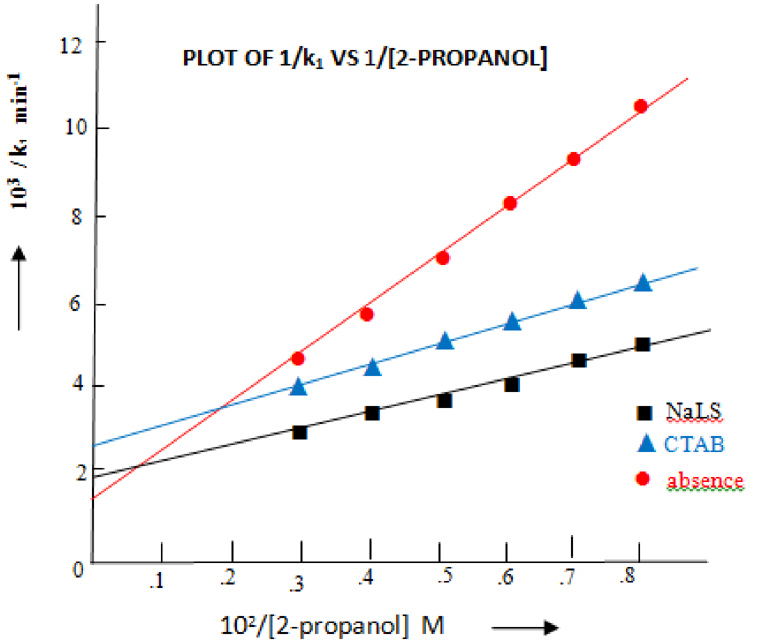


Figure 1 [NBSA] = 2.0 x 10^{-3}M, [Hg $(0Ac)_2$] = 1.0 x 10^{-2}M, [CTAB] = 5.0 x 10^{-6}M, [NaLS] = 5.0 x 10^{-5}M, HOAc–H_2O = 40%(v/v), Temp = 30^0C

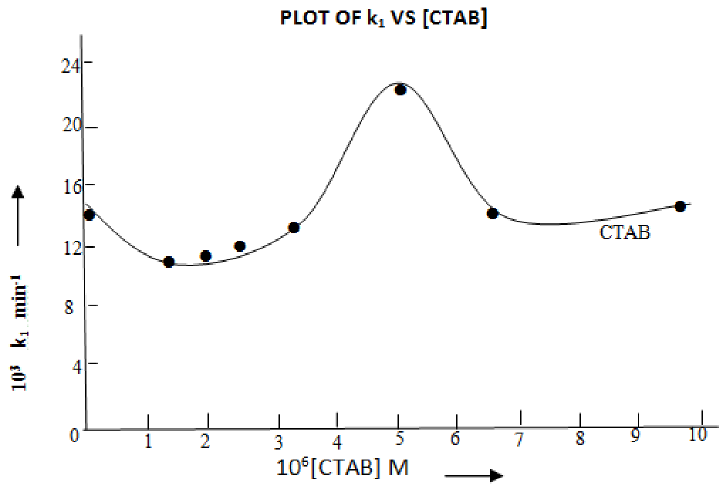


Figure 2 [NBSA] = 2.0 x 10^{-3}M, [Hg $(0Ac)_2$] = 1.0 x 10^{-2}, [2-Propanol] = 2.0 x 10^{-2}M, HOAc – H_2O = 40%(v/v), Temp = 30^0 C

Dependence of rate on perchloric acid concentration

The effect of variation in the concentration of perchloric acid on the reaction rate was examined at different initial concentrations of perchloric acid. For both micellar catalyzed and uncatalysed reactions the pseudo first order rate constant increases with increasing concentration of acid suggesting that the reaction follows acid catalysed as well as uncatalysed path. However, the plots of log (k_1- k_0) against log [$HClO_4$] are linear (**Figure 3**) with slope value nearly one confirming the order in perchloric acid is one.

Dependence of rate on saccharin

Addition of saccharin to 2-propanol- NBSA system in the presence and absence of micelles shows retarding effect (**Table 2**), this retarding effect of saccharin may be attributed to its involvement in pre equilibrium hydrolysis of oxidant.

