Kinetic and Mechanistic Study of Oxidation of Diethylamine by N-Sodio-N-Bromobenzene Sulphonamide (Bromamine-B) in Acid Solution: Catalyzed by Ru(III)

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ABSTRACT: Kinetics of oxidation of diethylamine (DEA) by Bromamine-B (BAB) has been investigated at 303 K in acid solution with Ru(III) as catalyst. The oxidation behavior obeys the rate law, rate = k [BAB] [DEA] [Ru(III)] [H+]x where 'x' is less than unity indicating retardation of rate by [H+]. Added halide ions, the reaction product benzenesulphonamide, variation of ionic strength and dielectric constant of the medium do not have any significant effect on the rate. The protonation constant of monobromamine-B evaluated for the reaction is 32.3 at 303 K. Activation parameters have been evaluated from Arrhenius plot. A mechanism consistent with experimental results has been proposed.

INTRODUCTION
Diethylamine (DEA) is an intermediate for rubber accelerators, pharmaceuticals, dyestuff, textile finishing agents and corrosion inhibitors. It is commonly used as an intermediate in the synthesis of procaine anesthetic and antihistamine. Diethylamine was oxidized by periodate by Hiremath et al. [1]. Recently, Jabhas et al. [2] have reported oxidation of Aliphatic amines including DEA by N-bromophthalalimide (NBP). However, a very few kinetic investigations of diethylamine oxidations have been reported. There is no information available on the oxidation by haloamines. The present studies were undertaken to investigate the kinetic aspects of oxidation of diethylamine by N-metallo-N-haloarylsulphonamides. Mechanistic studies of the oxidation of diverse organic substrates by these organic...
haloamines have been reported previously [3–5]. We now report a detailed investigation of the kinetics of oxidation of diethylamine (DEA) by Bromamine-B in acid solution catalyzed by Ru(III) at 303 K.

**EXPERIMENTAL**

The oxidant, BAB, was prepared and purified using the standard methods [6,7]. Its purity was checked isodometrically and through IR and NMR spectral data. Aqueous solution of BAB was prepared, standardized to 307 mol dm$^{-3}$ NaClO$_4$ (E. Merck) and stored in amber glass bottles whose outer surfaces were coated black to eliminate photochemical effects. Requisite amount of glass tubes whose outer surfaces were coated black to eliminate photochemical effects. Requisite amount of BAB and DEA were equilibrated at 307°C. Reaction mixtures containing different compositions of BAB and DEA were equilibrated at 30°C and 1500 rpm for 2 hours. The equilibration was monitored iodometrically for two hours. The iodometric determination of unreacted BAB in the reaction mixture at regular time intervals. The pseudo-first-order rate constants $k_1$ calculated were reproducible within ± 3%.

**Kinetic Measurements**

The kinetic runs were carried out in stoppered pyrex glass tubes whose outer surfaces were coated black to eliminate photochemical effects. Requisite amount of the amine substrate, NaClO$_4$, RuCl$_3$, and HCl solutions and water (to maintain a constant total volume of 20 ml for all runs) were taken in the tubes and thermostatically equilibrated in a water bath, set at a given temperature (30 ± 0.1°C). To this solution was added a measured amount of preequilibrated standard BAB solution of known concentration. The progress of the reaction was monitored isodometrically for two half-lives by withdrawing aliquots of the reaction mixture at regular time intervals. The pseudo-first-order rate constants $k_1$ calculated were reproducible within ± 3%.

