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Kinetic and mechanistic studies in the oxidation of Isoamyl alcohol by p-Methoxy-N-Bromobenzamide

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ABSTRACT

Kinetics Studies of The oxidation of Isoamyl alcohol by p-methoxy-N-bromobenzamide has been made in aqueous acetic acid in the 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.

Keywords: Kinetics, Oxidation, Isoamylalcohol, p-Methoxy-N-Bromobenzamide.

INTRODUCTION

A great deal of the survey of the literature reveals that the mechanism of oxidation by chloramine-T[1], chloramine-B [2], N-bromsuccinimide [3] N-bromobenzamide [4-6], p-Methyl [7] and other halo amides [8], but` very little is known about the modes of the redox reaction of p-methoxy N-bromobenzamide as an oxidant . By substituting benzene ring of such benzamide with different groups, it is possible to tune oxidation potential of N-halo amides and thereby developing a tuning oxidant ,such oxidant are very much useful in controlling a number of free radical polymerization [9]reactions and also useful in different analyzing procedures. The different mechanistic pathways reported for the structurally related N-halo amides [10-13] promoted us to undertake the present investigation.

MATERIALS AND METHODS

Alcohol used were of S. Merck grade and were 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 alcohol 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^{0}C Preliminary experiments showed that the reaction is not sensitive to ionic strength hence no attempt was made to keep it constant.

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.

$$\text{R-CH}_2\text{OH} + \text{CH}_3\text{OC}_6\text{H}_4\text{NHBr} \longrightarrow \text{R–CH}_3\text{OC}_6\text{H}_4\text{NH}_2 + \text{HBr}$$

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 = 323K

S. No.	(Oxidant) ×10^{-3} (mol dm^{-3})	i-AmOH (k ×10^{-3} min-^{1})
1.	2.50	2.8698
2.	3.75	2.5680
3.	5.00	2.0127
4.	6.25	2.5676
5.	7.50	3.4420
6	8.75	5.7010

Dependence of substrate concentration: The plot of log k vs. log [oxidant] was found to be linear and it gives a slope value of unity, indicating that the order of the reaction with respect to substrate is one; the results are summarized in table-2.

Effect of added Benzamide: Reaction rate decreases by addition of Benzamide. The results are presented as follows in table 3.

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.

TABLE-2

(HClO$_4$)=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 =323K

S.No.	Substrate (mol dm^{-3})	i-AmOH (k ×10^{-3} min-^{1})
1.	0.2	1.8084
2.	0.3	1.8664
3.	0.4	2.5215
4.	0.5	2.8462
5.	0.6	2.8900
6.	0.8	2.6330
7.	1.0	5.6780

TABLE-3

[Substrate]=1.0 mol dm^{-3}, [Oxidant]=5.0×10-^{3}mol dm^{-3},[HClO$_4$]=1.0 mol dm^{-3},
[Hg (OAc)$_2$]= 5.0×10^{-3}mol dm^{-3},HOAc= 50% (v/v), Temperature=323K

S.NO	Benzamide ×10-^{3}(mol dm^{-3})	i-AmOH (k ×10^{3} min^{-1})
1.	0.0	5.1850
2.	1.0	5.4720
3.	2.0	5.0708
4.	5.0	4.2640
5.	8.0	2.4799
6.	10.0	1.0223

Activation parameter: The reaction was studied at temperatures to evaluate activation parameters .the results are summarised in Table 4 and 5.

TABLE-4

[Substrate]=1.0mol dm^{-3}, [HClO$_4$]=1.0 mol dm^{-3}, [Oxidant] = 5.0 × 1^{-3}mol dm^{-3}
HOAc= 50 %(v/v) [Hg (OAc)$_2$] = 5.0× 10^{-3}mol dm^{-3}

S.NO.	TEMP. (K)	i-AmOH (k ×10^{-3} min^{-1})
1.	313	1.7059
2.	318	2.0829
3.	323	4.6780
4.	328	6.4394

TABLE-5

Substrate	ΔE (KJmol^{-3})	ΔH (KJ mol^{-3})	ΔPZ (Dm^{3} mol^{-1}min)	ΔS (J mol^{-1})	ΔG (KJ mol^{-1})
Isoamyl alcohol	97.89810	95.2472	1.974 × 10^{-3}	68.3209	-2.16307

The rate of oxidation of alcohol increases with in the initial concentration of bromide ion. It indicates that the protonation of HOBr give a cationic bromide species. The protonation may however hydrolysis of p-methoxy-N-bromobenzamide and it is not possible to distinguish kinetically between the reaction I, II, III and IV. A plot log k$_1$ against the increase of dielectric constant of acetic acid water mixture is linear with positive slop which points out that (H$_2$OBr$^+$) is an active oxidising species.

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

$$CH_3OC_6H_4CONH_2Br^{+}+2H_2O \underset{k_1^{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3OC_6H_4CONH_2 + HOBr^{+} +H_2O \qquad (I)$$

$$\text{R-CH}_2\text{OH} + \text{H}_3\text{O}^+ \underset{k_2^{-1}}{\overset{k_2}{\rightleftharpoons}} \text{R-CH}_2\text{O}^+\text{H}_2\text{+H}_2\text{O} \quad \text{(II)}$$

$$\text{R-CH}_2\text{-OH}_2 \text{ +HOBr} \xrightarrow{\text{Slow}} \text{R-CH}_2\text{O - Br + H}_3\text{O}^+ \qquad \text{(III)}$$

$$\text{RCH}_2\text{OBr} \xrightarrow{\text{Fast}} \text{R-CHO + HBr} \qquad \text{(IV)}$$

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REFERENCES

[1] K.K.Banarji , *Indain J. Chem.*,**1977,**16A, 595

[2] G.GopalKrishen, B.R.Pai and N.Venktasubramanian, *Indian J.Chem.*, **1980,**19B, 293.

[3] D .H.R. Barton and W.J.Rosenfelder, *J .Chem. Soc.*, **1951,** 2381.

[4] A.Poorey, L.V. Shaastry, V.K.Seeriya and V.R.Shaastry, *Asian. J Chem.*, **1992,** 4,744.

[5] Brijesh pare, AjitChoube, V.W.Bhagwat and AshaRadhakrishanan, *AsianJ. Chem.*, **2002,** 14 (2), 602-606.

[6] Y.Y.Huang, H.C Lin and Wong Lin,K.-M.Cheng, W.-N.Su, K.-C. Sung,T.-P.Lin, J.-J.Huang, S.-k.Lin and Wong, *Tetrahedron*, **2009,** 65,9592.

[7] O.N. Choubey and V.K. Seeriah, *Int. J. Chem. Sci.*, **2004, 2**, 275.

[8] Youunis L.Hassan and Noor H.M.Saeed, *Oriet. J. Chem.*, **2010,** 26 (2), 415-410.

[9] S. Zhu and A.E. Hamietec, *Macromolecular Symposia*, **1993,** 1169, 247.

[10] N. S. Shrinivasan and N. Venkatasubramanian**,** *Tetrahadron*, **1974,** 30**,**419.

[11] N. Venkatasubramanian and V.Thiangarajan, *Tetrahedron Lett*., **1967,** 3349.

[12] V. Thiangarajan and N. Venkatasubramanian**,** *Indian J.Chem*., **1967,** 6**,** 809.

[13] S.C. Negi and K.K. Banerji, *Indian, J. Chem., Sect. B*, **1982,** 21,846.