



## Kinetic and mechanistic investigations on the oxidative reactions of aromatic aldehydes with 1-bromobenzimidazole in aqueous acetic acid medium

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### ABSTRACT

The oxidation kinetics of aromatic aldehydes by 1-bromobenzimidazole (BBI) has been studied in 80% (v/v) acetic acid – water mixture in presence of mercuric acetate. The reaction exhibits first order dependence each in [BBI], [Aldehyde] and  $[H^+]$  ions. Increase in acetic acid content of the solvent medium increases the rate of reaction. The rate of reaction is not influenced by the addition of electrolyte like sodium perchlorate. Thermodynamic parameters have been calculated. Electron donating groups increase the rate while electron-withdrawing groups decrease the rate while electron-withdrawing groups decrease the rate.  $(H_2OBr)^+$  has been postulated as the reactive oxidizing species. Suitable mechanism consistent with the observed kinetic data is proposed.

**Key words:** Kinetics, BBI, Oxidation, Aldehyde, Mechanism.

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### INTRODUCTION

Kinetics of oxidation of organic compounds by N-halo compounds have received considerable attention [1-9]. Oxidation of aromatic aldehydes by Trichloro isocyanuric acid(TCICA)[10], N-bromobenzamide(NBB)[11], N-bromosuccinimide(NBS)[12] and 1-chlorobenzimidazole(CBI)[13] have been studied. In the present investigation, the new N-halo oxidant, 1-bromobenzimidazole(BBI)[14] has been utilized in the oxidation kinetics of aromatic aldehydes in aqueous acetic acid medium.

### EXPERIMENTAL SECTION

1-Bromobenzimidazole (BBI) (Fig.1) was prepared and purified by literature method[14]. Acetic acid was purified by standard method and the fraction distilling at 118<sup>o</sup>C was collected. Benzaldehyde (B.D.H, AnalaR) was used after distillation (b.p 179-179.5<sup>o</sup>C). All other aromatic aldehydes were the purest samples available from Fluka and were used as such. Other chemicals were analytical grade samples from B.D.H and sodium perchlorate was from E.Merck.

#### Product Analysis

Product analysis shows the presence of benzoic acid, the major product which is confirmed by physical constant, TLC and by spectral analysis. The stoichiometry of the reaction was found to be 1:1.

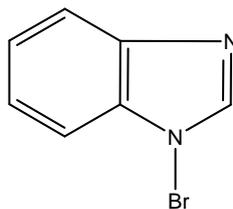


Fig.1. 1-bromobenzimidazole

### Kinetic Measurements

The pseudo-first order conditions were maintained by keeping a large excess (10 fold or more) of aldehyde over BBI. The reactions were followed potentiometrically upto 70% completion, by following the potentials of the reaction mixture containing varying concentrations of [BBI]/[BI] couple (BI=Benzenimidazole) at regular time intervals using a Platinum-Saturated Calomel Electrode assembly. The pseudo-first order rate constant,  $k_1$ , was computed from the linear ( $r > 0.98$ ) plots of  $\log(E_t - E_\infty)$  Vs time.

Where,  $E_t$ - potential at time  $t$   
 $E_\infty$ -potential at infinity

When the kinetic run was done by iodometry, the same result was obtained within  $\pm 2\%$ . Preliminary experiments showed that the rate of oxidation is not sensitive to ionic strength constant.

### RESULTS AND DISCUSSION

The oxidation of benzaldehyde 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. The function of added mercuric acetate is only to fix up  $\text{Br}^-$  formed in the course of reaction as  $\text{HgBr}_4^{2-}$ .

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

(i). The reactions have first order dependence as revealed by the constancy of the  $k_1$  values obtained from the integrated first order equation, linearity of the  $\log(E_t - E_\infty)$  Vs time plot and the invariance of  $k_1$  on varying initial [BBI].

(ii).The order in substrate is unity,  $k_1$  is directly proportional to [benzaldehyde] as evident from the constant values of  $k_2$  (Table 1). Plots of  $\log k_1$  Vs  $\log[\text{substrate}]$  are also linear with a slope of unity.

