Kinetics and mechanism of oxidation of substituted ethanols by bromamine-T in acid medium

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The kinetics of oxidation of seven primary alcohols, \( RCH_2CH_2OH \) (where \( R = -H, -OC_2H_5, -OCH_3, -NH_2, -Cl, -Br \) and \( -NO_2 \)) by bromamine-T in the presence of HCl has been studied at 45°. The rates show first order dependence on [BAT] and fractional order each on [alcohol], [H\(^+\)] and [Cl\(^-\)]. Variations of ionic strength and dielectric constant of the medium and addition of reaction product (toluene sulphonamide) have no effect on the rate. Formation constants and decomposition constants of alcohol-BAT complexes have been determined. The rates do not correlate satisfactorily with Taft substituent constants.

We report herein, the hitherto unreported results on the kinetics of oxidation of unsubstituted and substituted ethanols, namely, 2-ethoxy, 2-methoxy, 2-amino, 2-chloro, 2-bromo and 2-nitro-ethanols by bromamine-T (BAT) in the presence of HCl at 45°.

Materials and Methods

The purity of BAT prepared in the laboratory was checked iodometrically and through its mass, UV, IR and \(^1\)H and \(^13\)C NMR data. An aqueous solution of BAT was prepared, standardised by the iodometric method and preserved in brown bottles. Alcohols (AR) were distilled before use. All other reagents were of AR grade. Triply distilled water was used for preparing aqueous solutions. Ionic strength was kept constant at 1.0 mol dm\(^{-3}\) by adding a concentrated solution of NaClO\(_4\). Heavy water (D\(_2\)O, 99.2%) was supplied by the Bhabha Atomic Research Centre, Trombay.

Regression analysis of experimental data was carried out on a TDC-316 (16 bits) computer supplied by Trombay Electronics and EC-72 statistical calculator.

Kinetic measurements

Solutions containing appropriate amounts of alcohol, HCl and water (to keep the total volume constant for all runs) were thermostatted at 45°. To this was added a measured amount of BAT solution, also thermostatted at the same temperature. The progress of the reaction was monitored by withdrawing aliquots from the reaction mixtures at regular time intervals and estimating the unreacted BAT by iodometric method. The course of the reaction was studied up to two half-lives. The pseudo-first order rate constants, \( k' \), calculated were reproducible within ±3%.

Stoichiometric runs carried out after the completion of the reaction (24 hr) revealed that 1 mole of BAT consumed 1 mole of ethanol in accordance with Eq. (1):

\[
\text{TsNBrNa} + RCH_2CH_2OH + TsNH_2 + RCH_2CHO + Na^+ + Br^- ...
\]

We report the hitherto unreported results on the kinetics of oxidation of unsubstituted and substituted ethanols, namely, 2-ethoxy, 2-methoxy, 2-amino, 2-chloro, 2-bromo and 2-nitro-ethanols by bromamine-T (BAT) in the presence of HCl at 45°.

The products of oxidation were identified under experimental conditions ([alcohol] >> [BAT]). The reaction product, p-toluene sulphonamide (TsNH\(_2\)), was detected by paper chromatography. The corresponding aldehydes were quantitatively estimated through their 2,4-dinitrophenylhydrazone derivatives (DNP).

Results and Discussion

At fixed [HCl] and [alcohol] and [substrate] in excess, plots of log [BAT] versus time are linear \((r > 0.9904)\) indicating a first order dependence in [BAT]. Values of pseudo-first order constants \((k')\) are constant for varying [BAT]. The rate increases with [alcohol] and plots of log \( k' \) versus log [alcohol] are linear \((r > 0.9974; s < 0.02)\) with fractional slopes (0.4-0.7).

The rate increases with increase in [HCl] and the plots of log \( k' \) versus log [HCl] are linear \((r > 0.9978; s < 0.01)\) with fractional slopes (0.4-0.5). At fixed [Cl\(^-\)] = 0.6 mol dm\(^{-3}\), maintained by adding NaCl, the rate increases with increase in [H\(^+\)] which was varied by adding HCl and the plot of log \( k' \) versus log [H\(^+\)] is linear \((r > 0.9948; s < 0.02)\) with fractional slopes (0.2-0.3). At fixed [H\(^+\)] = 0.1 mol dm\(^{-3}\), the
rate increases by the addition of NaCl and a plot of log $k'$ versus log [Cl$^-$] is linear ($r > 0.9952; s = 0.02$) with a slope $\sim 0.2$.