**Stoichiometry and Product Analysis**

Reaction mixtures containing different compositions of BAB and DEA were equilibrated at 30°C in presence of 6.0 × 10$^{-4}$ mol dm$^{-3}$ HCl and 19.28 × 10$^{-5}$ mol dm$^{-3}$ Ru(III) for 24 hours. The iodometric determination of unreacted BAB in the reaction mixture showed that two moles of BAB were consumed per mole of the DEA according to Eq. (1).

$$\text{C}_3\text{H}_7\text{NH}_2\text{CH}_2\text{H}_2 + 2\text{PH}_{2}\text{SO}_2\text{NBrNa} + 2\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{CHO} + 2\text{PH}_{2}\text{SO}_2\text{NH}_3 + \text{NH}_3 + 2\text{Na}^+ + 2\text{Br}^- \quad (1)$$

The presence of aldehyde which is the oxidation product of DEA in the reaction mixture was detected by preparing its 2,4-dinitrophenylhydrazone derivative and by using Tollens reagent and chromic acid tests [8]. The other product, ammonia, was quantitatively estimated by the standard microkjeldahl procedure. In a typical experiment, $5 \times 10^{-3}$ moles of BAB were mixed with $2 \times 10^{-3}$ moles of diethylamine in a total volume of 20 ml under experimental conditions. The NH$_3$ formed was distilled and absorbed in 2% boric acid solution. It was then titrated against 0.01 M HCl using a mixed indicator (methyl red—bromocresol green). The solution consumed 2.5CC of 0.01M HCl corresponding to the formation of $2.5 \times 10^{-3}$ moles of NH$_3$. The reaction product benzene sulphonamide was detected by paper chromatography, using benzyl alcohol saturated with water as the solvent system with ascending irrigation and using 0.5% vanillin in 1% HCl in ethanol as the spray reagent ($R_f = 0.905$).

**RESULTS**

The reaction performed in the presence of Ru(III) and HCl, under pseudo-first-order conditions of [DEA] > [BAB], gave a linear plot of log [BAB] versus time ($r > 0.9981$). The linearity of these plots together with the constancy of the slope at various [BAB], indicate a first-order dependence of the reaction rate on [BAB]. The pseudo-first-order rate constants, $k_2$, obtained at 303 K are listed in Table I. The reaction rate increased with increase in [DEA], and plot of log $k_2$ versus log [DEA] was linear ($r = 0.998$) with unit slope showing a first-order dependence of the rate on [DEA], (Table I, Fig. 1). At fixed [BAB], and [DEA], the rate of reaction decreased with increase in [HCl] (Table I). The plot of log $k_2$ versus log [HCl] was linear ($r = 0.998$) with slope equal to −0.5, indicating inverse fractional order in [HCl]. Addition of Cl$^-$ or Br$^-$ ions in the form of NaCl or NaBr at known [H$^+$] and ionic strength did not affect the rate. Hence, the dependence of the rate on [HCl] reflected the effect of [H$^+$] only on the reaction. The rate increased with an increase in [Ru(III)] and plot of log $k_2$ versus log[Ru(III)] was linear with unit slope showing a first-order dependence on [Ru(III)] (Table III, Fig. 2). Addition of reaction product benzene sulphonamide ($2.0 \times 10^{-4}$ – $8.0 \times 10^{-4}$ mol dm$^{-3}$) and the variation of ionic strength of the medium by adding

<table>
<thead>
<tr>
<th>Short</th>
<th>Standard</th>
<th>Long</th>
</tr>
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</table>

The variation of ionic strength of the medium by adding

...
Table I Effect of Varying Reactant Concentrations on the Rate

\[ \begin{array}{cccc}
[BAB] \times 10^4 & [DEA] \times 10^2 & k' \times 10^4 (s^{-1}) \\
3.0 & 3.5 & 4.39 (1.01) \\
4.0 & 3.5 & 4.37 (0.96) \\
5.0 & 3.5 & 4.31 (0.99) \\
6.0 & 3.5 & 4.35 (1.02) \\
7.0 & 3.5 & 4.30 (0.97) \\
8.0 & 3.5 & 4.32 (0.98) \\
6.0 & 2.0 & 2.47 (0.57) \\
6.0 & 2.5 & 3.12 (0.69) \\
6.0 & 3.0 & 3.71 (0.86) \\
6.0 & 3.5 & 4.35 (0.98) \\
6.0 & 4.0 & 4.95 (1.14) \\
6.0 & 4.5 & 5.56 (1.28) \\
6.0 & 5.0 & 6.18 (1.38) \\
6.0 & 5.5 & 6.88 (1.53)
\end{array} \]

The values in parenthesis are for the uncatalyzed oxidation of DEA by BAB in HCl medium.

