KINETICS OF OXIDATION OF ALIPHATIC PRIMARY AMINES BY CAB IN ALKALINE MEDIUM CATALYZED BY β- CYCLODEXTRINE

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ABSTRACT
Kinetics of oxidation of a typical aliphatic primary amines namely n-propyl amine (nPA) and n-butyl amine (nBA) by Chloramine –B(CAB) has been studied in alkaline medium using β- Cyclodextrin(βCD) as catalyst at 50 °C. The rate shows first order dependence of rate on CAB and zero order dependence of rate on both [amine] which tends to fractional order dependence of rate on catalyst was observed, when [OH-] = 0.01 mol dm-3. The reaction is almost independent of [OH-] and other effects, like chloride, sulphate ions, Benzenesulphonamide(BSA). Effect of ionic strength and dielectric constant of medium has also been studied. The reaction has been studied at different temperatures and a mechanism conforming to the kinetic observations is suggested.

Keywords: Kinetics, Oxidation, Amines, CAB, β -Cyclodextrine

INTRODUCTION
Considerable attention has centered around the chemistry of N-metallo-N-arylhalosulphonamides generally known as organic halamines, because of their versatility in behaving as mild oxidants, halogenating agents and N-ions, which act as both bases and nucleophiles. The important chlorine compound Chloramine-T(CAT),which is a byproduct during saccharin manufacture, is well known as an analytical reagent for the determination of diverse substrates. Mechanistic aspects of many of these reactions have been documented. These investigations have shown that the aromatic amine oxidations are independent of changing [OH-]. Gupta and Agrawal have observed and the compound can be easily prepared from benzenesulphonamide and chlorine.

Some kinetics studies of reactions of aromatic amines and their derivatives with chloramines-T(CAT) have been reported by Ramaiah and Rao and Radhakrishnamurthy and Rao. These investigations have shown that the aromatic amine oxidations are independent of changing [OH-]. Gupta and Agrawal have found that the kinetics of α-butylation oxidation by CAT shows a retarding effect of alkali. However, there is no information available in the literature on the kinetics of oxidation of aliphatic primary amines by Chloramine-B in presence of βCD. The present article reports our studies on the kinetics of oxidation of two aliphatic primary amines viz. n-propylamine(nPA) and n-butylamine(nBA) catalyzed by β-Cyclodextrin in Chloramine-B.

Experimental
In a typical experiment, appropriate amount of primary amines, alkali, sodium perchlorate solution and water were taken in a reaction vessel and thermostated at desired temperature (30–60 °C) for thermal equilibrium. A measured amount of oxidant solution (CAB) also thermostated at same temperature was rapidly added to the mixture which is in the reaction vessel. The progress of the reaction was monitored by iodometric determination of unreacted oxidant in measured aliquot of the reaction mixture at different intervals of time. This was done by pipetting 5ml aliquot of the reaction mixture at regular intervals and run into conical flask containing quenching mixture (Ice cold mixture of 10ml of 10%KI, 10ml of 2N H2SO4, and 50ml of ice cold water).

The liberated iodine was than titrated against standard sodium thiosulphate, using starch as internal indicator near the end point. The course of the reaction was followed for two half lives. The titer at t = 0 gives the value of ‘a’ the titer at any instant of time denotes (a-x).

Plot of log (a-x) (log [oxidant]) vs time; or log Vo/v vs time were made. The values of pseudo first order rate constants k' obtained were reproducible within ± 3%. Regression analysis of the experimental data to obtain regression co-efficient ‘r’ was carried out on a CASIO fx-991ES scientific calculator.

MATERIAL AND METHODS
CAB was prepared as reported previously. An aqueous solution was prepared, standardized iodometrically and stored in brown bottle to prevent its photochemical degradation. Amines (Aldrich) were of accepted grades of purity and were used without further purification. All other reagents were of analytical grade. Doubly distilled water was employed in the preparation of aqueous solutions. The ionic strength of the system was maintained at a constant high value using concentrated solution of NaClO4.

Product analysis
The reaction products of the amines, in the reaction mixture were detected by preparing their 2,4-dinitrophenylhydrazone derivatives, and by using Tollen’s regent test and chromic acid test. (DNP derivatives of propanaldehyde, mp.153.3 °C observed and 155 °C lit.1), 4-buteraldehyde, mp.122 °C observed and 123 °C lit.1). The other product ammonia was quantitatively estimated by the standard micro-Kjeldahl procedure. The reduced product of CAB, benzene sulphonamide was identified by paper chromatography using benzyl alcohol saturated with water as the solvent system and 0.5% vanillin in 1% HCl in EtOH as the visualizing reagent (Rf = 0.905).

