

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

ARCHANA POOREY, L. V. SHAASTRY, V. K. SEERIYA AND V. R. SHAASTRY

*School of Studies in Chemistry,
Vikram University Ujjain-456 010, India*

Kinetic studies in the oxidation of some secondary alcohols by 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 near about one with respect to the substrates. The order with respect to perchloric acid varies with the change in perchloric acid 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.

INTRODUCTION

Reports are available in the literature on the mechanism of oxidations by chloramine-T¹, Chloramine-B², N-bromosuccinimide³ and other haloamides. However, very little information is available about the modes of the oxidation reactions of N-bromobenzamides *i.e.* NBB. The different mechanistic pathways reported for the structurally related N-haloamides⁴⁻⁷ prompted us to undertake the present investigations.

EXPERIMENTAL

Alcohols used were of S. Merck grade and were purified by the method described in the literature.⁸ Acetic acid was distilled over chromic acid before use. Perchloric acid was used as a source of hydrogen ions. All the chemicals other used were of BDH 'AR' and SM 'GR' quality. The reaction vessels were coated with black paint to exclude any photochemical effects.

The reactions were carried out under pseudo first order conditions by keeping a large excess of alcohol over NBB. The temperature was kept constant within $\pm 0.1^\circ\text{C}$. The solvent used was 1:4 (v/v) acetic acid-water, unless mentioned otherwise. The reactions were followed iodometrically for over 70% of the reaction. The pseudo first order rate constants (k_1) were computed from the plot of $\log [\text{NBB}]$ against time. Duplicate kinetic runs indicate that the reaction rate constants are reproducible within $\pm 4.0\%$. Preliminary experiments showed that the reaction is not sensitive to ionic strength, hence no attempt was made to keep it constant.

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 cases of the oxidation of alcohols by N-bromosuccinimide⁴⁻⁶. The second faster reaction is attributed to either the oxidation of alcohols by bromine or to the reaction of bromine with respective carbonyl products⁴. The second faster reaction was suppressed by the addition of $0.005 \text{ mol dm}^{-3}$ of mercuric acetate.

RESULTS AND DISCUSSION

Dependence of the Rate on the Oxidant Concentration

The time order of the reaction is found to be one with respect to oxidant. Results obtained are in the Table 1.

TABLE 1
[Substrate] : 0.5 mol dm^{-3} ; $[\text{Hg}(\text{OAc})_2]$:
 $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{HClO}_4]$: 1.0 mol dm^{-3} ;
Temperature : 318°K HOAc : 20% (v/v)

S.No.	NBB $\times 10^{-3}$ mol dm^{-3}	$k_1 \times 10^3 \text{ min.}^{-1}$	
		2-Propanol	2-butanol
1.	5.00	3.19	7.65
2.	3.75	3.31	7.65
3.	2.50	3.46	7.73
4.	1.87	3.21	7.62
5.	1.25	3.65	7.65

Dependence of the Rate on the Substrate Concentration

The rate constants corresponding to different initial concentrations of the respective substrates have been obtained. The order with respect to substrate is near about one. The results are summarised in the Table 2.

TABLE 2
[NBB] : $2.5 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{HClO}_4]$: 1.0 mol dm^{-3}
[$\text{Hg}(\text{OAc})_2$] : $5.0 \times 10^{-3} \text{ mol dm}^{-3}$;
Temperature : 318°K ; HOAc : 20% (v/v)

S. No.	Substrate mol dm^{-3}	$k_1 \times 10^3 \text{ min.}^{-1}$	
		2-propanol	2-butanol
1.	0.3	3.90	10.22
2.	0.5	6.91	15.73
3.	0.6	7.73	18.47
4.	0.8	9.77	23.18
5.	1.0	11.51	27.98

Dependence of the Rate on Perchloric Acid Concentration

It has been found that the reaction rate increases with the increasing concentration of perchloric acid. Interestingly, the order with respect to perchloric acid varies with the change in the perchloric acid concentration (Tables 3a and 3b).

