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Kinetics and mechanism of oxidation of aliphatic and aromatic alcohols by *in situ* generated bromine in reaction between oxone and bromide ion

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Oxidation of aliphatic and aromatic alcohols by oxone catalyzed by bromide ions has been studied in acidic medium, to avoid formation of alkoxide. Since no prior protonation equilibrium is involved, the rate of the reaction is independent of *p*H. The reaction is initiated by the oxidation of bromide to bromine, which abstracts a hydride ion from the alcohol in a rate determining step to form $R_1R_2COH^+$ cation. This cation loses a proton to give the corresponding carbonyl compound in a fast step. A mechanism for the bromide ion mediated oxidation is proposed and the rate law is derived based on the mechanism. Effect of relative permittivity, ionic strength and temperature is also studied; these effects also support the proposed mechanism.

Keywords: Kinetics, Reaction mechanism, Oxidation, Oxone, Bromide ion, Alcohols, Aliphatic alcohols, Aromatic alcohols

Oxidation of alcohols by liquid bromine is a well-known process in both industry as well as in research[1,2]. Although bromine is used for oxidation of alcohols due to its ready availability, other protocols using bromine species are being developed to avoid its direct use[2-4]. The alternatives for aqueous bromine is necessary as bromine is hazardous and sometimes side products like bromo-substituted compounds are obtained. The reagents that can replace aqueous bromine are generally a combination of an oxidant in presence of bromide[2, 5] or salts of bromine like quarternary ammonium tribromide[6-8]. Such types of alternatives are also environmentally green protocols for conventional metal ion catalyzed reactions[2].

The mechanistic aspects of oxidations by bromine is also complicated by the presence of various bromine species generated in solution[2,9]. Depending upon the *p*H of the solution, bromine will be in equilibrium with other species like HOBr and Br_3^- which may change the course of the reaction and the products formed. In our earlier study, we have noticed that the mixture of oxone and bromide in acidic solution leads to the formation of bromine which has been studied by examining the UV-vis spectrum of the reaction mixture. The absorption maximum obtained at 394 nm indicated the formation of bromine in the reaction mixture[10]. The other possible species, Br_3^-, was absent as the solution did not contain enough bromide ions for its formation. Therefore, we thought it would be worthwhile to study the mechanistic aspects of oxidation by such an *in situ* generated bromine species

Experimental

All solutions were prepared in doubly distilled water. The solutions of aliphatic alcohols (methanol, ethanol, propane-2-ol, butane-2-ol) (Highmedia) were prepared by dissolving in water, while the solutions of aromatic alcohols (benzyl alcohol, 4-methylbenzyl alcohol and 2-nitrobenzyl alcohol) (SD Fine) were prepared in 50% acetic acid (SD Fine). The solution of oxone (Spectrochem) was prepared by dissolving in water. The solution of sodium thiosulphate was freshly prepared every day and standardized against standard KIO_3 solution iodometrically. The solution of oxone was standardized by titrating known volume of oxone with standard sodium thiosulphate (SD Fine) solution iodometrically. The solution of catalyst KBr (Thomas Baker) was prepared by dissolving it in water. Standard H_2SO_4 (SD Fine) solutions of 2 *M* and 1 *M* were also prepared.

The reactions of oxone with aliphatic alcohols were carried out in aqueous solutions and with aromatic alcohols in 50% acetic acid solutions, under pseudo-first order conditions at a constant temperature of 24.5±0.6 °C. The reaction was initiated by mixing the previously thermostated solutions of alcohols and oxone, which also contained the required amount of catalyst KBr and H_2SO_4. The reaction was followed by determining the concentration of unreacted (remaining) oxone iodometrically. The rate constants were reproducible within ±0.6 %

The stoichiometry for all alcohols were determined by analyzing the reaction mixtures containing alcohol (6×10^{-3} mol dm^{-3}), (KBr) bromide (5.0×10^{-3} mol dm^{-3}), sulphuric acid (0.03 mol dm^{-3}) and excess of oxone