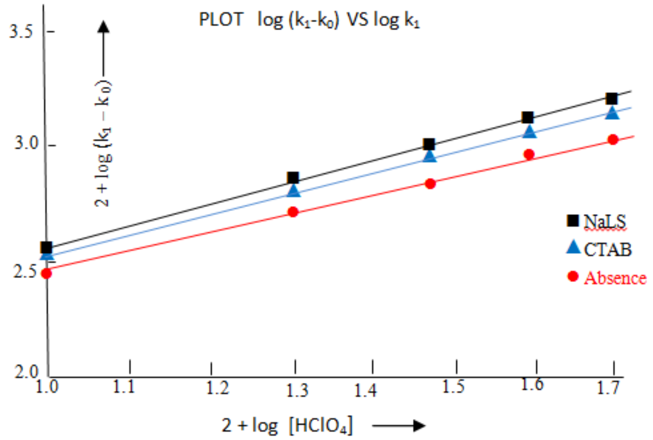


Figure 3 [NBSA] = 2.0 x 10^{-3}M, [Hg (0Ac)$_2$] = 1.0 x 10^{-2}M, [2-Propanol] = 2.0 x 10^{-2}M, HOAc – H_2O = 40%(v/v), [CTAB] = 5.0 x 10^{-6}M, [NaLS] = 5.0 x 10^{-5}M, Temp = 30^0 C

Table 2 Dependence of rate on the concentration of saccharin

S.No.	**[Saccharin] 10^3 M**	**10^3 k_1 min^{-1}**		
		Without Micelles	With CTAB	With NaLS
1	0.0	14.65	22.18	31.85
2	1.66	14.23	19.65	24.64
3	2.00	13.45	16.60	21.28
4	2.50	11.72	13.88	16.48
5	3.33	9.78	11.97	13.20
6	5.00	9.05	9.46	11.35
7	10.00	8.85	9.22	10.42

[NBSA] = 2.0 x 10^{-3}M,[Hg (OAc)$_2$] = 1.0 x 10^{-2}M, [2-Propanol] = 2.0 x 10^{-2}M, HOAc – H_2O = 40% (v/v), [CTAB] = 5.0 x 10^{-6} M, [NaLS] = 5.0 x 10^{-5} M, Temp = 30^0C

Dependence of rate on mercuric acetate

The plot of k_1 versus [mercuric acetate] (**Figure 4**) is obtained linear passing through origin and then bends towards x-axis i.e. at higher concentration range of Hg(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.

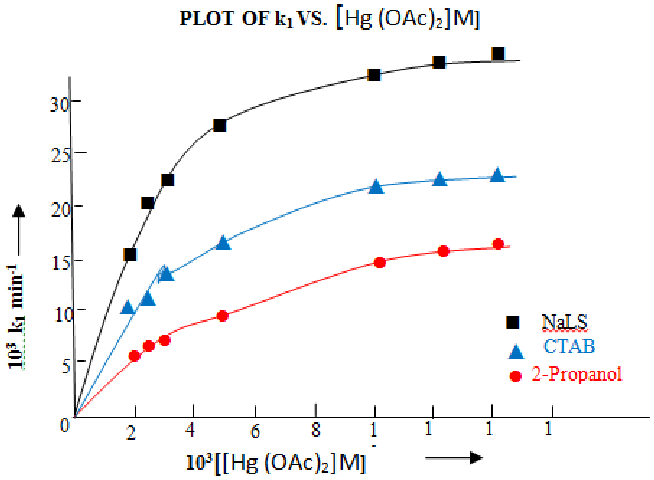


Figure 3 [NBSA] = 2.0 x 10^{-3}M, [2-Propanol] = 2.0 x 10^{-2}M, HOAc-H_2O =40%(V/V), [CTAB] = 5.0 x 10^{-6} M, [NaLS] = 5.0 x 10^{-5}M, Temp = 30°C.

Dependence of rate on medium

The effect of variation in dielectric constant of the medium was investigated with binary mixture of different composition 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. 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.