TABLE 3a

[Substrate] : 9.5 mol dm^{-3} ; [NBB] : $2.5 \times 10^{-3} \text{ mol dm}^{-3}$;
HOAc : 20% (v/v); $[\text{Hg}(\text{OAc})_2]$: $5.0 \times 10^{-3} \text{ mol dm}^{-3}$;
Temperature : 318°K

[HClO ₄] mol dm ⁻³	$k_1 \times 10^3 \text{ min.}^{-1}$	
	2-propanol	2-butanol
0.2	2.38	6.91
0.4	2.93	7.31
0.6	3.84	9.23
0.8	5.21	12.82
1.0	6.91	15.73
1.2	7.77	19.04
1.4	9.32	23.39
1.6	10.66	27.10
1.8	12.42	29.53
2.0	13.96	34.93

TABLE 3b

[Substrate] : $1.0 \times \text{mol dm}^{-3}$; [NBB] : $2.5 \times 10^3 \text{ mol dm}^{-3}$;
HOAc : 20% (v/v); $[\text{Hg}(\text{OAc})_2]$: $5.0 \times 10^{-3} \text{ mol dm}^{-3}$;
Temperature : 318°K

[HClO ₄] mol dm ⁻³	$k_1 \times 10^3 \text{ min.}^{-1}$	
	2-propanol	2-butanol
0.2	4.60	11.29
0.4	6.91	16.57
0.6	8.28	21.62
0.8	9.88	25.27
1.0	11.51	27.98
1.2	13.90	33.19
1.4	16.20	39.00

The Effect of the Added Benzamide

It has been found that the reaction rate decreases due to the initial addition of benzamide. The results are presented in the Table 4.

TABLE 4

[Substrate]: 0.5 mol dm^{-3} ; [NBB]: $2.5 \times 10^{-3} \text{ mol dm}^{-3}$
 [HClO₄]: 0.5 mol dm^{-3} ; [Hg(OAc)₂]: $5.0 \times 10^{-3} \text{ mol dm}^{-3}$
 HOAc: 20% (v/v); Temperature: 318°K

S.No.	[Benzamide] $\times 10^{-3}$	$k_1 \times 10^3 \text{ min}^{-1}$	
		2-propanol	2-butanol
1	1.25	2.71	6.49
2	2.50	2.38	5.58
3	3.75	2.25	5.07
4	5.00	1.98	4.13
5	7.50	1.55	3.25

The Effect of the Temperature Variation and the Activation Parameters

The reaction was studied at various temperatures to evaluate the activation parameters. The data regarding activation parameters are tabulated in the Tables 5a and 5b.

TABLE 5a

[Substrate]: 0.5 mol dm^{-3} ; [NBB]: $2.5 \times 10^{-3} \text{ mol dm}^{-3}$;
 [Hg(OAc)₂]: $5.0 \times 10^{-3} \text{ mol dm}^{-3}$; [HClO₄]: 1 mol dm^{-3}
 HOAc: 20% (v/v)

S. No.	Temperature in Kelvin scale	$k_1 \times 10^3 \text{ min}^{-1}$	
		2-propanol	2-butanol
1	323	12.00	—
2	318	6.91	15.73
3	313	3.51	9.24
4	308	1.59	4.87
5	303	—	2.49

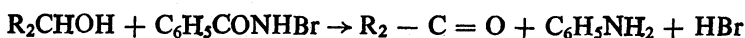
TABLE 5b

[Substrate]: 0.5 mol dm⁻³; [NBB]: 2.5 × 10⁻³ mol dm⁻³;
 [Hg(OAc)₂]: 5.0 × 10⁻³ mol dm⁻³; [HClO₄]: 1 mol dm⁻³;
 HOAc: 20% (v/v)

