Kinetics and mechanism of oxidation of acetylacetone by chloramine-T and bromamine-T in the presence of hydrochloric acid

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Oxidation of acetylacetone (AA) by chloramine-T (CAT) and bromamine-T (BAT) in the presence of HCl (0.1-0.6 mol dm$^{-3}$) at constant ionic strength (1.0 mol dm$^{-3}$) over the temperature range (303-318 K) obeys the rate law, rate = $k_{rx}[Ox][AA][HCl]^x$ where x and y are less than unity. Addition of the reaction product, p-toluenesulphonamide and variation of ionic strength of the medium have no effect on rate. The rate increases in D$_2$O medium. Activation parameters for the overall reactions have been computed. Michaelis-Menten type of kinetics has been proposed and activation parameters for the rate limiting step have been computed. The mechanism involves simultaneous catalysis by H$^+$ and Cl$^-$ ions and the interaction of haloamine species with the enol form of the diketone.

Analytical applications and mechanistic aspects of the reactions of chloramine-T ($\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2^-\text{NCINa.3H}_2\text{O or CAT}$) with diverse substrates are well documented$^{1,2}$. However, similar information on the bromine analogue, bromamine-T (BAT) is scanty. Oxidation of aliphatic ketones by organic haloamines has been carried out in acidic, basic and buffer media$^{3,4}$ and diketones are found to be the products. There are very few reports on the oxidation of diketones in literature and it was therefore of interest to investigate further oxidation of diketones by haloamines assisted by chloride. The present paper reports the kinetics and mechanism of oxidation of acetylacetone (AA) with CAT and BAT in the presence of HCl at 40°C.

Materials and Methods

Chloramine-T (E. Merck) was purified by repeatedly washing the sample with aliquots of CCl$_4$. An aqueous solution of CAT was prepared, standardised by the iodometric method and preserved in brown bottles to prevent photochemical deterioration.

Bromamine-T was prepared by the method reported in literature$^5$ and was characterised by its Br content and also by UV, IR and FT-NMR ($^1$H and $^13$C) spectra$^6$.

Analar grade acetylacetone (IDPL, India) was further distilled and aqueous solution of desired strength was prepared. All other reagents were of analar grade.

Triply distilled water was used for preparing aqueous solutions. Ionic strength was kept constant at 1.0 mol dm$^{-3}$ using a concentrated solution of NaClO$_4$. Heavy water (D$_2$O 99.2%) was supplied by the BARC, Trombay.

Regression analysis of experimental data to obtain regression coefficient r and standard deviation s was carried out on a EC-72 statistical calculator.

Kinetic measurements

The reaction was carried out in glass stoppered pyrex boiling tubes whose outer surface was coated black to eliminate photochemical effects. Solutions containing appropriate amounts of acetylacetone, HCl, NaClO$_4$ and water (to keep the total volume constant for all runs) were taken in the tube and thermostated at 40°C. A measured amount of oxidant (CAT or BAT) also thermostated at the same temperature was rapidly added to the mixture and the progress of reaction was monitored by iodometric determination of unreacted oxidant in a measured aliquot of the reaction mixture at regular intervals of time. The course of the reaction was studied up to two half lives. The pseudo-first order rate constants $k'$ calculated were reproducible within ±3%.

Stoichiometry

Varying ratios of oxidant to substrate in the presence of 0.2 mol dm$^{-3}$ HCl under conditions [reductant]$>[oxidant]$ and [oxidant]$>[reductant]$ were
equilibrated at 40°C for 24 hr and the stochiometry given in Eq. (1) was observed.

\[ \text{CH}_3\text{COCH}_2\text{COCH}_3 + 3\text{RNX Na} + 4\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{COOH} + \text{HCOOH} + 3\text{RNH}_2 + 3\text{Na}^+ + 3\text{X}^- \]  

(1)

where R = p-CH\text{C}_6\text{H}_4\text{SO}_2\text{Cl} for CAT and BAT with X = Cl or Br. p-Toluenesulphonamide (RNH\text{2} or TsNH\text{2}) was detected by paper chromatography. Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl in ethanol as spray reagent (R\text{f} = 0.905). Formic acid was identified by the chromotropic acid procedure after reducing it with magnesium and HCl. Acetate ion was identified by spot tests.