RESULTS
Effect of reactants on the rate of reaction
The kinetic run was carried out with stoichiometric excess of substrate at constant [NaOH] and [βCD]. Plots of log [CAB] vs time were linear with slope equal to unity table-1. fig.1 indicating first order dependence of the reaction rate on [CAB]. The value of pseudo first order rate constant ‘k’ is given in table-2 under the same experimental conditions. An increase in [amine] has no effect on the rate, thus indicating zero – order dependence on [amine] table -3.
Table 1: Rate of primary amines of oxidation by CAB

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>log [CAB]</th>
<th>log [CAB]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.198</td>
<td>1.290</td>
</tr>
<tr>
<td>10</td>
<td>1.017</td>
<td>1.093</td>
</tr>
<tr>
<td>15</td>
<td>0.939</td>
<td>0.991</td>
</tr>
<tr>
<td>20</td>
<td>0.850</td>
<td>0.903</td>
</tr>
<tr>
<td>25</td>
<td>0.763</td>
<td>0.806</td>
</tr>
<tr>
<td>30</td>
<td>0.672</td>
<td>0.707</td>
</tr>
<tr>
<td>40</td>
<td>0.505</td>
<td>0.572</td>
</tr>
<tr>
<td>50</td>
<td>0.230</td>
<td>0.203</td>
</tr>
</tbody>
</table>

$r = 6.397 \times 10^{-4} \text{sec}^{-1}$

$[\text{CAB}] = 5 \times 10^{-3} \text{mol dm}^{-3}$, $[\text{Amine}] = 10 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{NaOH}] = 5 \times 10^{-2} \text{mol dm}^{-3}$

Table 2: Effect of varying [CAB] on the rate of reaction of primary amines

<table>
<thead>
<tr>
<th>$10^3 \text{[CAB]}$ mol dm$^{-3}$</th>
<th>$10^4 \text{k sec}^{-1}$ nPA nBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>6.30</td>
</tr>
<tr>
<td>2.5</td>
<td>6.38</td>
</tr>
<tr>
<td>5.0</td>
<td>6.39</td>
</tr>
<tr>
<td>7.0</td>
<td>6.35</td>
</tr>
<tr>
<td>9.0</td>
<td>6.38</td>
</tr>
</tbody>
</table>

$[\text{Amine}] = 10 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{NaOH}] = 5 \times 10^{-2} \text{mol dm}^{-3}$, $[\beta CD] = 5 \times 10^{-3} \text{mol dm}^{-3}$ and $T = 323K$

Table 3: Effect of varying [amine] on the rate of oxidation by CAB

<table>
<thead>
<tr>
<th>$10^2 \text{[Amine]}$ mol dm$^{-3}$</th>
<th>$10^4 \text{k sec}^{-1}$ nPA nBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>6.40</td>
</tr>
<tr>
<td>7.5</td>
<td>6.38</td>
</tr>
<tr>
<td>10.0</td>
<td>6.39</td>
</tr>
<tr>
<td>15.0</td>
<td>6.35</td>
</tr>
<tr>
<td>30.0</td>
<td>6.43</td>
</tr>
</tbody>
</table>

$[\text{CAB}] = 5 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{NaOH}] = 5 \times 10^{-2} \text{mol dm}^{-3}$, $[\beta CD] = 5 \times 10^{-3} \text{mol dm}^{-3}$ and $T = 323K$

Effect of NaOH on the rate of reaction

At constant [CAB], [amine], [NaOH] and temperature, the rate of a reaction increased with increase in [NaOH] ($1 \times 10^{-2} \text{mol dm}^{-3}$ to $10 \times 10^{-2} \text{mol dm}^{-3}$). The plots of log k vs log [NaOH] were linear with a slope less than unity ($\approx 0.40$) indicating fractional order dependence on [NaOH] table-4, fig.2.

