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Kinetics and Mechanism of Oxidation of Some Primary Alcohols by N-Bromobenzamide

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Kinetic studies in the oxidation of n-butyl alcohol and amyl alcohol with N-bromobenzamide has been made in aqueous acetic acid in presence of mercuric acetate. The reaction is first order, each with respect to oxidant and substrate. Order with respect to perchloric acid is fractional or first order depending upon the substrate concentration. Suggest protonation of the substrate in course of reaction. A mechanism consistent with the result has been proposed.

INTRODUCTION

The literature of mechanism of oxidation by chloramine-T[1], chloramine-B[2], N-bromosuccinimide[3] and other N-halomides[4–7] are available, but less information is available about the modes of the redox reaction of N-bromobenzamide (NBB)[8–10]. In present work, we report the kinetics and mechanism of n-butyl alcohol and amyl alcohol with N-bromobenzamide (NBB).

EXPERIMENTAL

All the chemicals used were BDH, AR and SM quality and purified by the reported method[11]. 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 effect.

The kinetics of oxidation of alcohols is found to be pseudo-first order reaction by keeping a large excess of alcohol over NBB. The reactions were followed iodometrically for over 70% of the reaction. The temperature was kept constant within ± 0.1°C. The pseudo-first order rate constants (k_1) were computed from the plot of log [NBB] against time. Duplicate kinetic runs indicate that the reaction rate constants were reproducible within ± 4%. Preliminary experiments showed that the reaction is not sensitive to ionic strength, hence no attempt was made to keep it constant.

RESULTS AND DISCUSSION

When the alcohol is in excess, the first order plots show that the reaction is composed of two successive steps: the initial slow reaction followed by a fast reaction. Such observations were made in the oxidation of alcohols by N-bromosuccinimide[4–6]. The second faster reaction is attributed to either oxidation of alcohol by bromine or to the reaction of bromine with carbonyl product[4]. This was suppressed by the addition of 0.005 M mercuric acetate.

Dependence on oxidant concentration: The time order of reaction and concentration order of reaction is found to be one with respect to oxidant by the independence of the rate constant on the initial concentration. Results are summarized in Table-1.

TABLE-1

[Substrate] = 1.0 mol dm^{-3}, [$Hg(OAc)_2$] = 5.0×10^{-3} mol dm^{-3},
[$HClO_4$] = 0.5 mol dm^{-3}, [AcOH] = 50% (v/v),
Temp. = 323 K

S. No.	[NBB] × 10^3 mol dm^{-3}	k × 10^3 min^{-1}	
		BuOH	AmOH
1.	2.50	4.64	4.90
2.	3.75	4.66	4.99
3.	5.00	4.66	4.57
4.	6.25	4.68	4.96
5.	7.50	4.60	4.91
6.	8.75	4.67	4.98

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

TABLE-2

[NBB] = 5.0×10^{-3} mol dm^{-3}, [$Hg(OAc)_2$] = 5.0×10^{-3} mol dm^{-3},
[$HClO_4$] = 0.5 mol dm^{-3}, [AcOH] = 50% (v/v),
Temp. = 323 K

S. No.	[Substrate] mol dm^{-3}	k × 10^3 min^{-1}	
		BuOH	AmOH
1.	0.2	1.05	1.12
2.	0.3	1.48	1.58
3.	0.4	1.93	2.04
4.	0.5	2.74	2.53
5.	0.6	2.84	3.02
6.	0.8	3.75	3.99

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}, [Hg(OAc)$_2$] = 5.0×10^{-3} mol dm^{-3}
[$HClO_4$] = 0.5 mol dm^{-3}, [AcOH] = 50% (v/v)
Temp. = 323 K, [NBB] = 5.0×10^{-3} mol dm^{-3}

S. No.	[Benzamide] × 10^{-3}	k × 10^3 min^{-1}	
		BuOH	AmOH
1.	0.0	4.66	4.98
2.	1.0	4.29	4.58
3.	2.0	4.07	4.34
4.	5.0	3.53	3.76
5.	8.0	2.68	2.86
6.	10.0	2.06	2.20

Effect of Bromide ions: Reaction rate is enhanced by the initial addition of potassium bromide. The results are summarized in Table-4.

TABLE-4

[Substrate] = 1.0 mol dm^{-3}, [Hg(OAc)$_2$] = 5.0×10^{-3} mol dm^{-3}
[$HClO_4$] = 0.5 mol dm^{-3}, [AcOH] = 50% (v/v)
Temp. = 323 K, [NBB] = 5.0×10^{-3} mol dm^{-3}

S. No.	[KBr] × 10^{-3}	k × 10^3 min^{-1}	
		BuOH	AmOH
1.	0.0	4.66	4.87
2.	1.0	4.80	5.11
3.	2.0	5.14	5.47
4.	4.0	5.36	5.69
5.	6.0	5.59	5.98
6.	8.0	7.22	7.72
7.	10.0	12.63	13.53

Dependence of rate on perchloric acid concentration: Results of acid variation may be summarized as follows:

(a) **At 0.5 mole dm^{-3} of substrate concentration:** Fractional order with respect to perchloric acid up to 0.5 mole dm^{-3} of perchloric acid concentration.