**Table 1 Effect of varying [Aldehyde]**

[Benzaldehyde] $\times 10^2$ (mol.dm <sup>-3</sup> )	$k_{\text{obs}} \times 10^4$ (s <sup>-1</sup> )	$k_2 \times 10^3$ (mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> )
3.0	8.14	27.13
2.5	6.65	26.60
2.0	5.42	27.10
1.5	3.97	26.50
1.0	2.71	27.10

(iii) Added perchloric acid increases the rate for eg, when  $[\text{HClO}_4]$  mol.dm<sup>-3</sup> increased from 0.1 to 0.5 mol.dm<sup>-3</sup>,  $k_1$  increases from  $1.63 \times 10^{-4}$  to  $8.14 \times 10^{-4}$  s<sup>-1</sup> under the conditions of [BBI]= $3.0 \times 10^{-3}$  mol.dm<sup>-3</sup>, [benzaldehyde]= $3.0 \times 10^{-2}$  mol.dm<sup>-3</sup>, [mercuric acetate]=0.05 mol.dm<sup>-3</sup> at 30°C in 80% aqueous acid(v/v). A plot of  $\log k_1$  vs  $\log [\text{H}^+]$  is linear with a slope of 0.96 indicating first order dependence on  $[\text{H}^+]$ . Further the plot of  $1/k_1$  Vs  $1/[\text{H}^+]$  is linear (zero intercept).

(iv).Initial addition of one of the products viz. benzimidazole to the reaction mixture affects the rate.

(v). Polymerization is not observed when acrylonitrile is added to the reaction mixture.

(vi).The oxidation of substituted benzaldehydes by BBI has been investigated under comparable conditions. All the substrates obey the same rate law as for the parent substrate. Electron donating groups increased the rate while electron withdrawing groups decreased the rate of oxidation (Table 2).

Table 2 Effect of substituents

[BBI] =  $3.0 \times 10^{-3}$  mol.dm<sup>-3</sup> [Aldehyde] =  $3.0 \times 10^{-2}$  mol.dm<sup>-3</sup>  
 [Mercuric acetate] = 0.05 mol.dm<sup>-3</sup> [HClO<sub>4</sub>] = 0.5 mol.dm<sup>-3</sup>  
 Solvent = 80% CH<sub>3</sub>COOH Temperature = 313 K

Substituents	k <sub>2</sub> x 10 <sup>3</sup> (lit. mol <sup>-1</sup> . s <sup>-1</sup> )
H	27.13
p-OCH <sub>3</sub>	88.40
p-CH <sub>3</sub>	76.30
m-OCH <sub>3</sub>	35.80
m-CH <sub>3</sub>	29.71
p-Cl	17.70
m-NO <sub>2</sub>	11.72
m-Br	10.82
p-NO <sub>2</sub>	8.72

The order of reactivity of different aldehydes with BBI is p-OCH<sub>3</sub> > p-CH<sub>3</sub> > m-OCH<sub>3</sub> > m-CH<sub>3</sub> > H > p-Cl > m-NO<sub>2</sub> > m-Br > p-NO<sub>2</sub>

(vii) Increase in temperature increases the rate of oxidation. Plots of log k<sub>2</sub> Vs 1/T are linear for all aldehydes. Activation parameters have been calculated for all the aromatic aldehydes (Table 3) and the Exner plot is found to be linear with a correlation coefficient of 0.9946. The linearity of Exner plot is suggestive of unified mechanism for the BBI oxidation of different aldehydes. From the slope of the Exner plot, the isokinetic temperature (β) calculated is 229.64 K. Since it is far away from the experimental range, the observed effect of substituent is real.

Table 3 Arrhenius parameters for the oxidation of Benzaldehyde by BBI

S.No	Thermodynamic functions	Substituents								
		H	p-OCH <sub>3</sub>	p-CH <sub>3</sub>	m-OCH <sub>3</sub>	m-CH <sub>3</sub>	p-Cl	m-NO <sub>2</sub>	m-Br	p-NO <sub>2</sub>
1	E <sub>a</sub> kJ mol <sup>-1</sup>	57.72	55.56	53.64	52.56	52.32	57.3	52.65	53.31	54.6
2	ΔH* kJ mol <sup>-1</sup>	55.13	52.96	51.04	49.96	49.72	54.7	50.05	52.71	52.96
3	ΔG* kJ mol <sup>-1</sup>	95.21	92.14	92.51	94.4	94.95	96.39	97.37	97.64	98.14
4	ΔS* Jk <sup>-1</sup> mol <sup>-1</sup>	-128.07	-125.19	-132.52	-142.01	-144.53	-133.22	-151.21	-143.54	-144.35
5	ln A	2.12	2.16	2.05	1.89	1.85	2.04	1.72	1.87	1.85

Hence any mechanism proposed for the oxidation of aromatic aldehydes by BBI should be capable of explaining the above observations. Further the oxidizing species has to be identified before any mechanistic investigation could be advanced.