Table 3 Dependence of rate on dielectric constant of the medium

S.No.	**HOAc-H_2O %(V/V)**	**10^3/D**	**10^3 k_1 min^{-1}**		
			Without Micelles	With CTAB	With NaLS
1	10	15.50	5.30	-	14.13
2	20	17.17	8.51	14.46	17.73
3	30	19.15	9.78	17.66	22.98
4	40	21.98	14.65	22.18	31.85
5	50	25.68	17.58	26.84	43.42
6	60	30.36	21.12	24.68	53.33
7	70	38.04	25.80	21.27	-

Dependence of rate on sodium perchlorate

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 temperature and activation parameters were evaluated (**Table 4**).

Table 4 Thermodynamic Parameters

	Ea kJ mol^{-1}	**A Sec^{-1}**	**ΔH* kJ mol^{-1}**	**ΔG * kJ mol^{-1}**	**ΔS* JK mol^{-1}**
Without Micelles	69.77	2.55×10^{-4}	89.52	85.25	51.90
With CTAB	58.97	4.63×10^{-4}	57.67	83.95	56.71
With NaLS	40.97	4.80×10^{-4}	38.41	83.32	148.22

Discussion and Mechanism

Based on kinetic results stoichiometry and product analysis a probable mechanism for the oxidation of 2-propanol 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 adding acrylonitrile ruling out the involvement of free radical intermediates.

Nature of Oxidant Species

In aqueous medium NBSA hydrolyses according to the following equation

$$\mathrm{NBSA} + H_2O \rightleftharpoons \mathrm{HOBr} + \mathrm{Sac}$$

In the presence of mineral acid, the above species get protonated yielding $NBSAH^+$ and $H_2O\overset{\oplus}{Br}$

$$\mathrm{NBSA} + H^{\oplus} \rightleftharpoons \mathrm{NBSAH}^{\oplus}$$

$$HOBr + \overset{\oplus}{H} \rightleftharpoons H_2\overset{\oplus}{O}Br$$

$$NBSA\overset{\oplus}{H} + H_2O \rightleftharpoons H_2\overset{\oplus}{O}Br + Sac$$

In NBSA oxidation of 2-propanol 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.

$$NBSA + H_2O \rightleftharpoons HOBr + Sac$$

Acid catalysis and retardation of oxidation rate by added saccharin points out Br$^+$ or H$_2$O$^+$Br as active oxidant species.

$$NBSA + \overset{\oplus}{H} \rightleftharpoons Br^+ + Sac$$

In aqueous solution it is difficult to distinguish between Br$^+$ and H$_2$O$^+$Br but since H$_2$O$^+$Br is more electrophilic than Br$^+$, it is the preferred species.