Table II Effect of Varying Hydrogen Ion Concentration on the Reaction Rate

\[ \begin{array}{cccc}
[H^+] \times 10^2 & k' \times 10^4 (s^{-1}) \\
3.0 & 6.85 (1.51) \\
4.0 & 5.73 (1.24) \\
5.0 & 4.96 (1.07) \\
6.0 & 4.35 (0.98) \\
7.0 & 3.93 (0.88) \\
8.0 & 3.60 (0.83) \\
9.0 & 3.35 (0.74) \\
10.0 & 3.15 (0.71)
\end{array} \]

The values in the parenthesis are for the uncatalyzed oxidation of DEA by BAB in presence of HCl.

NaClO₄ (0.01–0.3 mol dm⁻³) had no effect on the reaction rate. The variation of the solvent composition using MeOH (0–15%) did not affect the rate effectively.

The reaction was studied at varying temperatures 298 K to 313 K. The activation parameters, namely

![Figure 1](image-url)
Table III  Effect of Varying [Ru(III)] Catalyst Concentration on the Reaction Rate

<table>
<thead>
<tr>
<th>[Ru(III)] × 10⁹ mol dm⁻³</th>
<th>k' × 10⁻⁵ (s⁻¹)</th>
<th>k₀ × 10⁻⁵ (s⁻¹)</th>
<th>K₀ = k₀/k′</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.82</td>
<td>1.04</td>
<td></td>
<td>1.203</td>
</tr>
<tr>
<td>9.64</td>
<td>2.14</td>
<td></td>
<td>1.562</td>
</tr>
<tr>
<td>14.46</td>
<td>3.24</td>
<td>0.98</td>
<td>1.747</td>
</tr>
<tr>
<td>19.28</td>
<td>4.35</td>
<td></td>
<td>1.842</td>
</tr>
<tr>
<td>24.10</td>
<td>5.42</td>
<td></td>
<td>1.922</td>
</tr>
<tr>
<td>28.92</td>
<td>6.54</td>
<td></td>
<td>2.012</td>
</tr>
<tr>
<td>38.56</td>
<td>8.74</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

DISCUSSION AND MECHANISM

Cady and Connick [9] and Connick and Fine [10] have determined the formula of aqueous ruthenium (III) complex species using the ion exchange resin properties and UV spectral studies. These studies have shown that the octahedral complex species such as [RuCl₆(H₂O)₆]³⁻, [RuCl₅(H₂O)₅]²⁻, [RuCl₄(H₂O)₃]⁻, and [RuCl₃(H₂O)₂]²⁻ do not exist in aqueous solutions of RuCl₃. Other studies have shown that the following equilibrium exists for Ru(III) in acidic solution [11–13]:

\[\text{[RuCl₃(H₂O)]}^⁺ + \text{H₂O} \rightleftharpoons \text{[RuCl₃(H₂O)₂]}^²⁻ + \text{Cl}^⁻ \]  

Singh et al. [14, 15] used the above equilibrium in the ruthenium (III) chloride catalyzed oxidation of primary alcohols by BAB and of ethylene glycols by N-bromocetamide in HClO₄ medium. In the present study, however, the chloride ion has no effect on the rate which indicates that the complex ion [RuCl₃]²⁻ is the reactive catalyst species that interacts with the amine to form a complex intermediate. Similar results were observed in the Ru(III) catalyzed oxidation of chloroacetic acids by bromamine-T (BAT) [16] and bromamine-B [17] and aliphatic primary amines by BAT [18].