#### Mechanism and Rate Law:

In acidified aqueous acetic acid solution of BBI, the possible oxidizing species are BBI itself or its protonated form, HOBr, H<sub>2</sub>O<sup>+</sup>Br and Br<sub>2</sub>.

The strict first order dependence of reaction rate on BBI rules out the possibility of molecular bromine as the oxidizing species.

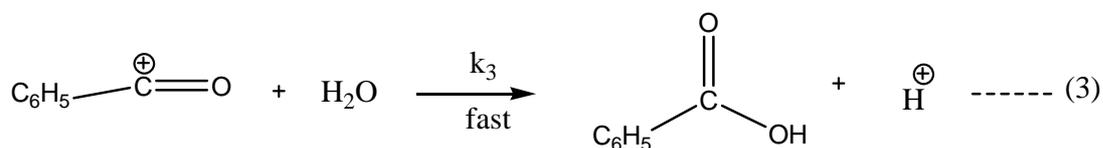
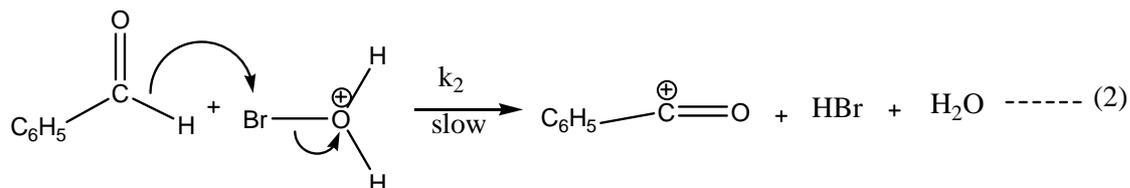
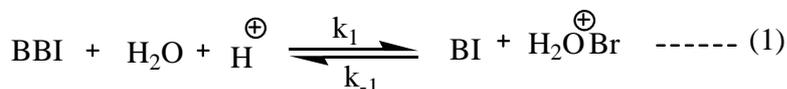
In the proposed mechanism, the involvement of BBI as such or HOBr as the active oxidizing species will lead to the rate law which will not explain the dependence of rate of oxidation on H<sup>+</sup> ions.

If BBIH<sup>+</sup> is the active oxidant, the reaction must show hydrogen ion dependence for the rate, which is true in this case. But the retardation of rate of oxidation with added benzimidazole indicates that the pre-equilibrium step involves a process in which benzimidazole is one of the products. Equation 1 explains the first order dependence of rate on [H<sup>+</sup>] suggesting H<sub>2</sub>O<sup>+</sup>Br as the oxidizing species obtained by the hydrolysis of BBI in equilibrium thus eliminating the possibility of BBIH<sup>+</sup> being an oxidizing species.

A plot of log k<sub>1</sub> against the inverse of dielectric constants of acetic acid-water mixture is linear (r = 0.9973) with a positive slope. This according to Amis[15], indicating a positive ion-dipole reaction. This is in accord with the suggestion that H<sub>2</sub>O<sup>+</sup>Br is the most probable oxidizing species.

The rate determining step (Equation 2) involving a reaction between an ion and a dipole  $\text{H}_2\text{O}^+\text{Br}$  accounts for the negligible electrolyte effect observed for the reaction, with a transfer of hydride ion from aldehyde molecule to the positive oxidizing species.

The following scheme has been proposed for oxidation of aldehydes by BBI.



$$\text{Rate} = \frac{-d[\text{BBI}]}{dt} = k_2 [\text{Aldehyde}] [\text{H}_2\text{O}^+\text{Br}] \quad \text{----- (4)}$$

From equation (1)

$$k_1 [\text{BBI}] [\text{H}_2\text{O}] [\text{H}^+] = k_{-1} [\text{BI}] [\text{H}_2\text{O}^+\text{Br}]$$

$$\text{or } [\text{H}_2\text{O}^+\text{Br}] = \frac{k_1 [\text{BBI}] [\text{H}_2\text{O}] [\text{H}^+]}{k_{-1} [\text{BI}]}$$

$$[\text{H}_2\text{O}^+\text{Br}] = \frac{K_a [\text{BBI}] [\text{H}_2\text{O}] [\text{H}^+]}{[\text{BI}]} \quad \text{----- (5)}$$

where  $K_a = k_1/k_{-1}$

substituting the value of  $[\text{H}_2\text{O}^+\text{Br}]$  from eq (5) in eq (4), we get

$$\text{Rate} = \frac{k_2 K_a [\text{BBI}] [\text{Aldehyde}] [\text{H}_2\text{O}] [\text{H}^+]}{[\text{BI}]} \quad \text{----- (6)}$$