Table 4: Effect of [NaOH] on the rate of oxidation of primary amines

<table>
<thead>
<tr>
<th>$10^3 \text{[NaOH]}$ mol dm$^{-3}$</th>
<th>$10^4 \text{k sec}^{-1}$ nPA nBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>3.41</td>
</tr>
<tr>
<td>2.5</td>
<td>4.84</td>
</tr>
<tr>
<td>5.0</td>
<td>6.39</td>
</tr>
<tr>
<td>7.5</td>
<td>8.04</td>
</tr>
<tr>
<td>10.0</td>
<td>9.77</td>
</tr>
</tbody>
</table>

$[\text{Amine}] = 10 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{CAB}] = 5 \times 10^{-3} \text{mol dm}^{-3}$, $[\beta CD] = 5 \times 10^{-3} \text{mol dm}^{-3}$ and $T = 323K$

Effect of [Cl$^-$] ion on the rate of reaction:

Effect of [Cl$^-$] was studied by adding NaCl to the reaction mixture ($0.1 \text{ mol dm}^{-3}$ to $0.5 \text{ mol dm}^{-3}$). It showed that the increase in [Cl$^-$] has no effect on the rate of a reaction table-6.

Table 5: Effect of [βCD] on the rate of reaction of primary amines

<table>
<thead>
<tr>
<th>$10^3 \text{[βCD]}$ mol dm$^{-3}$</th>
<th>$10^4 \text{k sec}^{-1}$ nPA nBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>3.52</td>
</tr>
<tr>
<td>2.5</td>
<td>4.82</td>
</tr>
<tr>
<td>5.0</td>
<td>6.39</td>
</tr>
<tr>
<td>7.5</td>
<td>7.34</td>
</tr>
<tr>
<td>10.0</td>
<td>8.18</td>
</tr>
</tbody>
</table>

$[\text{Amine}] = 10 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{CAB}] = 5 \times 10^{-3} \text{mol dm}^{-3}$, $[\text{NaOH}] = 5 \times 10^{-2} \text{mol dm}^{-3}$ and $T = 323K$

Effect of β-Cyclodextrine on the rate of reaction

At constant [CAB], [amine], [NaOH] and temperature, the rate of a reaction increased with increase in [βCD] ($1 \times 10^{-3} \text{mol dm}^{-3}$ to $10 \times 10^{-3} \text{mol dm}^{-3}$). The plots of log k vs log [βCD] were linear with slope less than unity ($\approx 0.40$) indicating fractional order dependence on [βCD] table-5, fig.3.

Fig. 1: Effect of concentration on rate of oxidation of primary amines by Chloramine-B

Effect of NaOH on the rate of reaction

At constant [CAB], [amines], [βCD] and temperature the rate increased with increase in [CAB] ($1 \times 10^{-2} \text{mol dm}^{-3}$ to $10 \times 10^{-2} \text{mol dm}^{-3}$). The plots of log k vs log [CAB] were linear with a slope less than unity ($\approx 0.40$) indicating fractional order dependence on [CAB] table-4, fig.2.
The reaction was studied at different temperatures in the range 318K - 333K and the value of 'k' were determined from the pseudo first order plot table-8, fig.5. The energy of activation 'Ea' was evaluated. The other activation parameters were calculated and are presented in table 9.

Table 8: Effect of temperature on the rate of reaction for the oxidation of primary amines by CAB in presence of β-Cyclodextrine catalyst

<table>
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<tr>
<th>T/K</th>
<th>10^4 k sec^{-1} nPA nBA</th>
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<tbody>
<tr>
<td>318</td>
<td>3.89</td>
</tr>
<tr>
<td>323</td>
<td>6.39</td>
</tr>
<tr>
<td>328</td>
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[βCD] = 5x10^{-3} mol dm^{-3} and T = 323 K

Table 9: Activation parameters for the oxidation of primary amines by CAB in presence of β-Cyclodextrine catalyst

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<td>Ea kJ/mol</td>
<td>11.24</td>
<td>9.75</td>
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<tr>
<td>ΔH° kJ/mol</td>
<td>86.65</td>
<td>77.08</td>
</tr>
<tr>
<td>ΔS° JK^{-1}mol</td>
<td>-36.49</td>
<td>-67.10</td>
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<tr>
<td>ΔG° kJ/mol</td>
<td>74.74</td>
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Test of free radicals on the rate of reaction:
The addition of reaction mixture to aqueous acrylamide monomer solution did not initiate polymerization indicating the absence of insitu formation of free radical species in the reaction sequence.

Stoichiometry
Reaction mixtures containing varying ratio of oxidant to amines were equilibrated in 5 x 10^{-2} mol dm^{-3} of NaOH and 5 x 10^{-3} mol dm^{-3}.

