Mechanism of oxidation of ethanolamines by sodium N-chloro-p-toluenesulphonamide in alkaline buffer medium: A kinetic study

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Kinetics of oxidation of monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) by sodium N-chloro-p-toluenesulphonamide (chloramine-T, CAT) in alkaline buffer medium has been studied at 313K. The reactions followed identical kinetics being first order in [CAT] and fractional order each in [substrate] and [OH-]. Under comparable experimental conditions the rate of oxidation increases in the order: DEA > TEA > MEA. Addition of the reaction product p-toluenesulphonamide retards the reaction rate. Added chloride ions and change in ionic strength of the medium do not have any effect on the rate of the reaction. Change in dielectric constant of the medium affects the reaction rate. Activation parameters for the rate determining step are evaluated and isokinetic relation is observed with [1]=390 K indicating that the reactions are enthalpy-controlled. Formation and decomposition constants of substrate -CAT complexes are evaluated. Suitable mechanisms and rate equations are proposed based on the observed kinetic data.

**Experimental**

Chloramine-T (E Merck) was purified by the method of Morris et al. An aqueous solution of CAT was prepared, standardised iodometrically and preserved in amber coloured bottles to prevent photochemical deterioration. Ethanolamines were of accepted grades of purity and were used without further purification. Standard buffer system (borax+NaOH) were employed. A constant ionic strength of the reaction medium was maintained at 0.50 mol dm$^{-3}$ by adding required amount of concentrated NaClO$_4$ solution. All other chemicals were of analytical grades. Doubly distilled water was used for preparing aqueous solutions.

**Kinetic measurements**

Mixtures containing requisite amounts of substrate, NaClO$_4$ and buffer were taken in stoppered pyrex glass tubes whose outer surface was coated with black paint. The tube was thermally equilibrated in a water bath (313±0.1K). A measured amount of CAT solution pre-equilibrated at the same temperature, was added and the reaction mixture was shaken. The progress of the reaction was monitored iodometrically by withdrawing aliquots (5 ml each) of the reaction mixture at regular time intervals. The course of the reaction was studied for two half lives. The pseudo-first order rate constants, $k$, calculated were reproducible within ±3%.

**Stoichiometry and product analysis**

Varying ratios of CAT to ethanolamines ([CAT]/[ethanolamine]) were equilibrated at 313K in the presence of alkaline buffer for 48h. Estimation of unreacted oxidant lead to stoichiometric reactions (1, 2 and 3).

\[
\begin{align*}
\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})+2\text{RNClNa}+2\text{H}_2\text{O} & \rightarrow \text{HCHO}+ \\
\text{HCOOH}+\text{NH}_3+2\text{RNHI}_2+2\text{NaCl} & \quad \ldots (1) \\
\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2+4\text{RNClNa}+4\text{H}_2\text{O} & \rightarrow 2\text{HCHO}+ \\
2\text{HCOOH}+\text{NH}_3+4\text{RNHI}_2+4\text{NaCl} & \quad \ldots (2) \\
\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2+4\text{RNClNa}+4\text{H}_2\text{O} & \rightarrow \text{CH}_2\text{CHO}+2\text{HCl} \\
\text{HO}+2\text{HCOOH}+\text{NH}_3+4\text{RNHI}_2+4\text{NaCl} & \quad \ldots (3) \\
\text{where } R=p-\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3&-
\end{align*}
\]

$p$-Toluenesulphonamide was identified among the reaction products by paper chromatography using benzyl alcohol saturated with water as the solvent and
Oxidation of ethanolamines by CAT was carried out at 313K in various buffer media. The reaction was found to be facile in the pH range 8.5-10.5. Hence a detailed investigation was made on the kinetics of oxidation of ethanolamines in alkaline buffer solution of pH 9.69.

Dependence of rate on [CAT] and [EA]

Kinetics of oxidation of ethanolamines by CAT in alkaline buffer solution of pH 9.69 was investigated at several initial [CAT]. Plots of log [CAT] versus time were linear indicating a first order dependence of rate on [CAT]. Similar results were noticed with other buffer solutions. The pseudo-first order rate constants, k, are independent of [CAT] and these values are given in Table 1. An increase in [ethanolamine] increases the rate of reaction (Table 1) and a plot of log k versus log [EA] was linear. The order in each of the ethanolamines was found to be fractional (0.50 for MEA, 0.40 for DEA and 0.75 for TEA). Under comparable experimental conditions the reaction rates were in the order: DEA > TEA > MEA.

