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Oxidation of Glycolic Acid by N-Bromosaccharin: A Kinetic and Mechanistic Study in Presence and Absence of Cationic Surfactant

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The oxidation of 2-hydroxyethanoic acid (glycolic acid) by N-bromosaccharin leads to the formation of the corresponding aldehydes. Oxidation kinetics has been studied in aqueous acetic acid in the presence of Hg(II) acetate and cationic surfactant (CTAB). The reaction shows first order dependence in oxidant while Michaelis-Menten type of kinetics has been observed with respect to reductant. The oxidation is inhibited by CTAB. Variation in [H^+] shows complex kinetics. Addition of reaction product, saccharin, retards the rate of reaction. Effect of variation of dielectric constant of the medium, ionic strength of the medium and concentration of Hg(II) acetate have also been investigated. Activation parameters have been computed. The observed results are explained by Piszkiewicz model, which concludes that reaction occurs in the aqueous acetic acid phase.

Key Words: Glycolic acid, Oxidation, N-Bromosaccharin, Cationic surfactant, Kinetics.

INTRODUCTION

α-Hydroxy acids have been subjected to kinetic oxidation studies[1–3]. In recent years, micelles, micro-emulsion, etc., have emerged as attractive reaction media for investigating the reactivity and selectivity of a number of chemical reactions[4, 5]. A literature survey reveals that the surfactant catalyzed oxidative decarboxylation of some α-hydroxy acids[6–10] has been explored by different workers, but glycolic acid has not received any attention as yet. The present study, therefore, concerns the influence of addition of the cationic surfactant, cetyltrimethyl ammonium bromide (CTAB), on the oxidation of glycolic acid (GA) by N-bromosaccharin (NBSA) in aqueous acetic acid.

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EXPERIMENTAL

N-Bromosaccharin (NBSA) was prepared by bromination of saccharin in alkaline medium at 0°C and its acetic acid solution was prepared by dissolving its appropriate amount in acetic acid and was standardized iodometrically. The reaction mixture was equilibrated in a thermostat (±0.1°C) at the desired temperature. The progress of the reaction was monitored by iodometric estimation of unreacted N-bromosaccharin.

Stoichiometry and product analysis

Stoichiometric studies revealed that 1 mol of hydroxy acid consumed 1 mol of NBSA in the presence as well as in the absence of CTBA, according to the following equation:

$$C_6H_4COSO_2NBr + CH_2(OH)COOH \rightarrow C_6H_4COSO_2NH + HCHO + CO_2 + HBr$$

RESULTS AND DISCUSSION

Kinetic studies were made under pseudo first order conditions. Mercury(II) acetate was added to each reaction mixture to prevent liberation and further reaction of bromine.

Under the conditions [GA][Hg] ≫ [NBSA], the plot of log (a – x) *vs.* time was found to be linear indicating first order dependence on NBSA. However, the first order rate constants decrease with decrease in the concentration of NBSA. This is probably due to the formation of some inactive oxidant species. The order with respect to glycolic acid is less than one, which is evidenced from the value of k_2 ($k_2 = k_1/[GA]$), which does not show constancy. A plot of $1/k_1$ and $1/[GA]$ is linear with an intercept on the rate co-ordinate. Thus Michaelis-Menten type of kinetics is observed with respect to glycolic acid in the presence and absence of CTAB.

The reaction was studied at different concentrations of cationic surfactant CTAB in the range $2.0–16.0 \times 10^{-5}$ mol dm^{-3}. CTAB inhibits the rate of oxidation (Table-1).

TABLE-1
EFFECT OF CTAB MICELLE ON THE OXIDATION OF GLYCOLIC ACID WITH NBSA

[CTAB] × 10^5 (mol dm^{-3})	$10^4 \times k_1$ (s^{-1})
0.0	2.61
2.0	1.81
4.0	1.72
6.0	1.31
8.0	1.69
16.0	1.97

[GA] = 6.66×10^{-2} mol dm^{-3}; [NBSA] = 3.33×10^{-3} mol dm^{-3}, HOAc-H_2O = 20% (v/v); [$Hg(OAc)_2$] = 1.0×10^{-2} mol dm^{-3}; Temp. = 323 K

The effect of variation in the concentration of perchloric acid on the reaction rate was examined at different concentrations of perchloric acid and at constant ionic strength (Table-2).