(b) **At 1.0 mole dm^{-3} of substrate concentration:** Fractional order with respect to perchloric acid up to 1.0 mole dm^{-3} and first order above 1.0 mole dm^{-3} of perchloric acid concentration.

Thus it seems that the effect of hydrogen ions must be traced to some factor involving the alcohol[12]. The results find an explanation on the assumption that alcohols are protonated in acidic solutions and the protonated form is kinetically active.

$$ROH + H^+ \longrightarrow RO^+H_2$$

Alcohols are known to be proton acceptors and protonation for many alcohols has been determined both kinetically and spectrophotometrically[13]

Temperature variation and activation parameter: The reaction was studied at various temperatures to evaluate activation parameter. The data of activation parameters are given in Table-5 and 6.

TABLE-5

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

S. No.	[Temp] K	k × 10^3 min^{-1}	
		BuOH	AmOH
1.	313	1.55	1.66
2.	318	2.66	2.84
3.	323	4.86	4.98
4.	328	8.11	8.66

TABLE-6

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

Substrate	ΔE* kJ mole^{-1}	ΔH* kJ mole^{-1}	PZ dm^3 mole^{-1} min^{-1}	ΔS* J K^{-1} mole^{-1}	ΔG* kJ mole^{-1}
BuOH	96.21	93.52	1.75 × 10^{13}	+7.95	90.96
AmOH	92.53	89.84	4.55 × 10^{12}	–3.26	90.89

Stoichiometry of the reaction: It was observed that one mole of substrate gets oxidized by one mole of the oxidant:

$$RCH_2OH + C_6H_5NHBr \longrightarrow RCHO + C_6H_5NH_2 + HBr$$

The retardation of the rate of oxidation with added benzamide suggested that pre-equilibrium step involves a process in which benzamide is one of the products (equation 2). The increase in the rate of oxidation with acidity points out the protonation of HOBr to give a cationic bromide species—a stronger electrophile and oxidant (equation 3). The reaction proceeds, albeit slowly, even in absence of perchloric acid. From this observation, it is likely that in the absence of added mineral acid and the oxidising species is HOBr. the protonation may, however, precede hydrolysis of $C_6H_5CONHBr$, and it is not possible to distinguish kinetically between the reactions (2) and (3) from (4) and (5). A plot of log k_1 against the inverse of dielectric constant of acetic acid-water mixture is linear with positive slope. According to Amis[14] this indicates a positive ion-dipole reaction in the oxidation of alcohol with NBB. This is in accordance with our suggestion that $(H_2OBr)^+$ is active oxidizing species.

$$C_6H_5CONHBr + H_2O \rightleftharpoons C_6H_5CONH_2 + HOBr \tag{1}$$

$$HOBr + H_3O^+ \rightleftharpoons (H_2OBr)^+ + H_2O \tag{2}$$

$$C_6H_5CONHBr + H_3O^+ \rightleftharpoons (C_6H_5CONH_2Br)^+ \tag{3}$$

$$C_6H_5CONH_2Br^+ + H_2O \rightleftharpoons (H_2OBr)^+ + C_6H_5CONH_2 \tag{4}$$

$$R\text{-}CH_2OH + (H_2OBr)^+ \xrightarrow{\text{(slow)}} R\text{-}CH(Br)OH + H_3O^+ \tag{5}$$

$$R\text{-}CH(Br)OH \xrightarrow{\text{fast}} R\text{-}CHO + HBr \tag{6}$$

or

$$C_6H_5CONH_2Br^+ + 2H_2O \rightleftharpoons (HOBr) + C_6H_5CONH_2 + H_3O^+ \tag{4A}$$

$$R\text{-}CH_2OH + H_3O^+ \rightleftharpoons R\text{-}CH_2O^+H_2 + H_2O \tag{5A}$$

$$R\text{-}CH_2O^+H_2 + (HOBr) \xrightarrow{\text{(slow)}} R\text{-}CH(Br)O^+H_2 + H_2O \tag{5B}$$

$$R\text{-}CH(Br)O^+H_2 + H_2O \xrightarrow{\text{fast}} R\text{-}CHO + HBr + H_3O^+ \tag{6A}$$

The formation of hypobromite ester (RCH_2OBr) in the rate determining step[15] may be excluded considering the values of entropy of activation. Hence, the proposed reaction mechanism for the oxidation of primary alcohol with NBB is very consistent with the experimental findings.

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