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OXIDATION OF SERINE BY IN-SITU GENERATED BROMINE: KINETIC AND MECHANISTIC STUDY

M. R. Thombare* and G. S. Gokavi

Kinetics and Catalysis Laboratory, Department of Chemistry,

Shivaji University, Kolhapur,416004, India

**Corresponding author E-mail: mrthombare1973@gmail.com*

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Abstract:

Oxidation of Serine by Oxone catalyzed by bromide ions has been studied in acidic medium. The reaction is initiated by the oxidation of bromide to bromine, which then react with the Serine. The formation of bromine is supported by the spectrophotometric examination of the reaction mixture. The proposed intermediate involves a complex formation between bromine and the anion of Serine. The rate of reaction is inhibited by an increase in the hydrogen ion concentration due to protonation equilibria of Serine. A mechanism is proposed and the derived rate law was verified graphically. Effect of ionic strength & temperature was also carried out and these effects are also in fever of the mechanism proposed.

Keywords: *Kinetics, Reaction Mechanism, Oxidation, Oxone, Bromide Ion, Serine.*

Introduction

Bromine and its compounds are used for bromination and oxidation of organic compounds. Aqueous bromine solution is a selective and mild oxidizing agent (1). The hazardous nature of bromine is the main drawback to use it in environmentally benign protocols; therefore, an attempt has been made to utilize the compounds like tetra alkyl ammonium salts which contains bromine in the form of tribromide ions (2,3). These salts when dissolved in a solvent, active bromine species which effect the desired reaction to occur. Hypo Bromus acid, HOBr is another active bromine species, which can be generated *in situ*. Variety of N-halo reagents are used for generation of hypohalous acids in solution for their application in synthesis and to study mechanism (4,5).

Hypo Bromus acid, HOBr, a reactive bromine species, is known to be generated during the disinfection process of water using chlorine or ozone containing bromide ion (6). Bromide ion concentrations in ground water are in the range of 0.01 to 3 mg L^{-1} (7). This reactive bromine species, HOBr, can also be prepared by the combination of bromide and an oxidizing agent. Such combination of bromide with oxidants, like bromate and Oxone has been utilized as a green protocol for bromination and oxidation in organic synthesis (8). Biological production of hypobromous acid is also reported during activation of eosinophils (9). The release of eosinophil peroxidase due

to respiratory burst catalyzes the reaction between hydrogen peroxide and bromide ions to form hypobromous acid. The HOBr, thus, produced kills the invading pathogens [9] and also plays an important role in damaging the tissues. It was also concluded that proteins are the major biological compounds reacting with HOBr (10). Therefore, we investigated kinetically the reaction between serine and Oxone in presence of bromide in acidic medium in order to understand the probable path of the reduction of in situ generated bromine species.

Experimental

All solutions were prepared in doubly distilled water. The solutions of serine and Oxone were prepared by dissolving in water. The solution of sodium thiosulphate was freshly prepared every day and standardized against standard KIO_3 solution iodometrically. The solution of Oxone was standardized by titrating known volume of oxone with standard sodium thiosulphate (SD Fine) solution iodometrically. The solution of catalyst KBr (Thomas Baker) was prepared by dissolving it in water. Standard H_2SO_4 (SD Fine) solution of 2M and 1 M were also prepared.

The reaction was initiated by mixing the previously thermos stated solutions of Serine and oxone which also contains the required amount of catalyst KBr and H_2SO_4.The reaction was followed by determining the concentration of unreacted oxone iodometrically. The pseudo first order rate constants were determined from the linear plots of log (oxidants) against time plots and the values were reproducible up to +0.6%.

Stoichiometry and product analysis

Stoichiometry was determined by analyzing reaction mixtures containing serine ($1x10^{-2}$ mol dm^{-3}) bromide ($5 x 10^{-3}$ mol dm^{-3}), sulphuric acid (0.03 mol dm^{-3}) and excess of oxidant (0.1 mol dm^{-3}). The reaction mixture containing excess of oxidant , Oxone was kept in a thermostat at required temperature for about 24 hours and remaining oxidant was iodometrically determined. The Stoichiometry was found to be one mole of Oxone per mole of serine. The product according to the stoichiometry is the corresponding glycolaldehyde.