(0.02 mol dm^{-3}), kept in a thermostat at the required temperature for one day. The concentration of unreacted oxone was determined after 24 h iodometrically. The stoichiometry was found to be one mole of oxone per mole of each alcohol. Further, the reaction mixtures (concentration of each reactant being twenty times that under kinetic conditions) were allowed to stand for 24 h and then distilled. The distillate was collected in a closed container and test for aldehydes and ketones. The distillate was treated with 2,4-DNP solution in 4 *N* H_2SO_4 when a yellow DNP derivative of the product was precipitated. It was filtered off, washed thoroughly, recrystalized and dried. The melting points of the derivatives were determined and compared with the reported values. The melting points of the 2,4-DNP derivatives of the products obtained agreed well with the literature values (Supplementary data, Table S1), confirming the formation of aldehydes and ketones as the oxidation products in the case of all the alcohols studied. Therefore, the stoichiometry of the reaction can be written as in Eq. (1).

$$R_1R_2CHOH + HSO_5^- \xrightarrow{Br^-} R_1R_2CO + 2H^+ + SO_4^- \quad \ldots(1)$$

Results and discussion

The reactions in the case of aliphatic alcohols were studied in water while that of aromatic alcohols were studied in 50 % *v/v* acetic acid solutions. Therefore, the concentrations of reactants, sulphuric acid and catalyst bromide were different. The effect of concentration of [alcohol] was studied by varying its concentration between 0.1 mol dm^{-3} and 1.0 mol dm^{-3} for aliphatic alcohols and between 0.01 mol dm^{-3} and 0.1 mol dm^{-3} for aromatic alcohols, keeping all other concentrations constant. The pseudo-first order rate constants, k_{obs}, increased (Tables 1 and 2) with increase in concentration of alcohol for both aliphatic and aromatic alcohols. The plots of k_{obs} against [alcohol] were found to be linear without any intercept for aliphatic as well as aromatic alcohols, indicating first order dependence of the reaction on the substrate concentration. Similarly, the effect of concentration of [oxone] was studied by varying its concentration from 2.0×10^{-3} mol dm^{-3} to 2.0×10^{-2} mol dm^{-3} for aliphatic alcohols and from 2.0×10^{-4} mol dm^{-3} to 2.0×10^{-3} mol dm^{-3} for aromatic alcohols, keeping all other concentrations constant. The pseudo-first order rate constants, k_{obs}, remained constant (Tables 1 and 2) as the concentration of oxidant for both aliphatic and aromatic alcohols is varied. The pseudo-first order plots of log[oxone] against time were also found to be

Table 1 – Effect of oxone, alcohols and KBr concentrations on k_{obs} values for oxidation aliphatic alcohols by oxone catalyzed by bromide at 25 °C. {[H_2SO_4] = 0.1 mol dm^{-1}; I = 0.2 mol dm^{-3}}

[Alcohol] (mol dm^{-3})	10^2[Oxone] (mol dm^{-3})	10^2[KBr] (mol dm^{-3})	10^4 k_{obs} (s^{-1})			
			Methanol	Ethanol	Propan-2-ol	Butan-2-ol
0.1	1.0	1.0	0.23	0.52	0.25	5.20
0.2	1.0	1.0	0.51	0.94	0.55	9.40
0.4	1.0	1.0	1.19	1.68	1.06	16.8
0.6	1.0	1.0	1.63	2.52	1.54	25.2
0.8	1.0	1.0	1.98	3.29	1.96	32.9
1.0	1.0	1.0	2.50	3.99	2.43	39.9
0.4	0.2	1.0	1.23	1.68	1.00	16.9
0.4	0.4	1.0	1.18	1.69	1.09	16.8
0.4	0.6	1.0	1.19	1.68	1.06	16.8
0.4	0.8	1.0	1.20	1.70	1.08	17.0
0.4	1.0	1.0	1.21	1.66	1.06	17.1
0.4	1.0	0.1	0.19	0.19	0.09	0.70
0.4	1.0	0.3	0.34	0.42	0.33	3.20
0.4	1.0	0.5	0.46	0.73	0.62	6.20
0.4	1.0	0.8	0.81	1.15	0.86	9.30
0.4	1.0	1.0	1.19	1.66	1.06	17.1
0.4	1.0	2.0	1.98	3.18	2.36	28.8
0.4	1.0	3.0	2.99	4.49	3.56	36.6
0.4	1.0	4.0	4.10	6.28	4.87	51.6
0.4	1.0	5.0	4.89	8.15	5.87	68.9

Table 2 – Effect of oxone, alcohols and KBr concentration on the k_{obs} values for oxidation aromatic alcohols by oxone catalyzed by bromide in 50% *v/v* acetic acid at 25 °C. {$[H_2SO_4]$ = 0.01 mol dm^{-1}}