[Substrate]	ΔE_{\neq} (KJ mol ⁻¹)	ΔH_{\neq} (KJ mol ⁻¹)	PZ (dm ³ mol min ⁻¹)	ΔS_{\neq} (JK mol ⁻¹)
1. 2-propanol	119.0	117.0	3.09 × 10 ¹⁷	89.40
2. 2-butanol	95.5	92.5	7.12 × 10 ¹⁶	77.5

Stoichiometry of the Reaction

The product analysis was made under the kinetic conditions. Alcohol (0.05 mol) and NBB (0.01 mol) made up to 50 ml in perchloric acid (1.0 mol dm⁻³) were kept in dark for 8 hrs., till the completion of the oxidation. The solution was then treated overnight with excess (200 ml.) of freshly filtered saturated solution of 2,4-dinitrophenyl hydrazine (DNP) in 2 mol dm⁻³ of hydrochloric acid. The precipitated 2,4-dinitrophenylhydrazone (DNPH) was collected by filtration. It was weighed, both after and before crystallisation. The difference in the crude yield and the yield determined after crystallisation was not more than 2%. Mixture melting point and mixture TLC of DNPH derivative of the respective of the products and that of the authentic samples confirmed that the products were the corresponding ketones and the reactions proceed as per the following general scheme of the stoichiometric equation:



The stoichiometry was further, ascertained by treating 0.01 mol of alcohol with 0.05 mol of NBB in the presence of perchloric acid (1 mol). The residual NBB was determined iodometrically.

1. The retardation of the rate of oxidation due to the added benzamide suggests that the pre-equilibrium step involves a process in which benzamide is one of the products.

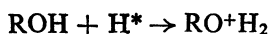
2. From the Tables 3a and 3b, we can make different observations leading to useful inferences.

(a) *At 0.5 mol dm⁻³ of Substrate Concentration:* The order is fractional with respect to perchloric acid upto 0.5 mol dm⁻³, and is first order above 0.5 mol dm⁻³ of its concentration.

(b) The order is fractional with respect to perchloric acid upto 1.0 mol dm⁻³, and is first order above 1.0 mol dm⁻³ of its concentration.

Thus, it seems that the effect of hydrogen ions must be traced in to some factor, involving the alcohol molecules.⁸ The results find an explanation on the assumption that alcohols are protonated in acidic solutions

and the protonated form is kinetically active.

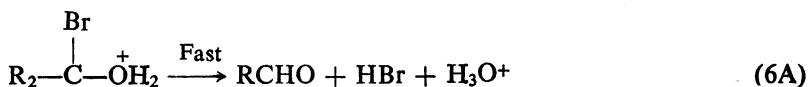
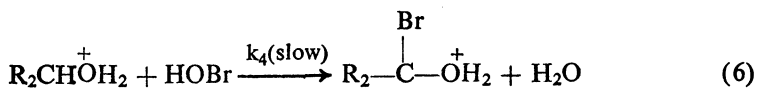
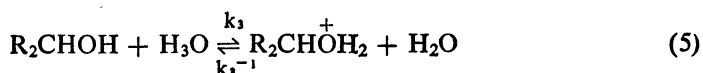
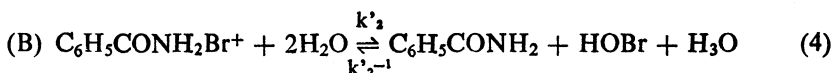
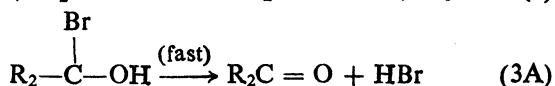
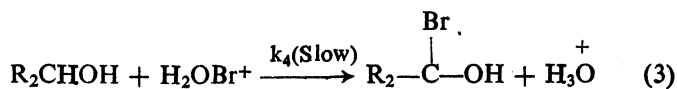
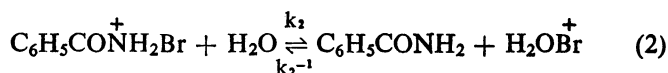
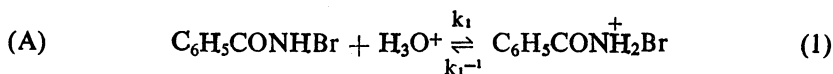