Addition of [Br$^-$] ion in the form of NaBr (0.0005-0.0020 mol dm$^{-3}$) has negligible effect on the rate. Also, NaClO$_4$ (0.2-1.0 mol dm$^{-3}$) or addition of the reaction product toluene-sulphonamide (0.0005-0.0020 mol dm$^{-3}$) has no influence on the rate. Variation of dielectric constant of medium (D) by adding different proportions (0-30% v/v) of methanol to the reaction mixture has negligible effect on the rate. Blank experiments showed that oxidation of methanol under these conditions is negligible.

Studies relating to kinetic isotope effects show that, while $k_0^*$ values are $5.56 \times 10^{-4}$ S$^{-1}$ and $4.49 \times 10^{-4}$ S$^{-1}$ respectively for ethanol and 2-bromoethanol, corresponding $k_{D,0}^*$ values are $5.72 \times 10^{-4}$ S$^{-1}$ and $4.64 \times 10^{-4}$ S$^{-1}$. The solvent isotope effect $k_{H,O}/k_{D,0} = 0.97$.

The reaction was studied at different temperatures (308-323K) and from the linear Arrhenius plots ($r > 0.9978$), values of activation parameters for the overall reaction have been computed and are given in Table 1.

Addition of reaction mixture to aqueous acrylamide solutions fails to initiate polymerization, ruling out the possibility of involvement of free radicals.

The possible oxidizing species in acidified BAT solutions are acid monobromamine T (TsNHBr), dibromamine T (TsNBr$_2$) and HOBr. If TsNBr$_2$ were to be the reactive species, a second order dependence of rate on [BAT] should be observed which is not so. Also, if HOBr is the active oxidant species, a first order retardation of rate by added $p$-toluenesulphonamide is expected. However, no such effect was noticed. Hardy and Johnston$^1$ made detailed calculations on the concentration dependence of conjugate acid, HOBr and BrO$^-$, on pH in aqueous BAB solutions (6 $\times$ 10$^{-3}$ mol dm$^{-3}$) in the pH range of 7-13. It was shown that [TsNHBr] was high at pH 7 and was of the order of $4.1 \times 10^{-5}$ mol dm$^{-3}$, while [HOBr] $\approx 6.0 \times 10^{-6}$ mol dm$^{-3}$ and [BrO$^-$] $\approx 10^{-7}$ mol dm$^{-3}$. Assuming that BAT is similar to the benzene analogue, it is likely that TsNHBr is the oxidizing species in acid medium, and its concentration is expected to increase with the decrease in pH. In view of these facts, proton catalysis of the oxidation of alcohols by BAT at constant [Cl$^-$] in the present studies can be explained by Scheme 1:

\[
\text{TsNHBr} + H^+ + S \rightarrow X
\]

\[
X + \text{products} \rightarrow \text{products}
\]

\[
\text{Scheme 1}
\]

From Scheme 1, if [BAT]$_t$ represents the total [BAT], then [BAT]$_t$ = [TsNHBr] + [X], from which rate law (2) can be derived:

\[
\frac{-d[\text{BAT}]}{dt} = \frac{k_2 K_{1}[\text{BAT}]_t [H^+] [S]}{1 + K_{1}[H^+] [S]}
\]

\[
\ldots (2)
\]

Rate law (2) is in agreement with the fractional orders noted with respect to [H$^+$] and [alcohol]$_t$, and the first order dependence of rate on [BAT]$_t$.

Since Rate $= k' [\text{BAT}]$, Eq. (2) can be transformed into Eqs. (3) and (4):

\[
k' = \frac{k_2 K_{1}[H^+] [S]}{1 + K_{1}[H^+] [S]}
\]

\[
\ldots (3)
\]

\[
\frac{1}{k'} = \frac{1}{k_2 K_{1}[H^+] [S] + k_2}
\]

\[
\ldots (4)
\]

From the slope and intercept of the double reciprocal plot, $1/k'$ versus $1/[H^+](r > 0.9882)$, values of

