



Research Article

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1-Bromobenzimidazole Oxidation of Aliphatic Alcohols -A Kinetic Perspective

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Abstract

The kinetics of oxidation of aliphatic alcohols by 1-bromobenzimidazole (BBI) has been studied in aqueous acetic acid medium in presence of mercuric acetate. The order of the reaction with respect to [BBI] and [alcohol] are unity. The reaction is fractional order with respect to $[H^+]$. The rate of oxidation increases with decrease in dielectric constant of solvent medium indicating ion-dipole interaction. The rate of the reaction is not influenced by the addition of electrolytes like sodium perchlorate. Polymerization was not observed with acrylonitrile. The reactions were studied at four different temperatures and thermodynamic parameters have been calculated. The oxidation of aliphatic alcohols shows a Taft ρ value of -0.722 suggesting an electron deficient transition state. $BBIH^+$ has been postulated as the reactive oxidizing species. A suitable mechanism in consistent with the observed kinetic data is proposed.

Keywords: aliphatic alcohols, 1-bromobenzimidazole, oxidation, kinetics.

Contents

1. Introduction	1137
2. Experimental	1138
3. Results and discussion	1138
4. Mechanism and Rate Law.	1139
5. Conclusion	1140
6. References	1140

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1. Introduction

The N-halo compounds are referred to as positive halogen compounds. The kinetics of oxidation of various organic substrates by N-halo oxidants has received considerable attention [1-12]. The kinetics of oxidation of alcohols by N-bromosuccinimide [13, 14], N-chlorosuccinimide [15], N-bromoacetamide [16], Bromamine-T [17], Chloramine-T [18], N-chloronicotinamide [19], N-bromophthalimide [20], 1-Chlorobenzotriazole [21], 1-Chlorobenzimidazole [3] and 1-Bromobenzimidazole [22] have already been reported in the literature. 1-Bromobenzimidazole (BBI) has been used as an oxidimetric titrant for a good number of reductants [23] and was used in the oxidation kinetics of benzaldehydes [24], furfural [25], cyclanols [26], cyclohexanone [27] and benzyl alcohols [22]. An extensive literature survey reveals that the oxidation of aliphatic alcohols with BBI has not been reported so far and hence an

attempt was made to study the reaction kinetics and mechanism of oxidation of aliphatic alcohols with BBI in aqueous acetic acid medium.

2. Materials and Methods

1-Bromobenzimidazole (BBI) was prepared and purified by literature method [28]. Acetic acid was purified by standard method and the fraction distilling at 118^oC was collected. Aliphatic alcohols and sodium perchlorate were the purest samples available from E-Merk and were used as such. Other chemicals were analytical grade samples from B.D.H.

2.1 Kinetic Measurements

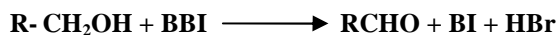
The pseudo-first order conditions were maintained by keeping a large excess of [alcohol] over [BBI]. The reactions were followed potentiometrically [3] upto 70% completion by following the potentials of the reaction mixture containing varying concentrations of [BBI]/[BI] couple (BI=Benzimidazole) at regular time intervals using a Platinum-Saturated Calomel Electrode [SCE] assembly. The pseudo-first order rate constant, k_1 , was computed from the linear ($r > 0.999$) plots of $\log(E_t - E_\infty)$ versus time.

where, E_t - potential at time t
 E_∞ - potential at infinity.

When the kinetic run was done by iodometry, the same results were obtained. The velocity constants were reproducible within $\pm 2\%$ error. Preliminary experiments showed that the rate of oxidation is not sensitive to change in ionic strength.

2.2 Product Analysis and Stoichiometry

Different ratios of BBI and methanol were equilibrated at 303 K in presence of requisite amounts of perchloric acid, mercuric acetate and acetic acid under the conditions of [BBI] \gg [alcohol]. The reaction mixture was kept for 48 hours to ensure the completion of the reaction. The solution was extracted with ether, washed with water. Formaldehyde was formed as the main product which was confirmed by its semicarbazone derivative and IR spectral analysis.



3. Results and Discussion

The oxidation of methanol was carried out in 80% acetic acid –20% water medium (v/v) in presence of a large excess of substrate and perchloric acid of suitable concentration as the catalyzing acid source and mercuric acetate. Mercuric acetate acts as a capture agent for any Br^- formed in the reaction. It exists as $HgBr_4^{2-}$ or unionized $HgBr_2$ and ensures that oxidation take place purely through BBI.