10[Alcohol] (mol dm^{-3})	10^2[Oxone] (mol dm^{-3})	10^3[KBr] (mol dm^{-3})	10^4 k_{obs} (s^{-1})		
			Benzyl alcohol	4-Methylbenzyl alcohol	2-Nitrobenzyl acohol
0.1	0.2	1.0	1.80	0.91	0.49
0.2	0.2	1.0	4.45	2.10	1.11
0.4	0.2	1.0	8.72	4.70	1.97
0.6	0.2	1.0	12.5	7.20	3.14
0.8	0.2	1.0	17.0	9.80	4.19
1.0	0.2	1.0	23.0	12.3	4.72
0.2	0.2	1.0	4.46	2.09	1.10
0.2	0.4	1.0	4.45	2.10	1.11
0.2	0.6	1.0	4.44	2.12	1.11
0.2	0.8	1.0	4.45	2.10	1.12
0.2	1.0	1.0	4.46	2.10	1.11
0.2	2.0	0.1	4.45	2.15	1.11
0.2	1.0	0.4	1.23	0.88	0.32
0.2	1.0	0.6	1.99	1.03	0.56
0.2	1.0	0.8	2.99	1.30	0.73
0.2	1.0	1.0	4.45	2.10	1.12
0.2	1.0	1.5	6.06	2.61	1.55
0.2	1.0	2.0	8.25	3.56	1.99
0.2	1.0	2.5	9.86	4.29	2.46
0.2	1.0	3.0	12.2	5.48	3.01
0.2	1.0	3.5	14.9	6.48	3.68
0.2	1.0	4.0	16.8	7.33	4.22

linear for aliphatic as well as aromatic alcohols, indicating first order dependence of the reaction on the oxidant concentration. The concentration of catalyst, KBr, was varied between 1.0×10^{-3} mol dm^{-3} and 5.0×10^{-2} mol dm^{-3} for aliphatic alcohols, and between 4.0×10^{-4} mol dm^{-3} and 4.0×10^{-3} mol dm^{-3} for aromatic alcohols, keeping all other concentrations constant. The pseudo-first-order rate constants, k_{obs}, increased (Tables 1 and 2) with increase in concentration of catalyst for both aliphatic and aromatic alcohols. The plots of k_{obs} against [KBr] were also found to be linear without any intercept for aliphatic(Fig. 1) as well as aromatic alcohols (Fig. 2) without any intercept, indicating that uncatalyzed reaction did not occur to any considerable extent under the reaction conditions and also first order dependence of the reaction on the catalyst concentration. The hydrogen ion concentration was studied from 0.04–0.4 mol dm^{-3} for alipahatic alcohols at an ionic strength of 0.5 mol dm^{-3} and from 0.005–0.05.0 mol dm^{-3} for aromatic alcohols at an ionic strength of 0.02 mol dm^{-3}. There was no change in the values of k_{obs} as the hydrogen ion concentration increased for both the alcohols, indicating that the reaction is independent of hydrogen ion concentration. The effects of ionic strength and dielectric constant were studied by varying the concentration of KNO_3 and acetic

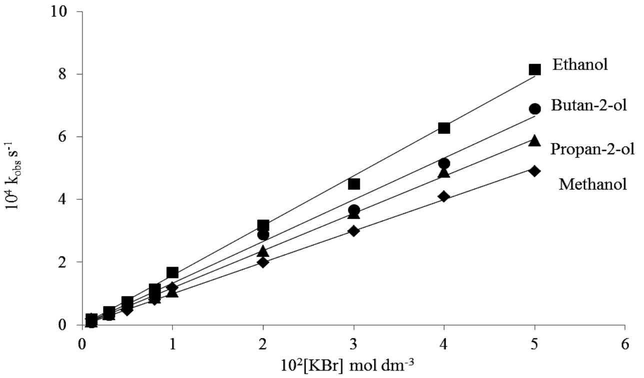


Fig. 1 – Plot of k_{obs} against [KBr] for oxidation of aliphatic alcohols by oxone catalyzed by bromide at 25 °C.