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of β-Cyclodextrine at 323K for about 24 hours with $[\text{oxid}]_0 > [\text{S}]_0$. The excess unreacted oxidant was estimated by iodometric titration with standard sodium thiosulphate. It was found that one mole of substrate consumed one mole of the oxidant to yield the corresponding aldehyde, conforming to equation (1).

$$\text{PhSO}_2\text{NCl} + \text{RCl} + \text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{R-CHO} + \text{PhSO}_2\text{NH}_2 + \text{NH}_3 + \text{Na}^+ + \text{Cl}^- \quad \text{(1)}$$

$\text{R} = \text{CH}_3\text{CH}_2$ for n-propyl amine

DISCUSSION

Pryde and Soper13, Morris et al14 and Bishop and Jennings15 have showed that the existence of similar equilibrium in acid/alkaline solution of $N$-metallo-$N$-halosulphonamide. CAB analogous to CAT, behaves as a strong electrolyte in aqueous solution, forming different species as shown in equation 2–6.

$$\text{PhSO}_2\text{NCl} + \text{H}_2\text{O} \leftrightarrow \text{PhSO}_2\text{NH}^+ + \text{OH}^- \quad \text{(2)}$$

In acidic medium the probable oxidizing species are free acid $\text{PhSO}_2\text{NCl}$, $\text{PhSO}_2\text{NH}_2$, $\text{HOCl}$ and $\text{H}_2\text{OCl}^+$. In the medium, where $\text{PhSO}_2\text{NCl}$ and $\text{H}_2\text{OCl}^+$ do not exist, the expected reactive species are $\text{PhSO}_2\text{NH}_2$, $\text{HOCl}$ and $\text{PhSO}_2\text{NCl}_2$. Hardy and Johnston16 have reported the existence of following equilibrium in alkaline solution of CAB.

As equation (8) indicates a slow hydrolysis, if $\text{HOCl}$ is the primary oxidizing species, a first retardation of the rate by the added BSA would be expected, which was not observed. If $\text{PhSO}_2\text{NH}_2$ were the reactive species, a retardation of the rate by $[\text{OH}^-]$ would be expected (eq.7), which has also not been observed. Therefore it is likely that the anion $\text{PhSO}_2\text{NCl}^-$ itself acts as the reactive species responsible for the oxidation of amines. The following Scheme 1 is therefore proposed to explain the experimentally observed reaction.

\begin{align*}
\text{PhSO}_2\text{NH}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{PhSO}_2\text{NCl}^- + \text{OH}^- \quad \text{(7)} \\
\text{PhSO}_2\text{NCl}^- + \text{BCD} & \rightleftharpoons \text{X} \quad \text{(Slow)} \quad \text{(10)} \\
\text{X} + \text{H}_2\text{O} & \rightarrow \text{X'} \quad \text{Slow and r.d.s} \quad \text{(11)} \\
\text{X'} + \text{S} & \rightarrow \text{Product} \quad \text{(12)}
\end{align*}

SCHEME 1

Where ‘S’ is primary amines (nPA or nBA) and X and X’ are the intermediate complexes. From the above scheme we can write from equations (9) and (10),

$$[\text{PhSO}_2\text{NCl}] = \frac{[\text{X}]}{K_2[\text{BCD}]} \quad \text{(14)}$$

And $[\text{PhSO}_2\text{NCl}] = \frac{[\text{X}][\text{H}_2\text{O}]}{K_4[\text{BCD}]} \frac{1}{[\text{H}_2\text{O}]} K_4[\text{OH}^-] \quad \text{(15)}$

By substituting for $[\text{PhSO}_2\text{NCl}]$ and $[\text{PhSO}_2\text{NH}_2]$ in equation (13) and rearranging we have.

$$[\text{X}] = \frac{K_1K_2[\text{BCD}][\text{OH}^-][\text{CAB}]}{[\text{H}_2\text{O}]} + \frac{K_4[\text{OH}^-]}{K_2K_4[\text{BCD}][\text{OH}^-]} \quad \text{(16)}$$

Since rate $= k_1 \cdot [\text{X}][\text{H}_2\text{O}]$ \quad \text{(17)}

On substituting equation (16) in (17)
A Plot of \(1/k'\) vs \(1/[\beta\text{CD}]\) and \(1/k'\) vs \(1/[\text{OH}^-]\) [\text{[OH]}\].