Table 1: Effect of varying [BBI], [alcohol], $[HClO_4]$ and % acetic acid
 $[Mercuric\ acetate] = 3.0 \times 10^{-2} \text{ mol.dm}^{-3}$; Temperature = 303 K

$[BBI] \times 10^3$ mol.dm^{-3}	$[Alcohol] \times 10^2$ mol.dm^{-3}	$[H^+] \times 10^2$ mol.dm^{-3}	% acetic acid	$k_{obs} \text{ s}^{-1} \times 10^4$
1.60	3.20	3.60	80	1.70
2.40	3.20	3.60	80	1.68
3.20	3.20	3.60	80	1.76
4.00	3.20	3.60	80	1.78
4.80	3.20	3.60	80	1.74
3.20	1.60	3.60	80	0.92
3.20	3.20	3.60	80	1.76
3.20	4.80	3.60	80	2.64
3.20	6.40	3.60	80	3.47
3.20	8.00	3.60	80	4.39
3.20	3.20	2.16	80	1.32
3.20	3.20	3.60	80	1.76
3.20	3.20	5.76	80	2.32
3.20	3.20	8.64	80	3.03
3.20	3.20	10.80	80	3.35
3.20	3.20	3.60	90	3.12
3.20	3.20	3.60	80	1.76
3.20	3.20	3.60	70	1.31
3.20	3.20	3.60	60	1.09

The oxidation kinetics of methanol by BBI has the following salient features.

- The reactions have first order dependence as revealed by the constancy of k_1 values obtained from the integrated first order equation, linearity of the $\log(E_t - E)$ versus time plot and the invariance of k_1 on varying initial [BBI] (Table 1).
- The order of the reaction with respect to [substrate] is unity, k_1 is directly proportional to [Methanol] as evident from the constant values of k_2 . Plots of $\log k_1$ versus \log [substrate] are also linear with a slope of unity (Table 1).
- Added perchloric acid increases the rate of the reaction for eg, when $[\text{HClO}_4]$ increased from 2.16×10^{-2} to $10.80 \times 10^{-2} \text{ mol.dm}^{-3}$, k_1 increases from 1.32×10^{-4} to $3.35 \times 10^{-4} \text{ s}^{-1}$ under the conditions of $[\text{BBI}] = 3.20 \times 10^{-3} \text{ mol.dm}^{-3}$, $[\text{Methanol}] = 3.20 \times 10^{-2} \text{ mol.dm}^{-3}$, $[\text{mercuric acetate}] = 3.0 \times 10^{-2} \text{ mol.dm}^{-3}$ at 303 K in 80% aqueous acetic acid (v/v). A plot of $\log k_1$ versus $\log [\text{H}^+]$ is linear with a slope of 0.59 indicating a fractional order dependence on rate with respect to $[\text{H}^+]$. (Table 1)
- The rate of oxidation increases with decreasing dielectric constant of the medium (Table 1). A plot of $\log k_2$ versus $1/D$ is linear with a positive slope.
- Initial addition of one of the products viz. benzimidazole to the reaction mixture does not affect the rate.
- Polymerization is not observed when acrylonitrile is added to the reaction mixture.
- The oxidation of other aliphatic alcohols viz. ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol by BBI has been investigated under comparable conditions. All the other aliphatic primary alcohols exhibit similar kinetic trend. (Table-2).
- Activation parameters have been calculated for all aliphatic alcohols (Table 3) and the Exner plot is found to be linear with a correlation coefficient of 0.999. The value of isokinetic temperature () evaluated from Exner's plot is 139.52 K. The linearity of the Exner plot suggests that all the alcohols are oxidized by the same mechanism and the changes in rates are governed by changes in both the enthalpy and entropy of activation.

Table 2: Effect of alcohols

$[\text{BBI}] = 3.20 \times 10^{-3} \text{ mol.dm}^{-3}$; $[\text{Alcohol}] = 3.20 \times 10^{-2} \text{ mol.dm}^{-3}$
 $[\text{HClO}_4] = 3.60 \times 10^{-2} \text{ mol.dm}^{-3}$; Solvent = 80% CH_3COOH
 $[\text{Mercuric acetate}] = 3.0 \times 10^{-2} \text{ mol.dm}^{-3}$; Temperature = 303 K

Alcohols	Methanol	Ethanol	1-Propanol	1-Butanol	1-Pentanol	1-Hexanol	1-Heptanol
$k_{\text{obs}} \times 10^4 \text{ s}^{-1}$	1.76	2.81	3.59	4.38	5.18	6.01	7.33

Table 3: Activation parameters at 303K for the Oxidation of Aliphatic alcohols by BBI

$[\text{BBI}] = 3.20 \times 10^{-3} \text{ mol.dm}^{-3}$; $[\text{Alcohol}] = 3.20 \times 10^{-2} \text{ mol.dm}^{-3}$
 $[\text{HClO}_4] = 3.60 \times 10^{-2} \text{ mol.dm}^{-3}$; Solvent = 80% CH_3COOH
 $[\text{Mercuric acetate}] = 3.0 \times 10^{-2} \text{ mol.dm}^{-3}$; Temperature = 303 K