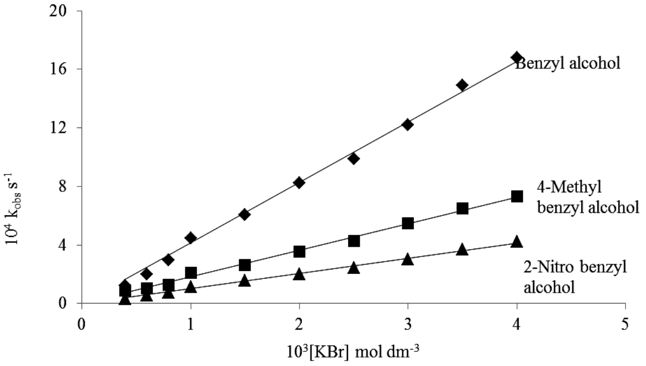


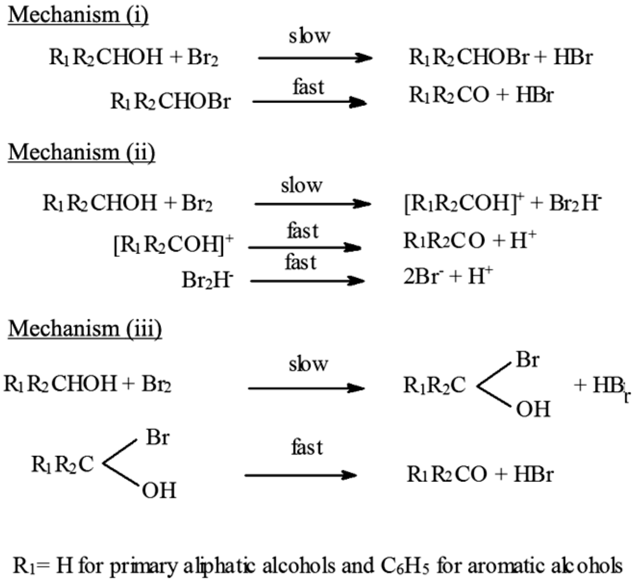
Fig. 2 – Plots of k_{obs} against [KBr] for oxidation of aromatic alcohols by oxone catalyzed by bromide in 50% *v/v* acetic acid at 25 °C.

acid respectively. The increase in ionic strength from 0.1–0.6 mol $dm^{-3}$for alipahatic alcohols and (1.0–8.0)×10^{-2} mol dm^{-3} for aromatic alcohols increased the k_{obs} values slightly.

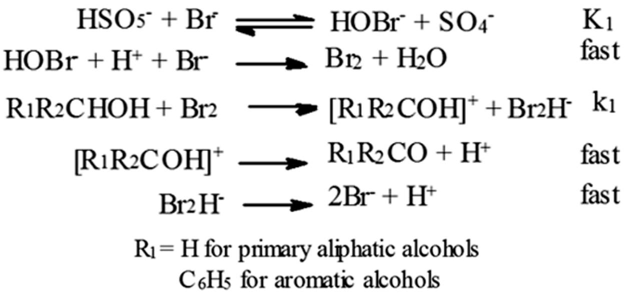
The variation of dielectric constant on the rate of the reaction was studied with acetic acid. For aliphatic alcohols, the acetic acid was varied from 0–50%, while for aromatic alcohols it was varied from 50–90%. The values of k_{obs} of both the alcohols decreased as the % acetic acid increased. The plot of log k_{obs} against $(1/D)$, where D is the dielectric constant of the medium, was linear with negative slope. The activation parameters for the reactions were determined by studying the reaction at five different temperatures. The activation energy and activation enthalpy were calculated from the plots of log k_{obs} and log (k_{obs}/T) against $(1/T)$ plots. The values of activation parameters for aliphatic alcohols and for aromatic alcohols are given in Table S2 (Supplementary data).

The structure of the oxidant, oxone or peroxomonosulphuric acid, contains a sulphur atom surrounded tetrahedrally by perhydroxyl and hydroxyl groups[10]. The proton of the hydroxyl group is equivalent to that of sulphuric acid proton and is highly ionized, while that of the perhydroxyl group is weakly ionized. The pK value of the perhydroxyl proton is reported to be 9.4, indicating that in strongly acidic pH the peroxymonosulphate exists mainly in the form of HSO_5^- ion. Since, the pH of the present study is > 1.3 for aliphatic alcohols and > 2.3 for aromatic alcohols, the oxidant is in the form of peroxomonosulphate anion, HSO_5^-. In our earlier study, it has been reported and spectrophotometrically indicated that only bromine is generated by the slow oxidation of bromide ion in acidic medium[10]. None of the alcohols used in the present study are known for their equilibrium with hydrogen ion in aqueous medium. The kinetic results obtained also support the observations that the reaction is independent of hydrogen ion concentration, indicating that no prior protonation equilibrium are involved in the reaction. Therefore, the reaction initiates by the rate determining generation of bromine.