Taking reciprocal equation (20) can be written as

\[
\frac{1}{k'} = \frac{1}{k_1 K_2 [\beta\text{CD}]} + \frac{1}{k_2}\left(\frac{1}{[\text{OH}^-]} + \frac{1}{k_3 K_1 [\beta\text{CD}]}\right)
\]

Where, \((k_1') = k_3 [\text{H}_2\text{O}])

On rearranging equation (21) it can be written as

\[
\frac{1}{k'} = \frac{1}{[\beta\text{CD}]} + \frac{1}{k_1 K_2}\left(\frac{1}{[\text{OH}^-]} + \frac{1}{k_3 K_1 [\beta\text{CD}]}\right)
\]

A Plot of \(1/k'\) vs \(1/[\beta\text{CD}]\) and \(1/k'\) vs \(1/[\text{OH}^-]\) is found to be linear.

The above rate law is in agreement with experimental data, which includes first order in \([\text{CAB}\]) fractional order in \([\beta\text{CD}]\) and \([\text{OH}^-]\).

\[
\text{Experimentally rate} = k'[\text{CAB}]
\]

Therefore \(k' = \frac{k_3 K_2 [\beta\text{CD}] [\text{OH}^-][\text{H}_2\text{O}]}{K_1 [\text{OH}^-] + K_2 K_1 [\beta\text{CD}]}\) .... (19)

\[
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\]

\[
\frac{1}{k'} = \frac{1}{k_1 K_2}\left(\frac{1}{[\beta\text{CD}]} + \frac{1}{k_2}\left(\frac{1}{[\text{OH}^-]} + \frac{1}{k_3 K_1 [\beta\text{CD}]}\right)\right)
\]

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\text{Where, } (k_1') = k_3 [\text{H}_2\text{O}])
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\]

A detailed mechanistic interpretation of \(\beta\text{CD}\) catalyzed oxidation of the primary amines by \(\text{CAB}\) in \(\text{NaOH}\) medium is presented in Scheme II. An anion of the oxidizing species, \(\text{(PhSO}_2\text{NCl)}\) coordinates through the sulphonamide nitrogen atom to activate \(\text{CAB}\) by stabilizing the charge on its nitrogen atom and polarizing the \(\text{N-Cl}\) bond in the complex species \(X\) in the slow step (step i).

Fairly large value \(\Delta G\) indicates that the activated complex is solvated as is given by the slow r.d.s step (eq.11) in Scheme I. A negative \(\Delta S\) indicates an ordered activated complex. The decrease in the rate constant with decreasing constant also supports this view in Scheme II.

From the slope and intercept of the plots, the values of \(k_1\), \(k_2\), and \(K_1\), are calculated (table-10). The fairly constant values of \(K_1\) and \(K_2\) for the step (9) and (10) respectively indicates that proposed Scheme I is correct.

An anion of the oxidizing species, \(\text{(PhSO}_2\text{NCl)}\) coordinates through the sulphonamide nitrogen atom to activate \(\text{CAB}\) by stabilizing the charge on its nitrogen atom and polarizing the \(\text{N-Cl}\) bond in the complex species \(X\) in the slow step (step i).


\[
\begin{align*}
\text{C}_{42}\text{H}_{70}\text{O}_{35} + \text{Cl}\cdot\text{N}\cdot\text{S}\cdot\text{Ph} & \quad \text{Slow} \quad \text{Cl} \cdot \text{N} \cdot \text{S} \cdot \text{Ph} \quad \text{(C}_{42}\text{H}_{70}\text{O}_{35}) \\
\text{R} - \text{C} - \text{N} & \quad \text{Fast} \quad \text{Cl} \cdot \text{N} \cdot \text{S} \cdot \text{Ph} \\
\text{PhSO}_2\text{N}^+ & \quad \text{H}_2\text{O} \\
\text{NH}_3 & \quad \text{H}_2\text{O}
\end{align*}
\]

In the next fast step III, the intermediate \(X'\) disproportionates into an N-chloromine species \(X''\) and \((\text{PhSO}_2\text{NCl})\) which on hydrolysis can form the reduction product \(\text{PhSO}_2\text{NH}_2\). The step IV involves a nucleophilic attack by \(\text{H}_2\text{O}\) followed by intramolecular rearrangements, forming an N-protonated amine intermediate which is attacked by \(\text{OH}^-\) to form the aldehyde, \(\text{NH}_3\) and \(\text{H}_2\text{O}\).
Here, Ph = C₆H₅ and R = CH₃CH₂ for nPA, CH₃CH₂CH₂ for nBA.

**SCHEME II**

**REFERENCE**