Dependence of rate on [OH-]

The reaction rate increases with increase in pH of the reaction medium. Plots of log k versus pH were linear with fractional slopes (0.30 for MEA, 0.46 for DEA and 0.32 for TEA), giving positive fractional orders in [OH-].

Effect of ionic strength and p-toluenesulphonamide on the rate

A constant ionic strength (0.5 mol dm-3, NaClO4) was maintained during oxidation. However, the effect of change in ionic strength of the medium (0.1-0.8 mol dm-3) on the reaction rate was found to be negligible. Addition of the reaction product, p-toluenesulphonamide to the reaction mechanism retarded the rate. Further, plots of log k versus log [RNH2] were linear with negative fractional slopes (~0.20 for MEA, ~0.18 for DEA and ~0.21 for TEA).

Effect of dielectric constant, temperature and solvent isotope on the rate

The effect of solvent dielectric constant on the kinetics of oxidation of ethanolamines was also studied by adding methanol to the reacting system. A decrease in the rate constant was noticed with decrease in the dielectric constant of the reaction. Plots of log k versus 1/T activation parameters (ΔG°, ΔS° and ΔH°) for the overall reactions were evaluated. These values are presented in Table 2. The reaction between CAT
Table 3—Values of $K_1$, formation constant $K_2$ and decomposition constant $k_3$ (from double reciprocal plots)

<table>
<thead>
<tr>
<th>Ethanolamine</th>
<th>$10^4 K_1$</th>
<th>$K_2$ (dm$^3$mol$^{-1}$)</th>
<th>$k_3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>7.77</td>
<td>47.3</td>
<td>2.87x10$^5$</td>
</tr>
<tr>
<td>DEA</td>
<td>5.69</td>
<td>61.0</td>
<td>1.82x10$^3$</td>
</tr>
<tr>
<td>TEA</td>
<td>10.0</td>
<td>28.8</td>
<td>3.44x10$^4$</td>
</tr>
</tbody>
</table>

(1.0x10$^{-3}$ mol dm$^{-3}$) and DEA (1.0x10$^{-2}$ mol dm$^{-3}$) was studied in D$_2$O medium containing buffer (pH 9.69) at 313K. The solvent isotope effect, $k$(H$_2$O)/$k$(D$_2$O), was found to be 0.94.

Oxidation potential of CAT-PTS system decreases with increase in pH of the medium$^{13}$. In alkaline solution of CAT, RNCl$_2$ or HOCl does not exist. In the present alkaline solution one could expect the presence of RNCl$^-$ anion and RNHCl. The latter, however, is formed in base retarding reactions$^{14}$.

Table 4—Values of the decomposition constant ($k_3$) of ethanolamine-CAT complex at different temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$10^3 k_3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>308</td>
<td>MEA 1.04 DEA 103 TEA 25.0</td>
</tr>
<tr>
<td>313</td>
<td>MEA 2.87 DEA 182 TEA 34.4</td>
</tr>
<tr>
<td>318</td>
<td>MEA 4.54 DEA 333 TEA 100</td>
</tr>
<tr>
<td>323</td>
<td>MEA 8.00 DEA 500 TEA 333</td>
</tr>
</tbody>
</table>

Hardy and Johnston$^{15}$ have indicated that there is considerable concentration of RNHCl even in alkaline CAT solution. Further with increase in [NaOH], RNHCl gives NaOCl. First order dependence of rate on [CAT], fractional order dependence each on [EA]

**Scheme-2a**
Table 5—Kinetic and thermodynamic parameters for the rate limiting step

<table>
<thead>
<tr>
<th>Ethanolamine</th>
<th>$Ea$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (JK$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>121</td>
<td>119</td>
<td>43.1</td>
<td>105</td>
</tr>
<tr>
<td>DEA</td>
<td>82.9</td>
<td>80.3</td>
<td>-41.2</td>
<td>93.3</td>
</tr>
<tr>
<td>TEA</td>
<td>112</td>
<td>109</td>
<td>40.1</td>
<td>96.4</td>
</tr>
</tbody>
</table>

and [OH$^-$] and the observed retardation of rate by the reaction product RNH$_2$ can be explained by Scheme 1:

$\text{RNHCl} + \text{OH}^-$ $\overset{K_1}{\longrightarrow} \text{RNH}_2 + \text{Cl}^-$ ... (i) fast

$\text{OCI} + \text{EA} \overset{K_2}{\longrightarrow} X$ ... (ii) fast
X $\rightarrow k_1 \rightarrow X'$

... (iii) slow and is

X + n OCl $\rightarrow k_2 \rightarrow $ Products

... (iv) fast

**Scheme 1**

Here n=1 for MEA, n=3 for DEA and TEA.