Pryde and Soper [19], Morries et al. [20], and Bishop and Jennings [21] have shown the existence of similar equilibrium in acid and alkaline solutions of N-metallo-N-haloarylsulphonamides. Bromamine-B (PhSO₂NBrNa), like chlorine analogue chloramine-T, behaves as a strong electrolyte in aqueous solutions forming different species as shown in Eqs. (3–7).

\[\text{PhSO}_₃\text{NBrNa} \rightleftharpoons \text{PhSO}_₃\text{NBr}^⁺ + \text{Na}^⁺ \]  
\[\text{PhSO}_₃\text{NBr}^⁺ + \text{H}^⁺ \rightleftharpoons \text{PhSO}_₃\text{NBrH}^⁺ \]  
\[2\text{PhSO}_₃\text{NBrH}^⁺ \rightleftharpoons \text{PhSO}_₃\text{NH}^₂ + \text{PhSO}_₃\text{NBr} \]  
\[\text{HOB}⁺ + \text{H}^⁺ \rightleftharpoons \text{H₂OBr}^⁻ \]

In acidic solution, the probable oxidizing species are the free acid (PhSO₃NBr), dibromamine-B (PhSO₃NBr₂), HOB, and H₂OBr⁻.

The involvement of PhSO₃NBr in the mechanism leads to a second-order rate law according to Eq. (8), which is contrary to the experimental observations. As Eq. (5) indicates a slow hydrolysis, if HOB were the primary oxidizing species, a first-order retardation of the rate by the added PhSO₃NH₂ would be expected, contrary to the experimental results. Hardy and Johnston [22], who have studied the pH-dependence of rel-

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Figure 2  Plot of log $k^\circ$ versus log[Ru(III)]. [BAB]$_o$ = $6.0 \times 10^{-4}$ mol dm$^{-3}$; [DEA] = $3.5 \times 10^{-2}$ mol dm$^{-3}$; [H$^+$] = $6.0 \times 10^{-2}$ mol dm$^{-3}$; $\mu$ = 0.3 mol dm$^{-3}$; Temp = 303 K.

Table IV  Temperature Dependence of the Reaction Rate and Activation Parameters of the Oxidation of Diethylamine by Bromamine-B  

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$k \times 10^5$ (S$^{-1}$)</th>
<th>Activation Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>2.71</td>
<td>$E_a$ = 56.8 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>303</td>
<td>4.35</td>
<td>$\Delta H^\circ$ = 54.2 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>308</td>
<td>6.62</td>
<td>$\Delta S^\circ$ = -130 JK$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td>313</td>
<td>10.23</td>
<td>$\Delta G^\circ$ = 94.0 kJ mol$^{-1}$</td>
</tr>
</tbody>
</table>

The second protonation constant for chloramine-T (p-Me-C$_6$H$_4$SO$_2$NHCl) and chloramine-B (C$_6$H$_5$SO$_2$NHCl), respectively.

p-CH$_3$C$_6$H$_4$SO$_2$NHCl + H$^+$ $\rightleftharpoons$ [p-CH$_3$C$_6$H$_4$SO$_2$NH$_2$Cl]$^-$  \hspace{1cm} (8)

C$_6$H$_5$SO$_2$NHCl + H$^+$ $\rightleftharpoons$ [C$_6$H$_5$SO$_2$NH$_2$Cl]$^-$  \hspace{1cm} (9)

The second protonation constant for chloramine-T (p-CH$_3$C$_6$H$_4$SO$_2$NHCl) and chloramine-B (C$_6$H$_5$SO$_2$NHCl) are 102 M$^{-1}$ and 61 ± 5 M$^{-1}$, respectively, at 298 K [23,24]. Gupta [25] believes that the values could be lower than those reported by the above workers. In the present case, the inverse fractional order in [H$^+$] suggests that the deprotonation of PhSO$_2$NHBr results in the formation of PhSO$_2$NHBr, which is likely to be the active oxidant involved in the mechanism of amine oxidation. And the zero effect of the ionic strength indicates that the slow step involves at least one neutral species.