Table 1: Effect of concentration of Serine and Oxone on the kobs values at 25°C

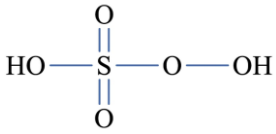
[KBr] = 5×10^{-3} mol dm^{-3} [H_2SO_4] = 3×10^{-2} mol dm^{-3} I = 0.1 mol dm^{-3}

10^{-3} [Oxone] mol dm^{-3}	10^{-2}[Serine] moldm^{-3}	$10^3 k_{obs}/s^{-1}$
2.0	5.0	0.491
2.0	8.0	0.921
2.0	1.0	1.33
2.0	2.0	3.12
2.0	3.0	4.32
2.0	4.0	5.54
2.0	5.0	6.96
0.2	2.0	3.12
0.4	2.0	3.11
0.6	2.0	3.10
0.8	2.0	3.12
1.0	2.0	3.12
2.0	2.0	3.12

For product analysis, the reaction mixture (concentration of reactant being twenty times that under kinetic condition) was allowed to stand for about a day, then distilled, the distillate being collected in a closed container. The distillate was treated with 2,4 -DNP solution in 4 (N) H_2SO_4 when a yellow derivative of the product was precipitated. It was recrystallized from water and dried. The melting point of derivative was 166^0C(lit..mp168^0C (11)

Mechanism

Accepted structure of oxidant (12), Oxone or peroxomonosulphuric acid used contains a sulphur atom surrounded tetrahedrally by perhydroxyl group and a hydroxyl group as shown below. The proton of hydroxyl group is high ionized [13] while that of perhydroxyl group is weakly ionized. The pK value of the perhydroxyl proton is reported to be 9.4 (13).



Scheme 1

Present study is carried out in acidic medium oxidant is in the form of peroxomonosulphate anion, HSO_5-. The oxidation of halide ions by peroxomonosulphate ion has been studied and an oxygen atom transfer mechanism is proposed (14,15). The mechanism involves slow oxidation of bromide ion in acidic medium containing stoichiometrically excess oxidant generating HOBr with rate constant [15] of 0.7 dm^3 mol^{-1} s^{-1}. In acidic medium HOBr undergoes various equilibrium and redox reactions as given in equations 1-4 with reported equilibrium and rate constants respectively. The pK value of the hypobromous acid is 8.8 (16), therefore under present conditions of the reaction, it exists in the protonated form, HOBr. In acidic medium the first rate determining step of oxidation of bromide ion by peroxomonosulphate, Oxone, is the formation of hypobromous acid followed by its fast oxidation generating bromine with a rate constant [16] of the order of 1.6×10^8 dm^6 mol^{-2}

Scheme 1

HOBr $\rightleftharpoons$ OBr - + H+ pK= 8.8 (1)

HOBr + H+ + Br - $\rightleftharpoons$ Br_2 + H_2O K= 1.6 × 10 8 dm^6 mol^{-2} (2)

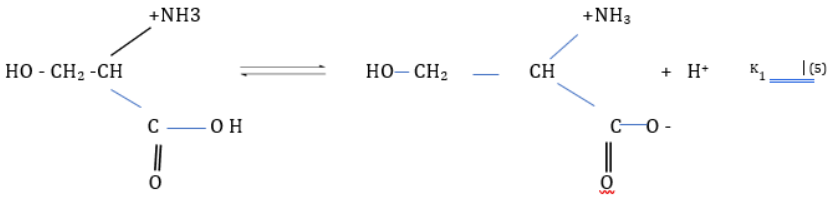
Br_2 + Br - $\rightleftharpoons$ Br_3 - K= 16.8 dm^3 mol^{-1} (3)

2 HOBr BrO_2 - + H + +Br - K= 2.3×10^{-3} dm^3 mol^{-1} sec^{-1} (4)

The amino acid serine has two protonated sites, the amino group and carboxylic group. The pK of amino group is more than 9.1of this amino acid [16] while that of carboxylic group is 2.35 for serine (17). Since the present study is carried out in acidic medium amino group is protonated and exists as -NH_3^+. Due to partial protonation of carboxylic acid group, both protonated -COOH and unprotonated -COO- species exist together.