Alcohols are known to be proton acceptors and protonation constants for many alcohols have been determined both kinetically and spectrophotometrically.⁹

3. It is revealed from the Table, that the rates of oxidation increase with the increase in the initial concentration of bromide ions. However, the increase in the values of the rate constants with increasing concentration of bromide ions can be assigned to the involvement of molecular bromine at very low concentrations, in the process of oxidation of alcohols, where the rate of oxidation depends upon the concentration of molecular bromine¹⁰.

4. A plot of $\log k_1$ against the inverse of dielectric constants of acetic acid-water mixture is linear with positive slope. This According to Amis¹¹ indicates a positive ion-dipole reaction. This is in accordance with our suggestion that $(\text{H}_2\text{OBr})^+$ is active oxidising species.

5. The consonance with the results obtained by us, the following two schemes of mechanism may be suggested for the oxidation of secondary alcohols by NBB:



From equation (3), we have

$$-\frac{d[\text{C}_6\text{H}_5\text{CONH}-\text{Br}]}{dt} = k_4[\text{H}_2\text{OBr}^+] [\text{ROH}] \quad (7)$$

on substituting the value of $[\text{H}_2\text{O}^+\text{Br}]$, we get

$$-\frac{d[\text{C}_6\text{H}_5\text{CONH}-\text{Br}]}{dt} = \frac{k_4 k_2 k_1 [\text{C}_6\text{H}_5\text{CONHBr}] [\text{ROH}] [\text{H}^+]}{k^{-1} + k_1 [\text{H}^+] [\text{C}_6\text{H}_5\text{CONH}_2]} \quad (8)$$

Similarly, from equation VI, we have

$$-\frac{d[\text{C}_6\text{H}_5\text{CONH}-\text{Br}]}{dt} = k' [\text{HOBr}] [\text{RCH}_2\overset{+}{\text{O}}\text{H}_2] \quad (9)$$

On substituting the value of $[\text{RCH}_2\overset{+}{\text{O}}\text{H}_2]$ in equation (9), we get

$$-\frac{d[\text{C}_6\text{H}_5\text{CONH}-\text{Br}]}{dt} = \frac{k'_4 k_3 [\text{ROH}] [\text{H}^+] [\text{HOBr}]}{k_3^{-1} + k_3 [\text{H}^+]} \quad (10)$$

Substituting the value of $[\text{HOBr}]$ in equation (10), we get

$$-\frac{d[\text{C}_6\text{H}_5\text{CONH}-\text{Br}]}{dt} = \frac{k'_4 k_3 k_1 k'_2 [\text{C}_6\text{H}_5\text{CONH}-\text{Br}] [\text{ROH}] [\text{H}^+]^2}{k_3^{-1} + k_3 [\text{H}^+] [\text{C}_6\text{H}_5\text{CONH}_2]} \quad (11)$$

The equations (8) and (11)

- (i) The order with respect to oxidant, $[\text{C}_6\text{H}_5\text{CONH}-\text{Br}]$ is one.
- (ii) The order with respect to alcohol is one.
- (iii) The order with respect to $[\text{H}^+]$ is either one or fractional, depending upon the values of $[\text{H}^+]$ and $k_1[\text{H}^+]$ for equation (11).

The formation of hypobromite ester $\begin{matrix} \text{R} \\ \diagdown \\ \text{CH}-\text{O}-\text{Br} \\ \diagup \\ \text{R} \end{matrix}$ in the rate determining step (as suggested by Banerji and Negi¹²) may be excluded considering the values of entropy of activation. Hence, the proposed reaction mechanism for the oxidation of 2-propanol by NBB is very much consistent with the experimental findings.

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