Furthermore, ultraviolet spectral measurements
showed that diethylamine solution has a sharp absorption band at 369 nm while a band around 217 nm was noticed for Ru(III), and 227 nm for BAB solution in presence of 0.06 mol dm$^{-3}$ HCl. A mixture of diethylamine and Ru(III) solution in presence of 0.06 mol dm$^{-3}$ HCl showed an absorption band at 318 nm while for the mixture of BAB and Ru(III) solutions there was no change in the $A_{max}$ at 227 nm, indicating that complex formation takes place only between Ru(III) and substrate. Based on the preceding discussion, a mechanism (Scheme I) is proposed for the reaction.

\[
\text{PhSO}_2\text{NHBr} + \text{H}^+ \rightarrow \text{PhSO}_2\text{NH}^+ + \text{Br}^- \quad \text{(i) fast}
\]

\[
\text{S} + \text{Ru(III)} \rightarrow \text{X} \quad \text{(ii) fast complex}
\]

\[
\text{PhSO}_2\text{NHBr} + \text{X} \rightarrow \text{X}^* + \text{PhSO}_2\text{NH}_2 \quad \text{(iv) fast complex}
\]

\[
\text{X}^* + \text{H}_2\text{O} \rightarrow \text{Products} \quad \text{(v) fast}
\]

**Scheme I**

From the slow step of the preceding Scheme I

\[
\text{rate} = -\frac{d[\text{BAB}]}{dt} = k_{obs}[\text{PhSO}_2\text{NHBr}][\text{X}] \quad (10)
\]

The total effective concentration of BAB, from Scheme I is given by Eq. (11).

\[
[\text{BAB}] = [\text{PhSO}_2\text{NHBr}] + [\text{PhSO}_2\text{NHBr}] \quad (11)
\]

By substituting for [PhSO$_2$NHBr] from equilibrium (i) into Eq. (11) and solving for [PhSO$_2$NHBr], one gets

\[
[\text{PhSO}_2\text{NHBr}] = \frac{k_r [\text{BAB}]}{[\text{H}^+] + K_1} \quad (12)
\]

From Scheme 1 step (ii)

\[
[\text{X}] = \frac{K_r [\text{S}][\text{Ru(III)}]}{[\text{H}^+] + K_1} \quad (13)
\]

Substituting [PhSO$_2$NHBr] and [X] in Eq. (10) we get the rate law Eq. (14).

\[
\text{rate} = -\frac{d[\text{BAB}]}{dt} = \frac{k_{obs} K_r [\text{BAB}][\text{S}][\text{Ru(III)}]}{[\text{H}^+] + K_1} \quad (14)
\]

Which is in good agreement with the experimental results. A detailed mechanism of Ru(III) catalyzed oxidation of DEA by BAB in HCl medium is given in Scheme II. An initial equilibrium involves deprotonation of PhSO$_2$NHBr forming the active oxidizing species of BAB, PhSO$_2$NHBr (step (i) in Scheme I, but not shown in Scheme II). In the next fast pre-equilibrium, the nitrogen atom of the amine coordinates to the metal center of the active catalyst species, [RuCl$_6$]$^{3-}$ to form a loosely bound metal complex anion X (step 1 of Scheme II) trapped in a solvent cage. This is similar to an associative interchange mechanism involving a fast pre-equilibrium in ligand substitution reactions of metal complexes. This kind of loose metal ion substrate complex formation has been used as an intermediate in some studies involving Ru(III) catalyst [11]. Then an electrophilic attack by PhSO$_2$NHBr at the amino nitrogen of X displaces [RuCl$_6$]$^{3-}$ to form the next intermediate species X$^*$ (step (ii) of Scheme II). In step (iii) the intermediate X$^*$ undergoes fast intramolecular rearrangements forming an intermediate X$^*$ and PhSO$_2$NH$_2$. In step (iv), a nucleophilic attack by H$_2$O on the $\alpha$-C$^-$ atom of the C-N bond of the neutral species X$^*$ and intramolecular rearrangements results in the formation of an $\alpha$-hydroxy amine intermediate X$^*$. This intermediate undergoes disproportionation to give acetaldehyde and ethylamine. Ethylamine further undergoes a similar type of oxidation consuming one equivalent of BAB resulting in the formation of CH$_3$CHO and NH$_3$. Overall, one molecule of diethylamine consumes two molecules of BAB for complete oxidation, liberating two molecules of CH$_3$CHO and one molecule of NH$_3$.

