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Kinetic and Mechanistic Studies in the Oxidation of *n*-Butanol by *p*-Methoxy-*N*-bromobenzamide†

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Kinetics studies of the oxidation of *n*-butanol by *p*-methoxy-*n*-bromobenzamide has been made in aqoues acetic acid in presence of mercuric acetate. The reaction is first order with respect to both, the oxidant and near about are with respect to the substrates. The order with respect to perchloric acid is fractional or first order depending upon the substrate concentration. The reaction is retarded by the initial addition of benzamide and is enhanced by the added potassium bromide. The activation parameters have been calculated and a suitable mechanism has been proposed.

Key Words: Kinetics, Oxidation, *n*-Butanol, *p*-Methoxy-*n*-bromobenzamide.

INTRODUCTION

Reports are available in the literature on the mechanism of oxidation of *n*-butanol by chloramine-T[1], chloramine-B[2], *N*-bromosuccinimide[3], *N*-bromobenzamide[4-6] *p*-methyl-*N*-chlorobenzamide[7,8] and other halomides, but very little is known about the modes of the redox reaction of *p*-methoxy-*N*-bromobenzamide (*p*-MeoNBB) as an oxidant. By substituting benzene ring of such bezamides with different groups, it is possible to tune oxidation potential of *N*-halomides and thereby developing a tuning oxidant, such oxidant are very much useful in controlling a number of free radical polymerization[9,10] reaction and also useful in different analyting procedures. Further different mechanistic pathways reported for the structurally related *N*-haloamides[11-14] to undertake the present investigation.

EXPERIMENTAL

n-Butanol used were of S. merck grade and was purified by the method described in the literature. All the chemical used were B.D.H. AR and S.M. GR quality. Alcohol were dried over anhydrous magnesium sulphate and then fractionally distilled. Acetic acid was distilled over chromic acid before use. Perchloric acid was use as a source of hydrogen ions. The reaction vessels were coated with black paints to exclude any photochemical effect. The kinetics of oxidation of *n*-butanol is found to be pseudo. First order reaction by keeping a large excess of alcohol over *p*-methoxy-*N*-bromobenzamide. The reactions were followed iodometrically for over 70 % of the reaction. The temperature was kept constant with in ± 0.1 ºC. Preliminary experiments showed that the reaction is not sensitive to ionic strength hence no attempt was made to keep it constants.

RESULTS AND DISCUSSION

The kinetics of oxidation of alcohol is found to be pseudo first order. A large excess of alcohol was maintained over *p*-methoxy-*N*-bromobenzamide. Stoichiometry of the reaction was also studied. It was observed that one equivalent of oxidant was consumed by on equivalent of alcohol.

Dependence on oxidant concentration: The data are summarized in Table-1.

TABLE-1		
[Substrate] = 1.0 mol dm^{-3}		Hg (OAc)$_2$ = 5.0 × 10^{-3} mol dm^{-3}
(HClO$_4$) = 1.0 mol dm^{-3}		HOAc = 50 % (v/ v)
Temperature = 323 K		
S. No.	(Oxidant) × 10^{-3} (mol dm^{-3})	n-BuOH (K × 10^{-3} min^{-1})
1.	2.50	1.5790
2.	3.75	1.5880
3.	5.00	1.5860
4.	6.25	2.0100
5.	7.50	1.5790
6.	8.75	1.5870

Dependence of substrate concentration: The plot of log K *vs.* log [oxidant] was found to be linear and it gives a slop value of unity, indicating that the order of the reaction

with respect to substrate is one; the results are summarized in Table-2.

TABLE-2

(HClO₄) = 1.0 mol dm⁻³		[Oxidant] = 5.0 × 10⁻³ mol dm⁻³
HOAc = 50 % (v/v)		Hg (OAc)₂ = 5.0 × 10⁻³ mol dm⁻³
Temperature = 323 K		

S. No.	Substrate (mol dm⁻³)	n-BuOH (k × 10⁻³ min⁻¹)
1.	0.2	2.5108
2.	0.3	2.7023
3.	0.4	2.6290
4.	0.5	2.0155
5.	0.6	2.6631
6.	0.8	3.7066
7.	1.0	3.0705

Effect of added benzamide: Reaction rate decreases by addition of benzamide. The results are presented as follows in Table-3.