Oxidation of alcohols by bromine, either generated *in situ* or used directly, has been studied extensively[11-15]. The major products of oxidation of alcohols reported by using direct or *in situ* generated bromine is the corresponding aldehydes for primary and ketones for the secondary alcohols. The diols also give the corresponding aldehydes[13]. The main feature of these oxidations is that the rate of reaction is independent of pH from 1 to 4 and increases above pH 6 due to the formation of alkoxide ion. The absence of primary kinetic isotope effect indicates the cleavage of O-H bond rather than the α-C-H bond[13]. In the present study as the pH for both aliphatic and aromatic alcohols (acetic acid medium) is < 4, formation of alkoxide ion is not considered and the oxidant, oxone, exists in the HSO_5^- form. As evidenced by the spectrophotometric examination of mixture of KBr and oxone in aqueous sulphuric acid solution, only bromine is generated[10]. Therefore, the mechanism of the oxidation of alcohols by oxone in the presence of bromide ion as a catalyst involves rate determining initiation of the reaction between oxidant and catalyst generating bromine without formation of other bromine species[10] like HOBr and Br_3^-. The bromine generated thus oxidizes the substrate alcohol in the next step. Various mechanisms have been considered and examined kinetically for different experimental conditions. The basic three mechanisms[15] are: (i) rate determining formation of hypobromite ester, (ii) transfer of hydride ion from carbon to bromine, and, (iii) replacement of hydrogen by bromine. All the three mechanisms are kinetically indistinguishable but Mechanism (i) is different from the other two. In mechanisms (ii) and (iii), the carbon-hydrogen bond is ruptured in the slow step while in (i), it is ruptured in the subsequent step. On the basis of large primary kinetic isotope effect for oxidation of ethanol it has been proposed that carbon-hydrogen bond is broken in the rate determining step of the reaction[15]. Since, mechanism (i) involves such carbon-hydrogen bond breaking after the slow step, it was ruled out as the probable mechanism for the oxidation of ethanol by bromine. In mechanism (iii), the transition state involves the exchange of hydrogen by bromine occurring in a second order reaction. Therefore, mechanism (ii) seems to the most probable, which explains the primary kinetic isotope effect suggesting the transfer of hydride ion from carbon to bromine in the rate determining step.



Therefore, considering mechanism (ii) as the probable path of oxidation of alcohols by bromine generated *in situ* in the present study, the general mechanism can be written as in Scheme 1.



Scheme 1

The corresponding rate laws are given in Eqs (2)-(4).

$$\text{Rate} = k_1[\mathrm{R_1R_2CHOH}][\mathrm{Br_2}] \qquad \ldots(2)$$

$$= k_1K_1[\mathrm{R_1R_2CHOH}][\mathrm{HSO_5^-}][\mathrm{Br^-}] \qquad \ldots(3)$$

$$K_{\mathrm{obs}} = \text{rate}/[\mathrm{HSO_5^-}] = k_1K_1[\mathrm{R_1R_2CHOH}][\mathrm{Br^-}] \qquad \ldots(4)$$

The rate law (4) indicates that k_{obs} values vary linearly with [alcohol] and [$\mathrm{Br^-}$] and are independent of both [oxone] and [$\mathrm{H_2SO_4}$]. The plots of k_{obs} against [alcohol] and [$\mathrm{Br^-}$] for all the alcohols were found to linear, thus justifying the rate law(4).

The reaction, as shown in Scheme 1, is initiated by the oxidation of bromide to bromine which abstracts a hydride ion from the alcohol in a rate determining step to form $\mathrm{R_1R_2COH^+}$ cation. This cation loses a proton to give the corresponding carbonyl compound in a fast step. Since in the present reaction, rate determining step involves a neutral $\mathrm{Br_2}$, the rate constant is expected to be unaffected by change in ionic strength. However, a moderate increase in the k_{obs} values as the ionic strength increases indicates the reaction between two negative ions in a prior equilibrium. The rate of the reaction decreases with decrease in relative permittivity of the reaction mixture and the plot of k_{obs} against ($1/D$) was linear with a negative slope. The transition state formed between $\mathrm{Br_2}$ and alcohol is more polar and decomposes into ionic species. The activation entropy was negative for all the alcohols .The polar nature of the transition state leads to immobilization of solvent molecules around the charged ends, which results in the loss of entropy as noticed in the present study.

Supplementary data

Supplementary data associated with this article, i.e., Table S1 and S2, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(02)182-186_SupplData.pdf.

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