TABLE-2
EFFECT OF H^+ ON THE OXIDATION OF GLYCOLIC ACID WITH NBSA

$[H^+]$ (mol dm^{-3})	$k_1 \times 10^4$ (s^{-1})	
	Without micelle	With CTAB
0.0	2.61	1.31
0.1	2.08	1.16
0.2	1.89	1.00
0.3	1.66	0.91
0.4	1.47	0.79
0.5	1.29	0.68

$[ClO_4] = 0.5$ mol dm^{-3}; [CTAB] $= 6.0 \times 10^{-5}$ mol dm^{-3}; other conditions same as in Table-1.

The results show that pseudo first order rate constant decreases with increase in the concentration of perchloric acid. The plot of k_1 *vs.* $[H^+]$ is linear with negative slope. The plot between k_1 and inverse of $[H^+]$ shows a limiting value at low $[H^+]$. The observed hydrogen ion dependence rules out the involvement of protonated species of oxidant, *viz.*, $NBSAH^+$, Br^+ or H_2O^+Br as active oxidant species according to the following equations:

$$NBSA + H^+ \rightleftharpoons NBSAH^+ \quad (1)$$

$$NBSA + H^+ \rightleftharpoons Sac + Br^+ \quad (2)$$

$$NBSA + H_2O \rightleftharpoons Sac + HOBr \quad (3)$$

$$HOBr + H^+ \rightleftharpoons H_2O^+Br \quad (4)$$

The oxidation of glycolic acid was studied in different compositions of acetic acid-water binary mixture, with increase in composition of acetic acid; the value of pseudo first order rate constant decreases in the presence and absence of CTAB. The plots of log k_1 and inverse of dielectric constant are linear with negative slope. These results suggest dipole-dipole interaction in the mechanistic step.

Addition of reaction product, saccharin, retards the rate of oxidation in the presence and absence of CTAB (Table-3).

TABLE-3
EFFECT OF SACCHARIN ON THE OXIDATION RATE OF GLYCOLIC ACID WITH NBSA

[Saccharin] $\times 10^3$ (mol dm^{-3})	$k_1 \times 10^4$ (s^{-1})	
	Without micelle	With CTAB
1.66	2.10	1.71
2.00	1.86	1.36
2.50	1.69	1.22
3.33	1.44	1.19
4.00	1.29	1.14

[CTAB] $= 6.0 \times 10^{-5}$ mol dm^{-3}; other conditions same as in Table-1.

Inhibition effect of saccharin suggests HOBr as active oxidant species according to eqn. (3), which is further supported by linearity of the plot between inverse of k_1 and [Sac] with positive intercept. A five-fold variation in the concentration of Hg(II) acetate and also addition of varying concentrations of sodium perchlorate do not affect the reaction rate. The reaction was also studied at different temperatures between 50–65°C and the activation parameters are computed (Table-4).

TABLE-4
ACTIVATION PARAMETERS

	E_a (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	$-\Delta S^*$ (kJ mol^{-1})
Without micelle	98.15 ± 0.27	95.73 ± 0.003	94.16 ± 0.05	4.73 ± 0.07
With [CTAB] = 6.0×10^{-5} mol dm^{-3}	106.03 ± 0.73	101.03 ± 2.18	95.16 ± 0.59	16.09 ± 0.20

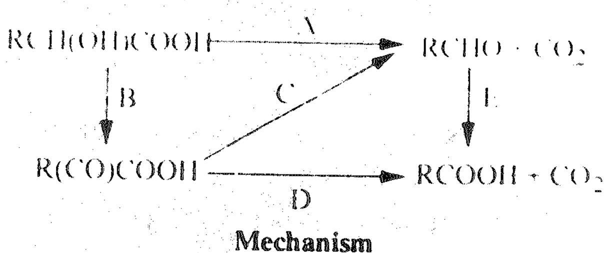
The oxidation of glycolic acid by NBSA undergoes polymerization by acrylonitrile in the presence as well as in the absence of CTAB.

Mechanism

In view of the absence of any effect of radial scavenger, acrylonitrile, on the reaction rate, it is unlikely that one electron reaction giving rise to free radical is operative in this oxidation. For the oxidative decarboxylation of glycolic acid, two mechanistic paths may be proposed.

In the absence of the surfactant

The mechanism and rate law have already been studied, which are as follows: α-hydroxy acids undergo oxidation in a number of ways.