From Scheme 1, assuming [CAT] $\rightarrow$ [RNHCl] $+$ [OCl]$^-$ $+$ [X]

Rate law (5) can be derived.

\[
\text{Rate} = \frac{d[CAT]}{dt} = \frac{k_1 k_2 [CAT] [EA] [OH^-]}{[RNH_2]_0 + K_{12} [OH^-]_0 + K_{23} [EA]} \tag{5}
\]

Rate law (5) is in accordance with the observed kinetic data and can be transformed into Eqs. (6) and (7).

Since rate $= k[CAT]$, where [CAT]$_0$ represents the total [CAT]

\[
1 = \frac{k_2 [EA] [OH^-]}{k_2 K_2 [EA] [OH^-]} + 1 \tag{6}
\]

\[
1 = \frac{1}{k_3} \frac{k_2 [EA]}{K_{12} [OH^-]} + 1 \tag{7}
\]

From the double reciprocal plots of 1/k versus 1/[EA] and 1/k versus [RNH$_2$], values of $K_1$ and decomposition constants $k_3$ were calculated (Table 3). $K_1$ values are fairly constant supporting the proposed mechanism. The values are small indicating the small equilibrium because of the acid – base character of the reaction. The formation constants $K_2$ are in the order DEA $>$ MEA $>$ TEA; on the other hand decomposition constants $k_3$ which indicate the stability of X are in the order DEA $<$ TEA $<$ MEA. The decomposition constant $k_3$ for the rate-limiting step was also determined by varying [EA]$_0$ at different temperatures (308-323K) and the values are given in Table 4. Using these values activation parameters for the decomposition step of the ethanamine -CAT complex [step (iii) of Scheme 1] were determined by an Arrhenius plot of log $k_3$ versus 1/T, these are shown in Table 5. A detailed mechanism of oxidation of ethanamines by CAT is shown in Scheme 2.

The non-bonding electron pair is important in the chemistry of amines, since it is responsible for the typical basic and nucleophilic properties of these compounds. In the series MEA, DEA and TEA since ethanol (CH$_2$CH$_2$OH) group has an $\text{ON}^+$ effect, the larger the number of these groups on nitrogen atom the greater will be the electron density on it. The increasing negative charge on the central nitrogen atom favours the attack of electron deficient oxidising species at this centre. It is anticipated that TEA should form complex with electrophilic species readily. However, in the present study the increasing order of the reaction rate is found to be DEA $>$ TEA $>$ MEA, which is anomalous compared to the expected order i.e., TEA $>$ DEA $>$ MEA. This is attributed to an increasing steric effect, which is operating in the case of TEA, where side chains may be hindering the approach of the reagent towards nitrogen atom. In the case of DEA both polar and steric factors are found to favour the reaction. It is noticed that TEA reaction is slow initially. As soon as a molecule of CH$_2$CHO is eliminated, the reaction is found to be faster as shown in Scheme 2C.

It is seen from Table 2 that the activation energy is highest for the slowest reaction, indicating that the reaction is enthalpy-controlled. Further, the values of $\Delta H^*$ and $\Delta S^*$ can be correlated linearly resulting in an isokinetic relationship. From the slope, the value of isokinetic temperature $\beta$ is found to be 390K, which is much higher than the experimental temperature indicating that the reaction is enthalpy-controlled. The reaction is characterised by a moderate energy of activation and the near constancy of $\Delta G^*$ values indicates that a similar mechanism is operative in the oxidation of ethanamines by CAT. Values of $\Delta G^*$ are negative and are in the order DEA $>$ TEA $>$ MEA. Thus the transition state appears to be more ordered and rigid for the diethanolamine while in the case of MEA the transition state more or less resembles the reactants.

For the limiting case of zero angle of approach, between two dipoles or an ion-dipole system, Amis$^{16}$ has shown that a plot of log $k$ versus $1/D$ is linear with a negative slope for a reaction between a negative ion and a dipole or between two dipoles, while a positive slope results for a positive ion-dipole interaction. The negative dielectric effect observed in the present studies clearly supports the ion-dipole interaction as given in Scheme 1. Solvent isotope studies show that $k$(H$_2$O)/$k$(D$_2$O) < 1. This is generally correlated with the fact that OD$^-$ is a stronger base$^{17}$ than OH$^-$ and hence in base catalysed reaction enhancement of rate in D$_2$O medium can be expected.

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