

KINETICS AND MECHANISM OF OXIDATION OF AMYL ALCOHOL BY p-METHYL-N-BROMOBENZAMIDE

O. N. CHOUBEY and V. K. SEERIAH*

Department of Industrial Chemistry, Govt. Narmada College of Excellence,
HOSHANGABAD-4611002 (M.P.) INDIA

* Govt. M. G. M. P. G. College, Itarsi (M.P.) INDIA

ABSTRACT

Kinetics studies of the oxidation of amyl alcohol by p-methyl 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 the substrate. The reaction is retarded by the initial addition of benzamide. The activation parameters have been calculated and a suitable mechanism has been proposed.

Key word : Kinetics, Oxidation, Amyl alcohol, p-Methyl-N-bromobenzamide

INTRODUCTION

A great deal of the survey of the literature reveals that the mechanism of oxidation of alcohol by chloramine-T¹, chloramine -B², N-bromosuccinimide³ and other halomides is available but very little is known about the p-methyl N-bromobenzamide as an oxidant.

EXPERIMENTAL

All the chemicals used were B.D.H. (A.R.) and S.M. quality. Alcohols were dried over anhydrous magnesium sulphate and then fractionally distilled. Acetic acid was distilled over chromic acid before use. Perchloric acid was used as a source of hydrogen ions. The reaction vessels were coated with black paint to exclude any photochemical effects. 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-methyl-N-bromobenzamide. Stoichiometry of the reaction was also studied. It was observed that one equivalent of oxidant was consumed by one equivalent of alcohol.



Dependence on oxidant concentration.**Table 1.**

[Substrate]	=	1.0 mol dm ⁻³	Hg[(OAc) ₂]	=	5.0 x 10 ⁻³ mol dm ⁻³
[HClO ₄]	=	1.0 mol dm ⁻³	HOAc	=	50% (v/v)
Temperature	=	323 K			

[Oxidant] x 10 ³ mol dm ⁻³	k x 10 ³ min ⁻¹
2.50	3.43
3.75	3.19
5.00	3.20
6.25	3.47
7.50	3.44
8.75	3.19

Dependence on substrate concentration

The plot of log K v/s log [Oxidant] was found to be linear and the slope of the plot was unity. It indicates that the order of the reaction with respect to the substrate is one.

Table 2.

[HClO ₄]	=	1.0 mol dm ⁻³	[Oxidant]	=	5.0 x 10 ⁻³ mol dm ⁻³
HOAc	=	50% (v/v)	[Hg(OAc) ₂]	=	5.0 x 10 ⁻³ mol dm ⁻³
Temperature	=	323°K.			

[Substrate] mol dm ⁻³	k x 10 ³ min ⁻¹
0.2	0.78
0.3	1.11
0.4	1.43
0.5	1.77
0.6	2.12
0.8	2.80
1.0	3.48

Effect of added benzamide

The rate of reaction decreases on addition of benzamide. The results are presented in the Table 3.

Table 3.

[Substrate] =	1.0 mol dm ⁻³	[oxidant] =	5.0 x 10 ⁻³ mol dm ⁻³
[HClO ₄] =	1.0 mol dm ⁻³	[Hg(OAc) ₂] =	5.0 x 10 ⁻³ mol dm ⁻³
HOAc =	50% (v/v)	Temperature =	323 K
[Benzamide] x 10 ³ mol dm ⁻³		k x 10 ³ min ⁻¹	
0.0		3.48	
1.0		3.20	
2.0		3.04	
5.0		2.63	
8.0		2.00	
10.0		1.54	

Effect of added mercuric (II) acetate – Initial addition of Hg(OAc)₂ suppresses completely the second faster stage and reduces the rate of the first state of oxidation of alcohol.

Activation parameters – The reaction was studied at different temperatures to evaluate activation parameters. The result are summarised in Tables 4 and 5.

Table 4.

[Substrate] =	1.0 mol dm ⁻³	[Oxidant] =	5.0 x 10 ⁻³ mol dm ⁻³
[HClO ₄] =	1.0 mol dm ⁻³	[Hg(OAc) ₂] =	5.0 x 10 ⁻³ mol dm ⁻³
HOAc =	50% (v/v)		
K		k x 10 ³ min ⁻¹	
313		1.16	
318		1.99	
323		3.48	
328		6.06	

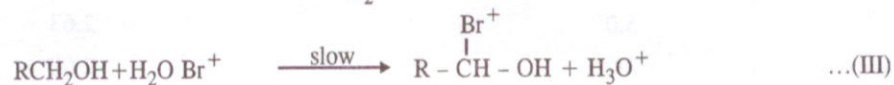
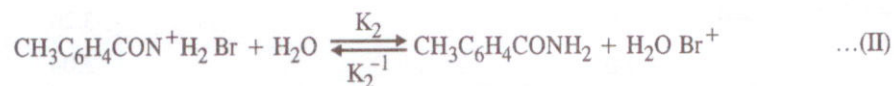
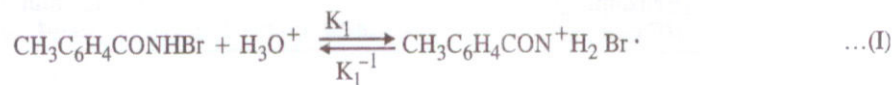
Table 5.

Substrate	ΔE kJ mol ⁻¹	ΔH kJ mol ⁻¹	ΔpZ dm ³ mol ⁻¹ min	ΔS J mol ⁻¹ K ⁻¹	ΔG kJ mol ⁻¹
Amyl Alcohol	92.53	89.84	3.6054 x 10 ⁻³	92.41	-7.97

The rate of oxidation of alcohol increases with an increase in the initial concentration of bromide ion. It indicates that the protonation of HOBr gives a cationic bromide species. The protonation may however hydrolyse p-methyl-N-bromobenzamide and it is not possible to distinguish kinetically between the reaction I, II, III and IV. A plot of log K against the increase

of dielectric constants of $\text{CH}_3\text{COOH}-\text{H}_2\text{O}$ mixture is linear with a positive slope, which points out the $\text{H}_2\text{O Br}^+$ is the active oxidising species.

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



The authors are thankful to the Principal, Govt. Narmada Mahavidyalya, Hoshangabad for providing laboratory facilities.

REFERENCES

1. Dr. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 2381 (1951).
2. G. Gopal Krishnan, B. R. Pai and N. Venkatasubramanian *Indian J. Chem., Sect B.* (1980).
3. N. S. Shrinivasan and N. Venkatasubramanian, *Tetrahedron.*, **30**, 419 (1974).

Accepted : 12.1.2004