Results

Effect of reactants

With the substrate in excess, at constant [HCl] and [AA]\text{0}, plots of log [Ox] versus time were linear (r > 0.9901) indicating a first order dependence of rate on [Ox]\text{0}. Values of first order constants k' increased with increase in [AA]\text{0} (Table 1). Plots of log k' versus log [AA]\text{0} were linear (r > 0.9918; s ~ 0.05) with a fractional slope (~ 0.3), thus indicating a fractional order dependence on [AA]\text{0}. Further, plots of k' versus [AA]\text{0} were linear with a Y-intercept, confirming the fractional order dependence on [AA]\text{0}.

Effect of [HCl]

The rate increased with increase in [HCl]. For example under the conditions [Ox]\text{0} = 10 \times 10^{-4} \text{ mol dm}^{-3}, [AA]\text{0} = 3 \times 10^{-2} \text{ mol dm}^{-3} and 40°C 10^4 k' increased from 0.76 to 2.71 s^{-1} for CAT and 2.70 to 9.85 s^{-1} for BAT when [HCl] was increased from 0.1 to 0.6 mol dm^{-3}. Plots of log k' versus log [HCl] were linear (r > 0.9996, s ~ 0.04) with fractional slope (~ 0.7). Further, plots of k' versus [HCl] are linear with a Y-intercept (Fig. 1).

Effects of [H\text{+}] and halide ions

Total [Cl\text{-}] in the reaction mixture was kept constant at 0.6 mol dm^{-3} by adding NaCl and then [H\text{+}] was varied using HCl. The rate increased with increase in [H\text{+}] (Table 2). A plot of log k' versus log [H\text{+}] was linear (r > 0.9986; s ~ 0.04) with a fractional slope ~ 0.5. Further a plot of k' versus [H\text{+}] was linear with an intercept.

At constant [H\text{+}] = 0.2 mol dm^{-3} maintained with HCl, the rate increased with the addition of NaCl (Table 2). A plot of log k' versus log [Cl\text{-}] was linear (r > 0.9914, s ~ 0.03) with a fractional slope ~ 0.25. But addition of Br\text{-} ions in the form of NaBr (10 \times 10^{-4}, 50 \times 10^{-4} \text{ mol dm}^{-3}) had negligible effect on the rate. Plot of k' versus [Cl\text{-}] was linear with an intercept.

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**Table 1---Effect of variation of reactant concentrations on the rate of reaction at 40°C**

<table>
<thead>
<tr>
<th>[HCl] = 0.2 mol dm^{-3}; [AA]_0 = 1.0 mol dm^{-3}</th>
<th>10^4 [Oxidant]_0 mol dm^{-3}</th>
<th>10^2 [AA]_0 mol dm^{-3}</th>
<th>10^4 k's^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAT</td>
<td>BAT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>3.0</td>
<td>1.18</td>
<td>4.52</td>
</tr>
<tr>
<td>9.0</td>
<td>3.0</td>
<td>1.23</td>
<td>4.48</td>
</tr>
<tr>
<td>10.0</td>
<td>3.0</td>
<td>1.20</td>
<td>4.55</td>
</tr>
<tr>
<td>11.0</td>
<td>3.0</td>
<td>1.21</td>
<td>4.53</td>
</tr>
<tr>
<td>12.0</td>
<td>3.0</td>
<td>1.22</td>
<td>4.59</td>
</tr>
<tr>
<td>13.0</td>
<td>3.0</td>
<td>1.20</td>
<td>4.56</td>
</tr>
<tr>
<td>10.0</td>
<td>5.0</td>
<td>1.38</td>
<td>5.60</td>
</tr>
<tr>
<td>10.0</td>
<td>7.0</td>
<td>1.59</td>
<td>6.10</td>
</tr>
<tr>
<td>10.0</td>
<td>9.0</td>
<td>1.61</td>
<td>6.82</td>
</tr>
<tr>
<td>10.0</td>
<td>12.0</td>
<td>1.80</td>
<td>7.40</td>
</tr>
</tbody>
</table>

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**Table 2---Effect of variation of [H\text{+}] and [Cl\text{-}] on the rate of reaction at 40°C**