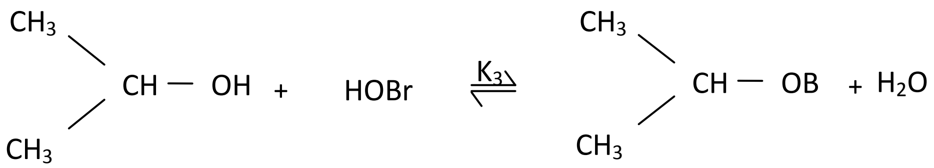
Nature of the substrate

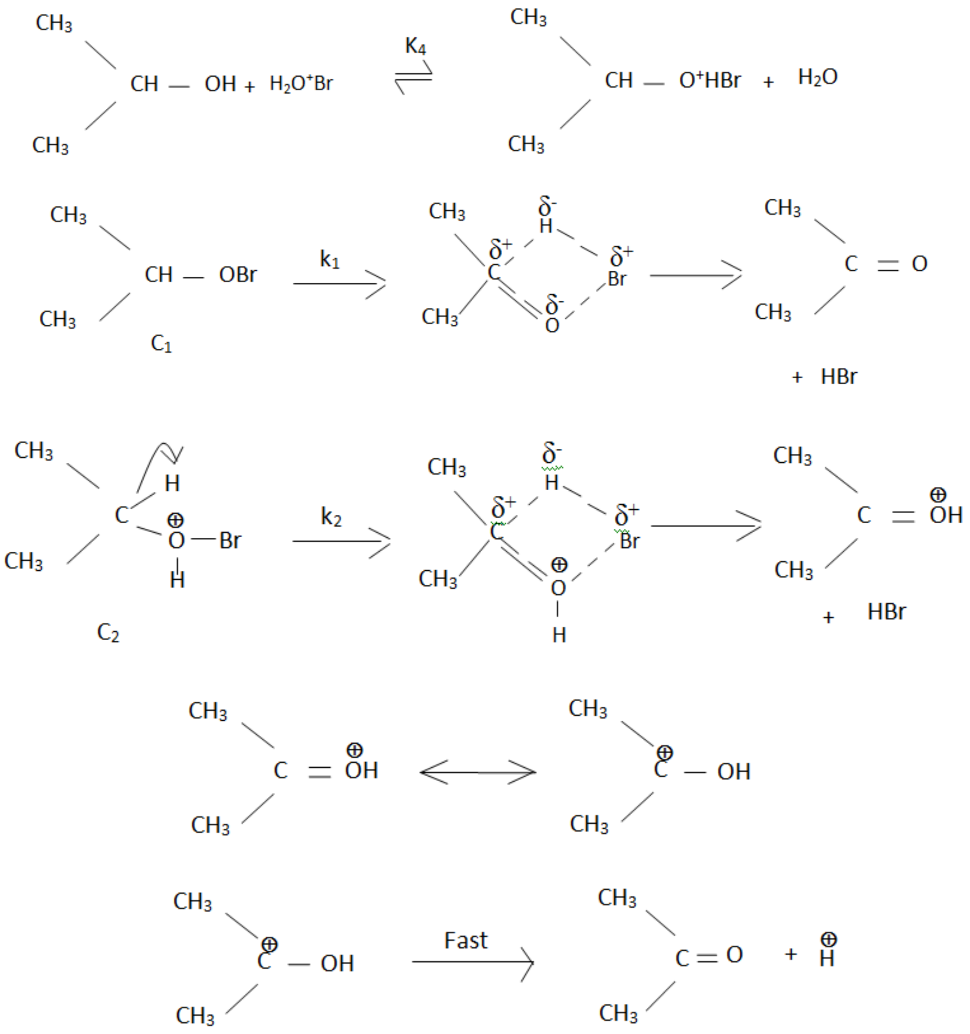
2-propanol is mono functional organic compound. Alcohols are nucleophilic in nature. In present investigation observed acid catalysis suggests the possibility of protonated alcohol as the active reductant species. In such case oxidation of tert-butyl alcohol would have been faster than secondary alcohol under similar experimental conditions. The slow oxidation of tert-butyl alcohol rules out the protonation of alcohol. 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. A probable mechanism for the oxidation of 2- propanol by N-bromosaccharin in the absence of micelles has been proposed.

Mechanism in the absence of micelles

$$NBSA + H_2O \overset{K_1}{\rightleftharpoons} HOBr + Sac$$

$$HOBr + \overset{\oplus}{H} \overset{K_2}{\rightleftharpoons} H_2O^+Br$$





$$\text{Rate} = k_1\,[C_1] + k_2\,[C_2]$$

$$\frac{\text{Rate}}{[\text{NBSA}]_T} = k = \frac{K_1\,[\text{Alcohol}]\,(K_3k_1 + K_2K_4k_2[H^+])}{[\text{Sac}] + K_1(1 + K_3\,[\text{alcahal}])}$$

Oxidation of 2- Propanol in presence of micelles

Rate enhancement for 2-propanol-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.

According to kinetic results oxidation of 2- propanol 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, H_2O^+ Br and the anionic miceller which bring both the reactant closer while the repulsive force between cationic micelle surface and H_2O^+ Br make CTAB less effective.

Table 5 Filling Parameters: Piszkiewicz Model

Surfactant	n	$\text{Log}[D]_{50}$	10^3K_D
CTAB	0.53	-0.84	4.365
NaLS	1.10	-0.67	131.83

The value of co-operative index "n" ,K_D, log $[D]_{50}$ are derived and given in table 5.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 4) gives additional support to the proposed mechanism. Ea decreases in the presence of surfactant, alcohol is oxidized at a faster rate in the presence of surfactant. The value of ΔH^*, ΔS^* and $\Delta G^*$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.

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 and follows both acid dependent and independent path the overall mechanistic sequence described here is consistent with all experimental evidences.

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