<table>
<thead>
<tr>
<th>RCH$_2$CH$_2$OH</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^*$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^*$ (JK$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta G^*$ (kJ mol$^{-1}$)</th>
<th>$\log A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>71.0</td>
<td>68.4 $\pm$ 0.0</td>
<td>$-93.3 \pm 0.1$</td>
<td>97.8 $\pm$ 0.2</td>
<td>9.5</td>
</tr>
<tr>
<td>O$_2$H$_3$</td>
<td>82.9</td>
<td>80.3 $\pm$ 0.0</td>
<td>$-62.0 \pm 0.1$</td>
<td>99.3 $\pm$ 0.1</td>
<td>11.2</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>83.7</td>
<td>81.1 $\pm$ 0.0</td>
<td>$-60.2 \pm 0.1$</td>
<td>100.1 $\pm$ 0.1</td>
<td>11.0</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>99.3</td>
<td>96.6 $\pm$ 0.0</td>
<td>$-27.8 \pm 0.2$</td>
<td>105.4 $\pm$ 0.1</td>
<td>13.1</td>
</tr>
<tr>
<td>Cl</td>
<td>88.8</td>
<td>86.2 $\pm$ 0.0</td>
<td>$-53.3 \pm 0.1$</td>
<td>103.0 $\pm$ 0.1</td>
<td>11.7</td>
</tr>
<tr>
<td>Br</td>
<td>76.4</td>
<td>73.7 $\pm$ 0.0</td>
<td>$-78.6 \pm 0.1$</td>
<td>98.5 $\pm$ 0.1</td>
<td>10.0</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>48.1</td>
<td>45.5 $\pm$ 0.0</td>
<td>$-157.6 \pm 0.1$</td>
<td>95.2 $\pm$ 0.3</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Table 1—Thermodynamic parameters for the oxidation of alcohols by BAT in presence of HCl calculated from plots of log $k'$ versus $1/T$.

$[\text{BAT}]_t = 9.0 \times 10^{-4}$ mol dm$^{-3}$; $[\text{RCH$_2$CH$_2$OH}]_t = 0.1$ mol dm$^{-3}$; $[\text{HCl}] = 0.1$ mol dm$^{-3}$; $\mu = 1.0$ mol dm$^{-3}$
formation constant $K_1$ and decomposition constant $k_2$ have been calculated (Table 2).

The decomposition constant $k_2$ for the rate-limiting step has also been determined by varying [alcohol]$_0$ at different temperatures (308-323K), and using these values activation parameters for the decomposition step of alcohol-BAT complex (Scheme 1) have been determined by the Arrhenius plot ($r > 0.9907$). These are given in Table 2.

The reaction is catalysed by Cl$^-$ ion and chloride catalysis at fixed [H$^+$] can be rationalised by Scheme 2:

$$k_1$$

TsNHBr$+\text{Cl}^- + S \rightarrow X$$

... (i) fast

$$X \xrightarrow{k_2} \text{Product}$$

... (ii) rate limiting

$$\text{H}_2\text{O}$$

Scheme 2

Scheme 2 leads to rate law (5) in the form:

$$\text{Rate} = \frac{k_2 K_1 [\text{BAT}] [S] [\text{Cl}^-]}{1 + K_1 [S] [\text{Cl}^-]}$$

Equation (5) can be transformed into equations (6) and (7):

$$k' = \frac{k_2 K_1 [S] [\text{Cl}^-]}{1 + K_1 [S] [\text{Cl}^-]} \quad \ldots (6)$$

$$1 = \frac{1}{k'} = \frac{1}{k_2 K_1 [S] [\text{Cl}^-]} + \frac{1}{k_2} \quad \ldots (7)$$

A double reciprocal plot of $\frac{1}{k'}$ versus $\frac{1}{[\text{Cl}^-]}$ ($r > 0.9809$) provides the values of $k_2$ and $K_1$ (Table 2).

Oxidation of alcohols by BAT is catalysed by H$^+$ and Cl$^-$ ions and the mixed order kinetics observed in [HCl] can be rationalised in terms of Eqs. (8) and (9):

$$\text{Rate} = k_{ob} [\text{BAT}] = a [\text{BAT}] [\text{H}^+] [\text{alcohol}] + b [\text{BAT}] [\text{Cl}^-] \quad \ldots (8)$$

$$k_{ob} = [a [S] + b] [\text{HCl}] \quad \ldots (9)$$

since [H$^+$] = [Cl$^-$] = [HCl] in aqueous solution.

Equation (9) predicts that a plot of $k_{ob} / [\text{HCl}]$ versus [S] should be linear ($r > 0.9931$). It is found to be so from which a and b were evaluated. The values of 10$^2a$ are 2.99, 1.83, 0.79, 0.21, 0.35, 1.47 and 5.02 and those of 10$^3b$ are 2.43, 1.27, 1.55, 0.12, 0.44, 2.93 and 7.93, respectively for ethanol and OC$_2$H$_5$, OCH$_3$, NH$_2$, Cl, Br and NO$_2$-substituted ethanols.