<p>| [oxidant]_0 = 10 \times 10^{-4} \text{ mol dm}^{-3}; [AA]_0 = 3.0 \times 10^{-2} \text{ mol dm}^{-3}; [\mu] = 1.0 \text{ mol dm}^{-3} |
|---|---|---|
| [H\text{+}] or ([Cl\text{-}]) mol dm^{-3} |
| 10^4 k's^{-1} |</p>
<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 (0.2)</td>
<td>1.26 (1.20)</td>
<td>4.15 (4.55)</td>
<td></td>
</tr>
<tr>
<td>0.2 (0.3)</td>
<td>1.70 (1.38)</td>
<td>5.65 (5.25)</td>
<td></td>
</tr>
<tr>
<td>0.3 (0.4)</td>
<td>1.98 (1.47)</td>
<td>7.00 (5.60)</td>
<td></td>
</tr>
<tr>
<td>0.4 (0.6)</td>
<td>2.25 (1.65)</td>
<td>8.12 (5.96)</td>
<td></td>
</tr>
<tr>
<td>0.5 (0.8)</td>
<td>2.47 (1.80)</td>
<td>8.90 (6.40)</td>
<td></td>
</tr>
<tr>
<td>0.6 (1.0)</td>
<td>2.70 (1.95)</td>
<td>9.85 (6.86)</td>
<td></td>
</tr>
</tbody>
</table>

a: Variation of [H\text{+}] on the rate of reaction at constant [Cl\text{-}] = 0.6 mol dm^{-3}.
b: Variation of [Cl\text{-}] on the rate of reaction at constant [H\text{+}] = 0.2 mol dm^{-3}.

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**Fig. 1---Plots of k' versus [HCl] ([Ox]_0 = 10 \times 10^{-4} \text{ mol dm}^{-3}; [AA]_0 = 3 \times 10^{-2} \text{ mol dm}^{-3}; [\mu] = 1.0 \text{ mol dm}^{-3})**
Effect of added p-toluene sulphonamide
Addition of the reaction product, p-toluene-sulphonamide (5 x 10^-4-30 x 10^-4 mol dm^-3) had no effect on the rate indicating that it is not involved in a pre-equilibrium to the rate limiting step.

Effect of ionic strength
Variation of ionic strength of medium by adding NaClO4 (0.2-1.0 mol dm^-3) had no effect on the rate.

Effect of temperature on the rate
The reaction was studied at different temperatures (303-318K) and from the linear Arrhenius plots (r> 0.9957) of log k' versus 1/T, values of activation parameters for the overall reaction were computed (Table 3).

Solvent isotope studies
Studies of rate in D2O medium for CAT and BAT revealed that while k' H2O is 1.20 x 10^-4 and 4.55 x 10^-4 s^-1, k'D2O was 1.30 x 10^-4 and 4.80 x 10^-4 s^-1 respectively. Thus, the solvent isotope effect, k'H2O / k'D2O was around 0.95.

Effect of varying dielectric constant of medium
Addition of methanol to reaction mixture (0-40%, v/v) increased the rate. Plot of log k' versus 1/D where D is the dielectric constant of medium was linear (r> 0.9986; s< 0.04) with positive slope. Blank experiments showed that oxidation of methanol by CAT and BAT during the experimental duration was negligible.

Test for free radicals
Addition of reaction mixture to acrylamide in an inert atmosphere did not initiate polymerization of the latter showing the absence of free radicals.

Discussion
Since the organic haloamines have similar chemical properties, it is expected that similar equilibria exist in solutions of these compounds. The haloamines behave like strong electrolytes in aqueous solutions, and the anion picks up a proton in acid solutions to give the free acid monohaloamine-T, RNXH. The free acid RNXH undergoes disproportionation/hydrolysis to give the dihaloamine (RNX2) and hypohalous acid (HOX).

The possible oxidizing species in acidified solutions of haloamines are therefore RNXH, RNX2 and HOX. If the dihaloamine were to be the reactive species the rate law predicts a second order dependence of rate on [haloamine] and a retardation by the sulphonamide (TsNH2). Also a first order retardation by the sulphonamide is expected, if the hypohalous acid HOX is involved. Since these were not observed, RNX2 and HOX are excluded from the reaction sequence and the likely oxidising species of diketone is the conjugate acid RNXH. Calculations of Hardy and Johnston on aqueous bromamine-B (BAB) solutions have shown that the concentration of RNBrH is considerable even in neutral pH and is greater than that of HOBr and BrO^- ion. Similar observations have been made by Bishop and Jennings with aqueous CAT solutions.

In the present investigations, oxidation of acetylacetone by CAT and BAT shows first order dependence of rate on [Ox]0 and fractional orders in [acid] and [substrate]. There is no involvement of toluenesulphonamide in pre-equilibrium with the oxidant and the absence of any ionic strength effect suggests that neutral species are taking part in the rate limiting step. Based on the above observations, the mechanism of reaction is best explained by Scheme 1 which predicts simultaneous catalysis by H^+ and Cl^- ions. Acetylacetone reacts in the enol form which is present up to 76% in an equilibrium solution.