Under higher concentration of  $\text{HClO}_4$  (0.5M),  $[\text{H}_2\text{O}]$  is negligible in eq. (6)

$$\therefore \text{Rate} = k_{\text{obs}} [\text{BBI}] [\text{Aldehyde}] [\text{H}^+] \quad \text{----- (7)}$$

$$\text{Where } k_{\text{obs}} = \frac{k_2 K_a}{[\text{BI}]}$$

The above mechanism is supported by the observed negative entropy of activation also.

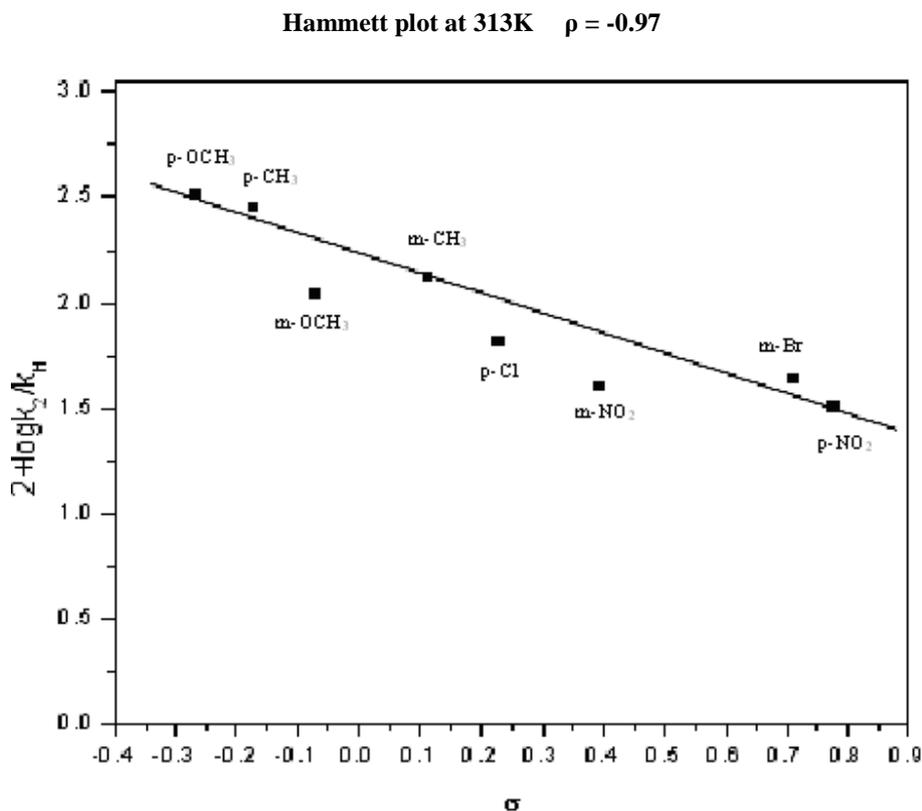


Fig.2 A plot of  $\log(k_2/k_H)$  Vs  $\sigma$

It was estimated from the Hammett plot (Fig.2) that the  $\rho$  value of the reaction is  $-0.97$  ( $r=0.9957$ ). The negative  $\rho$  value indicates that the reaction is favored by the formation of carbocation in the slow step, which is obtained by the hydride transfer[11] from the aldehyde to  $H_2O^+Br$ . Such a scheme demands that the electron withdrawing groups such as p-NO<sub>2</sub> should retard the rate while the electron donating groups such as p-OCH<sub>3</sub> should have an accelerating influence on the rate, which is true in our present investigation landing sufficient support for the suggested mechanism.

### CONCLUSION

The kinetic studies clearly demonstrate that oxidation of aromatic aldehydes by BBI involves the formation of carbocation in the slow step by the hydride transfer leading to products. High dielectric constant of the medium facilitates the reaction. First order each in oxidant, substrate and perchloric acid is supported by the derived rate law.

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