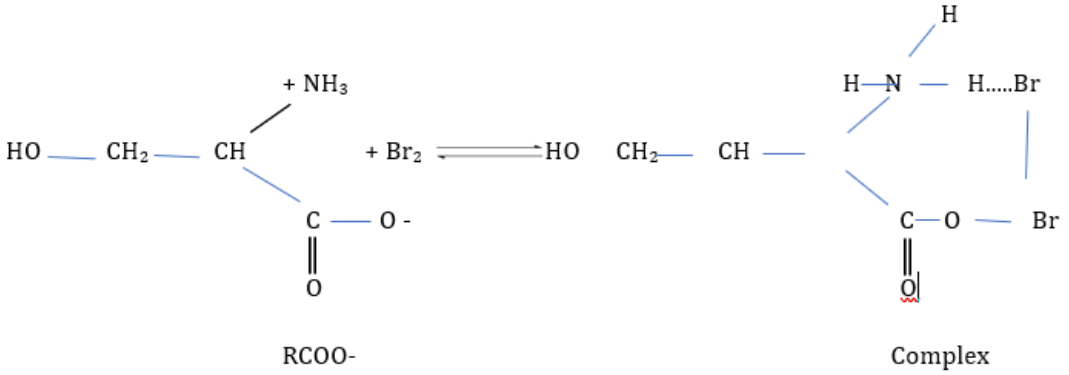
The k_{obs} value found to decrease as hydrogen ion concentration increases. Since in acidic solution amino group is protonated form formation of bromamine is not feasible. Therefore, electrophilic attack of Br_2 on the carboxylate anion of serine would be more probable (18). Kinetic results are also in support the following mechanism.

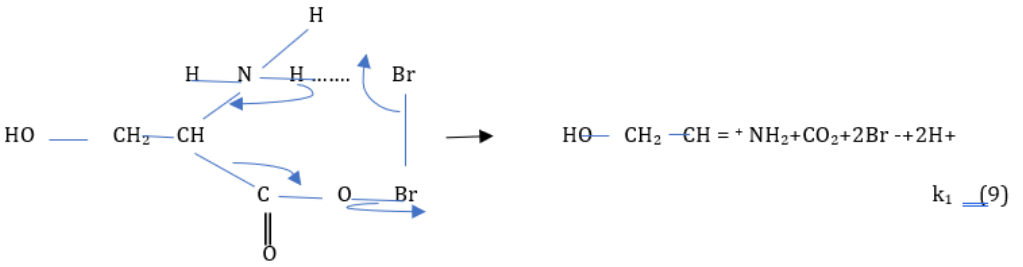
Mechanism



$HSO_5^- + Br^- \rightleftharpoons HOBr + SO_4^{2-}$ K_2 (6)

$HOBr + H^+ + Br^- \longrightarrow Br_2 + H_2O$ Fast (7)





$HO - CH_2 - CH = NH_2 + H_2O \longrightarrow HO - CH_2 - CHO + NH_4^+$ Fast (10)

Scheme 2

Consider unprotonated serine anion as active species, reacts with Br_2 generated as a result of reaction between HSO_5^- and bromide ion. The mechanism and rate law is as follows.

Rate = k_1 [Complex] (11)

Rate = k_1 K = [RCOO-] [HOBr-] (12)

[Br2] = K_2 [HSO_5^-] [Br-] (13)

Rate = k_1 K_2 K_3[RCOO-] [HSO_5^-] [Br-] (14)

$[RCOOH]_t = [RCOOH]_f + [RCOO^-] = [RCOOH]_f + (K_1[RCOOH]_f / [H^+])$ (15)

$[RCOO^-]=[RCOOH]_t / ([H^+] + K_1)$ (16)

$Rate = k_1 K_2 K_3[RCOOH]_t [HSO_5^-][Br^-] / ([H^+] + K_1)$ (17)

$k_{obs} = k_1 K_2K_3 [RCOOH]_t [Br^-] / ([H^+] + K_1)$ (18)

$1/k_{obs} = \frac{([H+]+K1)}{k1K2K3[RCOOH]t[Br-]}$ (19)

The reaction as shown in the scheme 2, initiated by the oxidation of bromide to bromine which oxidizes serine in RDS

Conclusion

Oxidation of Serine by Oxone was found to proceed through formation of bromine. Electrophilic attack of the bromine on the carboxylate anion of the serine leads to the formation of an intermediate complex in fast prior equilibrium. The complex thus formed, decomposes in a slow step. Since the amino group is in the protonated form, formation of bromamine intermediate is less feasible. Negative value of entropy indicating polar nature of transition state, leads to immobilization of solvent molecules around the charged ends which results in to loss of entropy as noticed in the present study.

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