Since rate $= k_{obs} [\text{BAB}]$, Eq. (14) can be transformed into Eqs. (15) and (16).

\[
1 = \frac{[\text{H}^+] + K_1}{k_{obs} K_r [\text{S}][\text{Ru(III)}]} \quad (15)
\]

\[
\frac{1}{k_{obs}} = \frac{[\text{H}^+] + K_1}{K_r K_r [\text{S}][\text{Ru(III)}]} + \frac{1}{K_1} \quad (16)
\]

From the plot of $1/k_{obs}$ versus [H$^+$] (Fig. 3) the value of $k_r K_r = 193.2$ and $K_1 = 3.1 \times 10^{-2}$ mol dm$^{-3}$ or protonation constant ($1/K_1 = K_p$) is 32.3 for the spe-
cies PhSO$_2$NHBr were evaluated from the intercept and slope, respectively. The protonation constant value obtained is in good agreement with the previously published work [18] which gives an indirect evidence for the proposed mechanism of the Scheme I.

It has been pointed out by Moelwyn and Hughes [26] that in the presence of the catalyst, the uncatalyzed and catalyzed reactions proceed simultaneously so that

$$k_1 = k_o + K_c \text{[catalyst]}$$

Successive addition of the catalyst brings about proportionate increase in the observed velocity, 'x' is unity and $K_c$ becomes a bimolecular constant. In the present study it has been found that the value of the rate constant is directly proportional to the concentration of the catalyst Ru(III) ion and therefore 'x' is unity and the relation will be

$$k_1 = k_o + K_c \text{[Ru(III)]}$$

Where $k_o$ is observed pseudo-first-order rate constant in the presence of the catalyst Ru(III), $k_1$ is the
OXIDATION OF DIETHYLAMINE BY N-SODIO-N-BROMOBENZENE SULPHONAMIDE

Figure 3  Plot of $1/k$ versus $[\text{H}^+]$ [BAB]$_0 = 6.0 \times 10^{-4}$ mol dm$^{-3}$; [DEA]$_0 = 3.5 \times 10^{-2}$ mol dm$^{-3}$; [Ru(III)] = 19.28 $\times$ 10$^{-3}$ mol dm$^{-3}$; $\mu = 0.3$ mol dm$^{-3}$; Temp = 303 K.

pseudo-first-order rate constant for the uncatalyzed reaction and $K_c$ is the catalytic constant. The values of $K_c$ obtained from

$$K_c = \frac{k_1 - k_o}{[\text{Ru(III)}]}$$

are found fairly constant and are given in Table III.

Variation of dielectric constant (D) of medium does not effect the rate. An explanation can be offered in terms of the Born treatment applied by Laidler [27] for dipole-dipole reaction.

$$\ln k' = \ln k_o + \frac{3}{2}kT (2/D-1) \mu_A^2/r_A^4 + \mu_B^2/r_B^4 - \mu_M^2/r_M^4$$  (17)

In Eq. (17) $k_o$ is the rate constant in a medium of infinite dielectric constant and $\mu$ and $r$ refer to the dipole moments and radii of reactants A and B and activated complex. It is seen from Eq. (17) that rates should be higher in a medium of lower dielectric constant when $r_A > r_B > r_M$ indicating that the extent of charge dispersal in the transition state is different. On the other hand $r_A > r_M > r_B$ implies the absence of dielectric effect of the solvent on rate as was observed in the present investigation.

BIBLIOGRAPHY