Table 3—Kinetic and thermodynamic parameters for the oxidation of acetylacetone by CAT and BAT in the presence of HCl

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>E_a (kJ mol^-1)</th>
<th>ΔH_+ (kJ mol^-1)</th>
<th>ΔS_+ (J K^-1 mol^-1)</th>
<th>ΔG_+ (kJ mol^-1)</th>
<th>log A</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAT</td>
<td>69.9 (62.3)</td>
<td>67.2 (59.7)</td>
<td>105.6 (-125.2)</td>
<td>100.4 (98.6)</td>
<td>8.6 (7.8)</td>
</tr>
<tr>
<td>BAT</td>
<td>59.0 (52.0)</td>
<td>56.4 (49.2)</td>
<td>129.2 (-146.1)</td>
<td>96.8 (94.8)</td>
<td>7.5 (6.8)</td>
</tr>
</tbody>
</table>

Values in parentheses are the activation parameters for the rate limiting step.
Step (iii) determines the overall rate,

\[
\text{rate} = \frac{-d[\text{Ox}]}{dt} = k_3[X^*] \quad \ldots (2)
\]

If \([\text{Ox}],\) represents the total concentration of the oxidant, then

\[
[\text{Ox}]_t = [\text{RNHX}] + [X'] + [XW],
\]

from which, solving for \([XW],\) and substituting its value in (2), rate law (3) can be derived

\[
\frac{1}{k'} = \frac{1}{k_3 K_2 [\text{AA}]_0} \left( \frac{1}{K_1 [\text{H}^+][\text{Cl}^-]} + 1 \right) + \frac{1}{k_3} \quad \ldots (3)
\]

Rate law (3) is in agreement with experimental results. Equation (3) can be transformed into Eq. (4).

\[
\frac{1}{k'} K_2 [\text{AA}]_0 \left( \frac{1}{K_1 [\text{H}^+][\text{Cl}^-]} + 1 \right) + \frac{1}{k_3} \quad \ldots (4)
\]

From the intercepts of the linear double reciprocal plots of \(1/k'\) versus \(1/[\text{AA}]_0\) at fixed \([\text{HCl}]_0,\) \(1/k'\) versus \(1/[\text{H}^+]\) and \(1/k'\) versus \(1/[\text{Cl}^-],\) values of decomposition constants \(k_3\) for CAT and BAT were found as \(2.1 \times 10^{-4} \text{ s}^{-1}\) and \(8.3 \times 10^{-4} \text{ s}^{-1},\) \(3.3 \times 10^{-4} \text{ s}^{-1}\) and \(14.3 \times 10^{-4} \text{ s}^{-1}\) and \(2.22 \times 10^{-4} \text{ s}^{-1}\) and \(8.70 \times 10^{-4} \text{ s}^{-1}\) respectively.

Since the rate was fractional in \([\text{AA}]_0,\) Michaelis-Menten kinetics\(^{12}\) were adopted to study the effect of \([\text{AA}]_0\) on rate at different temperatures (Fig. 2) by plotting \(1/k'\) versus \(1/[\text{AA}]_0\). Values of \(k_3\) obtained for CAT and BAT were \((\times 10^5 \text{ s}^{-1})\): 9.6 and 42.5 (303 K), 13.7 and 62.5 (308 K), 21.1 and 86.9 (313 K) and 30.5 and 133.0 (318 K) respectively. Activation parameters (Table 3) for the rate limiting step were computed from the Arrhenius plots of \(\log k_3\) versus \(1/T (r > 0.9908).\)

The increase in rate with decrease in permittivity of the medium suggests a charge dispersal in the transition state and the rate increases only slightly in D\(_2\)O medium contrary to expectations\(^{13}\) for pre-equilibrium proton transfer reactions. This could be due to the hydrolysis step (Scheme 1) wherein the normal kinetic isotope effect \((k_{14}^H/k_{14}^D > 1)\) counterbalances the solvent isotope effect \((k_{14}^{H,O}/k_{14}^{H,D,O} < 1)\) resulting in a net effect, \(k_{14}^H/k_{14}^D > 1.\) The high negative \(\Delta S^\ddagger\) value suggests that the transition state is fairly rigid.

A detailed mode of oxidation of acetylacetone by CAT and BAT is given in Scheme 2. The interhalog-
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References