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**Table 2**—Values of formation constants $K_1$ and $K'_1$; and decomposition constants $k_1$ and $k_2'$ from double reciprocal plots

<table>
<thead>
<tr>
<th>RCH$_2$CH$_2$OH</th>
<th>$10^4k_2$</th>
<th>$10^4k_2'$</th>
<th>$K_1$</th>
<th>$K'_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>13.6 (8.9)</td>
<td>186.7 (157.7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$C$_2$H$_5$</td>
<td>8.0 (5.3)</td>
<td>183.8 (147.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>4.7 (3.8)</td>
<td>294.1 (169.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_2$</td>
<td>0.9 (0.5)</td>
<td>156.3 (188.7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>2.0 (1.4)</td>
<td>200.0 (140.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>9.1 (6.9)</td>
<td>270.3 (172.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_2$</td>
<td>31.0 (20.5)</td>
<td>178.6 (185.2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3**—Kinetic and thermodynamic parameters for the oxidation of alcohols by BAT in presence of hydrochloric acid calculated from the values of $k_2$

<table>
<thead>
<tr>
<th>RCH$_2$CH$_2$OH</th>
<th>$E_a$</th>
<th>$\Delta H^*$</th>
<th>$\Delta S^*$</th>
<th>$\Delta G^*$</th>
<th>log A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ mol$^{-1}$</td>
<td>kJ mol$^{-1}$</td>
<td>JK$^{-1}$ mol$^{-1}$</td>
<td>kJ mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>65.4</td>
<td>62.8 ± 0.0</td>
<td>-100.1 ± 0.1</td>
<td>94.4 ± 0.2</td>
<td>9.2</td>
</tr>
<tr>
<td>O$_2$C$_2$H$_5$</td>
<td>86.8</td>
<td>84.1 ± 0.0</td>
<td>-36.5 ± 0.2</td>
<td>95.7 ± 0.2</td>
<td>12.5</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>81.3</td>
<td>78.6 ± 0.0</td>
<td>-61.4 ± 0.1</td>
<td>98.0 ± 0.3</td>
<td>10.9</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>111.1</td>
<td>108.4 ± 0.0</td>
<td>+22.4 ± 0.1</td>
<td>101.4 ± 0.1</td>
<td>15.7</td>
</tr>
<tr>
<td>Cl</td>
<td>94.1</td>
<td>91.4 ± 0.0</td>
<td>-28.0 ± 0.2</td>
<td>100.3 ± 0.1</td>
<td>12.9</td>
</tr>
<tr>
<td>Br</td>
<td>78.3</td>
<td>75.6 ± 0.0</td>
<td>-65.9 ± 0.1</td>
<td>96.4 ± 0.1</td>
<td>10.7</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>43.7</td>
<td>41.1 ± 0.0</td>
<td>-163.9 ± 0.1</td>
<td>92.8 ± 0.2</td>
<td>5.7</td>
</tr>
</tbody>
</table>
A plot of log \( k_2 \) versus \( \sigma^* \) is non-linear (Fig. 1), suggesting that oxidation follows a concerted mechanism, the degree of concertedness depending on whether the hydride transfer from the C-H bond to the oxidant is synchronous with the removal of a proton from O-H group by a water molecule. In the earlier work on the oxidation of primary alcohols by BAt and BAB, it has been noted that electron donating groups increase the rate. It indicates that the rupture of the C-H bond gets precedence over O-H cleavage creating a carbonium ion center which is stabilized by the electron donating character of alkyl groups. In the present case (Scheme 3a) decrease in rate with electron withdrawing groups is in agreement with this observation. On the other hand, the rate is higher when the substituent is NO₂. Under these circumstances O-H bond cleavage gets precedence over C-H bond cleavage and the carbon atom becomes electron rich in the transition state, which is stabilized by the electron withdrawing nitro group. Further, the enormous three-fold increase in the rate in case of nitroethanol may alternatively be explained by Scheme 3b where slight ionization of nitroethanol is a likely process facilitating the electrophilic attack by the positive halogen. However, a satisfactory explanation for the enhancement of rate with nitroethanol cannot be offered at this stage.

Isokinetic temperature \( (\beta) \) was calculated from the linear plot \((r=0.9965)\) of \( \Delta H^* \) versus \( \Delta S^* \) to be 360K, which is much higher than the temperature range employed in the present work. The value of \( \beta \) was also calculated from Exner plot and was found to be 368K.

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References