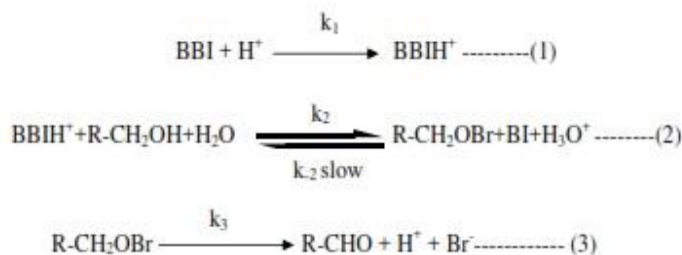
S.No	Activation parameters	Aliphatic Alcohols						
		Methanol	Ethanol	1-Propanol	1-Butanol	1-Pentanol	1-Hexanol	1-Heptanol
1	$E_a \text{ KJ mol}^{-1}$	31.96	32.73	30.02	31.04	29.72	29.02	29.10
2	$H^\ddagger \text{ KJ mol}^{-1}$	29.44	30.21	27.50	28.52	27.20	26.50	26.58
3	$G^\ddagger \text{ KJ mol}^{-1}$	96.00	94.86	94.20	93.69	93.28	92.93	92.53
4	$S^\ddagger \text{ KJ mol}^{-1}$	-219.66	-213.36	-220.15	-215.08	-218.09	-219.24	-217.66
5	$\ln A$	4.04	4.81	3.98	4.59	4.23	4.10	4.25

4. Mechanism and Rate Law

In acidified aqueous acetic acid solution of BBI, the possible oxidizing species reported were BBI itself, protonated oxidant BBIH^+ , HOBr and H_2OBr^+ . In the proposed mechanism, the involvement of BBI as such as the active oxidizing species will lead to the rate law which will not explain the dependence of rate of oxidation on H^+ ions. The retardation of reaction rate with the added benzimidazole rules out the possibility of HOBr and H_2OBr^+ as the active oxidizing species. Hence the most probable oxidizing species is the protonated oxidant, BBIH^+ which is revealed by H^+ ion dependence on the reaction rate. The protonation of N-halo compounds as a pre-equilibrium step has already been proposed in the oxidation of benzyl alcohols by CBT [29] and BBI [22], aliphatic primary alcohols by NCN [1], cyclanols by CBI [7] and BBI [26] and α -hydroxy acids by CBT [30]. The rate of the reaction increases with

decrease in dielectric constant of the medium and the plot of $\log k_2$ versus $1/D$ is linear with positive slope indicating ion-dipole [31] type of interaction in the rate determining step. The negligible ionic strength effect observed for the reaction indicates an interaction between an ion and a dipole in the rate determining step followed by the abstraction of a proton by water molecule [32&22] leading to the formation of alkyl hypobromite. The formation of hypobromite intermediate in the rate determining step has been documented in the oxidation of secondary alcohols by N-bromoacetamide [16] and benzyl alcohols by BBI [22]. Hypohalites are known to decompose to carbonyl products [33].

Therefore the following scheme has been proposed for the oxidation of aliphatic alcohol by BBI.



The rate law based on the above scheme is represented by the following equation

$$\frac{-d[\text{BBI}]}{dt} = \frac{k_{\text{obs}} [\text{Aliphatic alcohol}] [\text{BBI}][\text{H}^+]}{1+K[\text{H}^+]}$$

It was estimated from the Taft plot (Fig-1) that the ρ^* value of the reaction is -0.722 ($r=0.998$). The negative ρ^* value is indicative of the development of positive charge in the transition state. The magnitude of ρ^* value is not supporting a fully developed positive charge. It appears that the reaction is susceptible to both polar and steric factors. This again confirms the electron deficiency in the transition state of the reaction and supports the above mechanism.

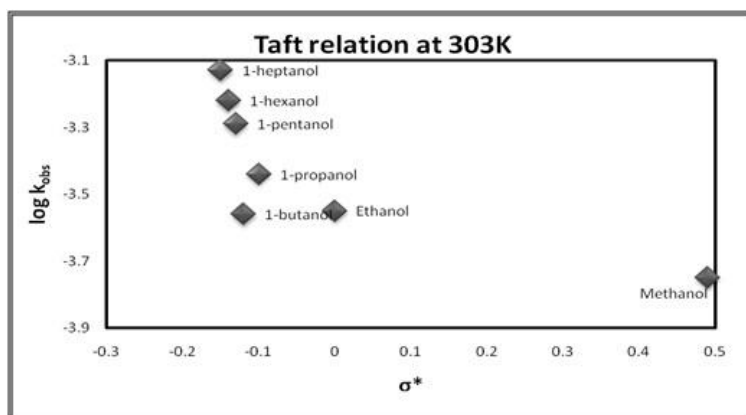


Figure 1

5. Conclusion

The kinetics of oxidation of aliphatic alcohols with 1-bromobenzimidazole (BBI) in aqueous acetic acid medium clearly shows that the order of the reaction with respect to [BBI] and [alcohol] are unity and order with respect to $[\text{H}^+]$ is fractional. The decrease in dielectric constant of the solvent medium increases the rate of reaction significantly. The rate of reaction increases with temperature and the various activation parameters have been evaluated. The mechanism proposed for oxidation kinetics is in accordance with the observed kinetic data.

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