NOTE

Kinetics of Oxidation of *n*-Butanol by *p*-Methyl N-Bromobenzamide

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Kinetic studies in the oxidation of *n*-butyl 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 the oxidant and unity with respect to 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.

Abundant literature is available about the mechanism of oxidation of alcohol by chloramine-T[1], chloramine-B[2], N-bromosuccinimide[3] and other haloamides, but very little about the *p*-methyl N-bromobenzamide.

All the chemicals used were BDH, AR and SM quality. Alcohals 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.

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

$$R\text{-}CH_2OH + CH_3C_6H_4NHBr \longrightarrow R\text{-}CHO + CH_3C_6H_4NH_2 + HBr$$

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

TABLE-1

[Substrate] = 1.0 mol dm^{-3} $Hg(OAc)_2 = 5.0 \times 10^{-3}$ mol dm^{-3}
$[HClO_4]$ = 1.0 mol dm^{-3} HOAc = 50% (v/v)
Temp. = 323 K

S.No	[Oxidant] $\times 10^{-3}$ (mol dm^{-3})	*n*-BuOH ($K \times 10^3$ min^{-1})
1.	2.50	3.2459
2.	3.75	3.2644
3.	5.00	3.2621
4.	6.25	3.2736
5.	7.50	3.2459
6.	8.75	3.2704

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Dependence of substrate concentration: The plot of log K *vs.* log [oxidant] was found to be linear and slope was unity, indicating that the order of the reaction with respect to the substrate is one (Table-2)

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}
Temp = 323 K

S.No.	Substrate (mol dm^{-3})	*n*-BuOH ($K \times 10^3$ min^{-1})
1.	0.2	0.7341
2.	0.3	1.0391
3.	0.4	1.3476
4.	0.5	1.9159
5.	0.6	1.9846
6.	0.8	2.6191
7.	1.0	3.2621

Effect of Added Benzamide: The rate of reaction decreases by the addition of benzamide. The results are presented in Table-3.

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) Temp = 323 K

S. No.	Benzamide $\times 10^{-3}$ (mol dm^{-3})	*n*-BuOH ($K \times 10^3$ min^{-1})
1.	0.0	3.2568
2.	1.0	3.0014
3.	2.0	2.8521
4.	5.0	2.4683
5.	8.0	1.8751
6.	10.0	1.4418

Effect of added mercuric(II) acetate: Initially addition of $Hg(OAc)_2$ suppresss completely the second faster stage and reduces the rate of the first stage of oxidation of alcohol.

Activation Parameters: The reaction was studied at different 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 of HOBr to give a cationic bromide species. The protonation may however proceed hydrolysis of *p*-methyl N-bromobenzamide and it is not possible to distinguish kinetically between the reactions (1), (2), (3) and (3a). A plot of log K against the increase of dielectric constants of $CH_3COOH–H_2O$ mixture is linear with positive slope which points out that H_2OBr^+ is an active oxidising species.

TABLE-4

[Substrate]= 1.0 mol dm^{-3}
$[HClO_4]$ = 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}

S. No.	Temp. (K)	BuOH $K \times 10^3$ min^{-1}
1.	313	1.0817
2.	318	1.8617
3.	323	3.4039
4.	328	5.6777

TABLE-5

[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} dm^{-3}
HOAc = 50% (v/v)

Substrate	ΔE (kJ mol^{-3})	ΔH (kJ mol^{-3})	ΔPZ (dm^3 mol^{-1} min)	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})
n-Butanol	88.61	85.924	3.5180×10^{-3}	88.134	–6.83

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

$$CH_3C_6H_4CONHBr + H_3O^+ \underset{K_1^{-1}}{\overset{K_1}{\rightleftharpoons}} CH_3C_6H_4CON^+H_2—Br \quad (1)$$

$$CH_3C_6H_4CON^+H_2—Br + H_2O \underset{K_2^{-1}}{\overset{K_2}{\rightleftharpoons}} CH_3C_6H_4CONH_2 + H_2OBr^+ \quad (2)$$

$$RCH_2OH + H_2OBr^+ \xrightarrow{\text{slow}} R—\underset{\displaystyle Br^+}{\underset{|}{CH}}—OH + H_3O^+ \quad (3)$$

$$\underset{\displaystyle Br^+}{\underset{|}{RCH}}—OH \xrightarrow{\text{fast}} RCHO + HBr \quad (3a)$$

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(*Received: 12 July 1999; Accepted*: 21 October 1999) AJC–1895