TABLE-3

[Substrate] =1.0 mol dm⁻³		[Oxidant] = 5.0 × 10⁻³ mol dm⁻³
(HClO₄) = 1.0 mol dm⁻³		Hg (OAc)₂ = 5.0 × 10⁻³ mol dm⁻³
HOAc = 50 % (v/v)		Temperature = 323 K

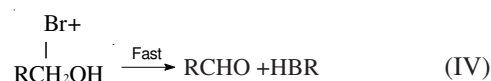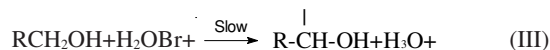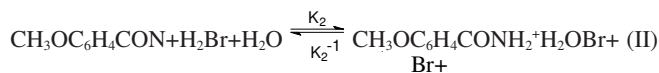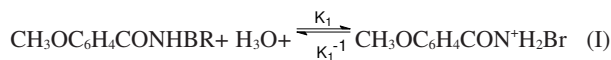| S. No.	Benzamide × 10⁻³ (mol dm⁻³)	n-BuOH (k × 10⁻³ min⁻¹)
1.	0.0	6.3050
2.	1.0	6.8460
3.	2.0	6.2810
4.	5.0	3.3430
5.	8.0	2.1083
6.	10.0	2.1428

Effect of added mercuric(II) acetate: Initially addition of Hg(OAc)₂ suppress completely the second faster stage and reduces the rate of the first stage of oxidation of alcohol.

Activation parameter: The reaction was studied at temperatures to evaluate activation parameters. The results are summarized in Tables 4 and 5. The rate of oxidation of alcohol increases with the increase in the initial concentration of bromide ion, it also proves the protonation may however precede hydrolysis of *p*-methoxy-*N*-bromobenzamide and it is not possible to distinguish kinetically between the reaction (1), (2), (3) and (3a). A plot of log K against the increase of dielectric constant of CH₃COOH + H₂O mixture is linear with positive slop which points out that H₂OBR+ is an active oxidising species.
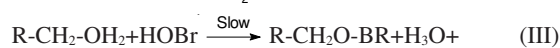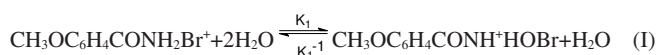
TABLE-4

[Substrate] =1.0 mol dm⁻³		[Oxidant] = 5.0 × 10⁻³ mol dm⁻³
(HClO₄) = 1.0 mol dm⁻³		Hg(OAc)₂ = 5.0 × 10⁻³ mol dm⁻³
HOAc = 50 % (v/v)		

S. No.	Temperature (K)	BuOH (K × 10⁻³ min⁻¹)
1.	313	3.1008
2.	318	3.1106
3.	323	3.6058
4.	328	6.1818

TABLE-5

Substrate	ΔE (KJ mol⁻³)	ΔH (KJ mol⁻³)	ΔPZ (Dm³ mol⁻¹ min)	ΔS (J mol⁻¹)	ΔG (KJ mol⁻¹)
n-Butanol	85.4423	82.80	2.052 × 10⁻³	66.382	+7.265

The information gained from the experimental data leads to the following probable mechanism which explains the observed results very well:

$$CH_3OC_6H_4CONHBR + H_3O+ \underset{K_1^{-1}}{\overset{K_1}{\rightleftharpoons}} CH_3OC_6H_4CON^+H_2Br \quad (I)$$

$$CH_3OC_6H_4CON+H_2Br+H_2O \underset{K_2^{-1}}{\overset{K_2}{\rightleftharpoons}} CH_3OC_6H_4CONH_2{}^+H_2OBr+ \quad (II)$$

$$RCH_2OH + H_2OBr+ \overset{Slow}{\longrightarrow} \underset{Br+}{\overset{|}{R\text{-}CH\text{-}OH}} + H_3O+ \quad (III)$$

$$\underset{RCH_2OH}{\overset{Br+ \;|}{}} \overset{Fast}{\longrightarrow} RCHO + HBR \quad (IV)$$

OR

$$CH_3OC_6H_4CONH_2Br^+ + 2H_2O \underset{K_1^{-1}}{\overset{K_1}{\rightleftharpoons}} CH_3OC_6H_4CONH^+HOBr+H_2O \quad (I)$$

$$R\text{-}CH_2OH + H_3O+ \underset{K_2^{-1}}{\overset{K_2}{\rightleftharpoons}} R\text{-}CH_2O+H_2+H_2O \quad (II)$$

$$R\text{-}CH_2\text{-}OH_2 + HOBr \overset{Slow}{\longrightarrow} R\text{-}CH_2O\text{-}BR+H_3O+ \quad (III)$$

$$RCH_2OBR \overset{Fast}{\longrightarrow} R\text{-}CHO + HBr \quad (IV)$$

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