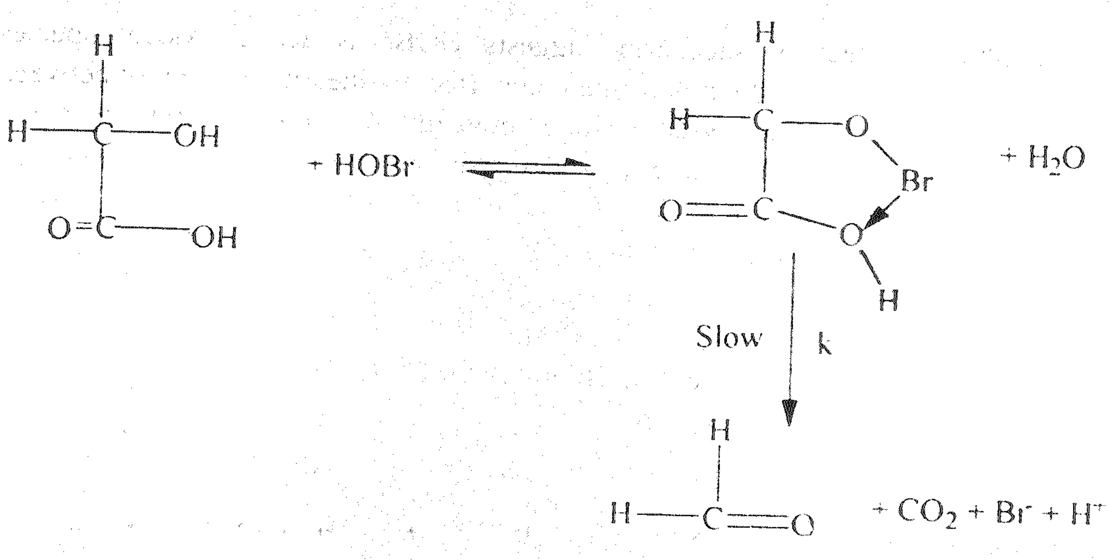
Mechanism

Isolation of formaldehyde as oxidation product and negative test for keto acid as intermediate suggest that oxidation of glycolic acid follows path-A. Hydroxy acid can react both as secondary alcohol and as carboxylic acid. In the same mechanistic steps may involve C—C or C—H fission. Since under similar experimental conditions benzilic acid is oxidized at a faster rate, hence the two mechanisms involved in C—C fission have been proposed.

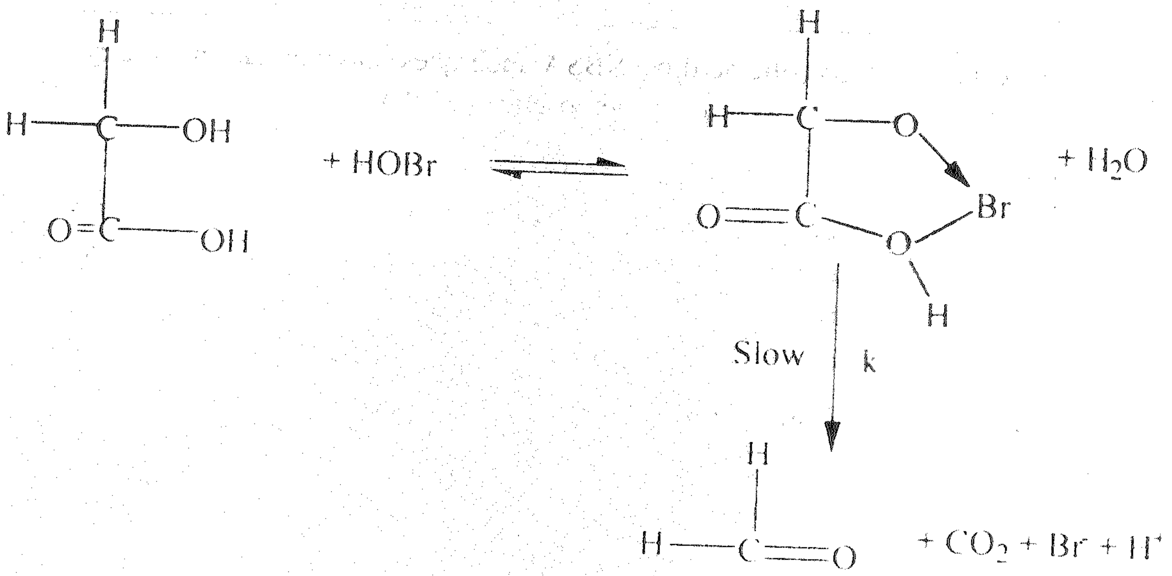
Scheme-1. Attack of HOBr at hydroxy function:

$$C_6H_4COSO_2NBr + H_2O \rightleftharpoons C_6H_4COSO_2NH + HOBr \quad (1)$$

$$HOBr + H^+ \rightleftharpoons H_2O^+Br \quad (2)$$



Scheme-2. Attack of HOBr at carboxyl function:



On the basis of the above schemes, rate law is obtained as:

$$\mathrm{NBSA + H_2O \overset{K_1}{\rightleftharpoons} Sac(S) + HOBr} \tag{1}$$

$$\mathrm{HOBr + H^+ \overset{K_2}{\rightleftharpoons} H_2O + Br} \tag{2}$$

$$\mathrm{GA + HOBr \overset{K_3}{\rightleftharpoons} Complex + H_2O} \tag{3}$$

$$\mathrm{Complex \underset{Slow}{\overset{k}{\rightleftharpoons}} Products} \tag{4}$$

$$\mathrm{Rate = k\ [Complex]} \tag{5}$$

$$k_{obs} = \frac{\mathrm{Rate}}{[\mathrm{NBSA}]_T} = \frac{kK_1K_3[\mathrm{GA}]}{[\mathrm{S}] + K_1 + K_1K_2[\mathrm{H^+}]K_1K_3[\mathrm{GA}]} \tag{6}$$

At low concentration of glycolic acid, assuming K_3 is much smaller than K_1, eqn. (6) reduces to

$$k_{obs} = \frac{kK_1K_3[GA]}{[S] + K_1 + K_1K_2[H^+]} \quad (7)$$

Eqn. (7) shows first order dependence in glycolic acid and oxidant and inverse dependence in hydrogen ion and saccharin concentration. At high concentration of glycolic acid assuming $K \ll K_3$ from eqn. (6) we obtain

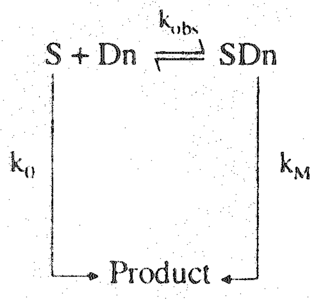
$$k_{obs} = k$$

i.e., rate is first order in oxidant and independent of glycolic acid and H^+ concentration.

In presence of surfactant

Cationic micelles of CTAB inhibit the oxidation of glycolic acid. This behaviour has been ascribed to the interaction between the surfactant and substrate, which induces micellization or submicellar aggregate.

Micellar effect on the oxidation rate has been analyzed by Piszkiewicz model[12]. Micelle and bulk aqueous medium are treated as distinct in reaction medium. The variation of rate constant surfactant is generally treated on the assumption that the substrate "S" is distributed between the aqueous and micellar pseudo phase.



$$nD + S \underset{K_D}{\rightleftharpoons} D_nS \quad (1)$$

$$D_nS \xrightarrow{k_M} \text{Product} \quad (2)$$

$$S \xrightarrow{k_0} \text{Product} \quad (3)$$

where n = aggregation number,

D_nS = non-covalent complex between substrate and micelles.

The above scheme leads to the following rate expression:

$$k_\Psi = \frac{k_M[D]^n + k_0K_D}{K_D + [D]^n} \quad (4)$$

K_D = Dissociation constant of micelles back to its free components, K_m and k_0 are rate constants in micellar and aqueous phase. Rearrangement of eqn. (4) gives

$$\log \frac{(k_\Psi - k_0)}{k_M - k_\Psi} = n \log [D] - \log K_D \quad (5)$$

According to eqn. (5) when $\log (k_\Psi - k_0)/(k_M - k_\Psi)$ is plotted against $\log [D]$

for glycolic acid-NBSA-CTAB system, a straight line is obtained which justifies the applicability of the model. From the plot the values of co-operative index (n) and log $[D]_{50}$ (Table-5) concentration of surfactant required for the half maximal catalysis or inhibition of the reaction are derived[13]. The value of n = 1.23 indicates positive co-operativity. This means that the substrate promotes micellization of the surfactant even before or below CMC.

TABLE-5
VALUES OF N AND K_D FOR THE OXIDATION OF GLYCOLIC ACID WITH NBSA

S. No.	Substrate	Surfactant	n	log $[D]_{50}$	log $[K_D]$
1.	Glycolic acid	CTAB	1.23	–0.086	–1.50

Conclusion

Kinetic results of N-bromosaccharin oxidation of glycolic acid in presence of cationic surfactant cetyltrimethyl ammonium bromide in aqueous acetic acid suggest that glycolic acid forms complex with pre-micellar aggregates, which is a less reactive or unreactive species due to which the oxidation rate is retarded.

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