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. © 1999 John Wiley & Sons, Inc. Int J Chem Kinet 31: 744–752, 1999

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-bromopthalamide (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-Nhaloarysulphonamides. Mechanistic studies of the oxidation of diverse organic substrates by these organic

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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 iodometrically and through IR and NMR spectral data. Aqueous solution of BAB was prepared, standardized by the iodometric method and preserved in amber colored bottles. Analar grade diethylamine (E. Merck) was used and aqueous solution of the substrate was prepared. Solution of RuCl₃ (Arora Matthey) in 0.5 mol dm⁻³ HCl was used as catalyst in acid solution. Allowance was made for the amount of HCl present in the catalyst solution while preparing solutions for kinetic runs. All other chemicals used were of accepted grades of purity. Triply distilled water was used for preparing aqueous solutions. Ionic strength of reaction mixture was kept at a high value with a concentrated solution of NaClO₄ (E. Merck).

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, NaClO₄, RuCl₃, and HCl solutions and water (to maintain a constant total volume for all runs) were taken in the tubes and thermally equilibrated in a water bath, set at a given temperature ($30 \pm 0.1^{\circ}$ C). To this solution was added a measured amount of preequilibrated standard BAB solution of known concentration. The progress of the reaction was monitored iodometrically for two half-lives by withdrawing aliquots of the reaction mixture at regular time intervals. The pseudo-first-order rate constants k' calculated were reproducible within $\pm 3\%$.

Stoichiometry and Product Analysis

Reaction mixtures containing different compositions of BAB and DEA were equilibrated at 30°C in presence of 6.0×10^{-2} 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).

$$C_{2}H_{5}NHC_{2}H_{5} + 2PhSO_{2}NBrNa + 2H_{2}O$$

$$\longrightarrow 2CH_{3}CHO + 2PhSO_{2}NH_{2}$$

$$+ NH_{3} + 2Na^{+} + 2Br \quad (1)$$

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 microkjeldhal procedure. In a typical experiment, 5×10^{-5} moles of BAB were mixed with 2×10^{-3} moles of diethylamine in a total volume of 20 ml under experimental conditions. The NH₃ 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 10⁻⁵ moles of NH₃. The reaction product benzenesulphonamide 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 $[DEA] \gg [BAB]$, 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', obtained at 303 K are listed in Table I. The reaction rate increased with increase in [DEA], and plot of log k' versus log [DEA]_o was linear (r = 0.998) with unit slope showing a first-order dependence of the rate on [DEA]_o (Table I, Fig. 1). At fixed [BAB]_o and [DEA], the rate of reaction decreased with increase in [HCl] (Table II). The plot of $\log k'$ 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 $\log k'$ 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 benzenesulphonamide $(2.0 \times 10^{-4} - 8.0 \times 10^{-4} \text{ mol dm}^{-3})$ and the variation of ionic strength of the medium by adding

DEA by BAB in HCl medium.

 Table I
 Effect of Varying Reactant Concentrations on the Rate

$\begin{array}{l} [\text{BAB}] \times 10^4 \\ \text{mol } \text{dm}^{-3} \end{array}$	$\begin{array}{l} \text{[DEA]}\times10^2\\ \text{mol dm}^{-3} \end{array}$	$k^\prime imes 10^4~({ m s}^{-1})$
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)

 $[H^+] = 6.0 \times 10^{-2} \text{ mol dm}^{-3}, [Ru(III)] = 19.28 \times 10^{-5}$ mol dm⁻³, $\mu = 0.3$ mol dm⁻³, Temp = 303 K

Table II	Effect of Varying	Hydrogen Ion	Concentra-
tion on th	e Reaction Rate		

 $[BAB]_{o} = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[DEA] = 3.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[Ru(III)] = 19.28 \times 10^{-5} \text{ mol dm}^{-3}$, $\mu = 0.3 \text{ mol dm}^{-3}$, Temp = 303 K

$[\mathrm{H^{+}}] \times 10^{2} \mathrm{~mol~dm^{-3}}$	$k^\prime imes 10^4~({ m s}^{-1})$
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)

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

NaCIO₄ (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 Plot of logk' versus log [DEA] [BAB]₀ = 6.0×10^{-4} mol dm⁻³; [H⁺] = 6.0×10^{-2} mol dm⁻³; [Ru(III)] = 19.28 $\times 10^{-5}$ mol dm⁻³; $\mu = 0.3$ mol dm⁻³ Temp = 303 K.

$[{ m H}^+]=6.0 imes 10^{-2}~{ m mol}~{ m dm}^{-3},~\mu=0.3~{ m mol}~{ m dm}^{-3},~{ m Temp}=303~{ m K}$			
$\frac{[\text{Ru(III)}] \times 10^5}{\text{mol dm}^{-3}}$	$k' imes 10^4 ({ m s}^{-1})$	$k_{ m o} imes 10^4 ({ m s}^{-1})$	$\mathrm{K_{c}} = \frac{k_{1} - k_{\mathrm{o}}}{[\mathrm{Ru(III)}]}$
4.82	1.04	\uparrow	_
9.64	2.14		1.203
14.46	3.24		1.562
19.28	4.35	0.98	1.747
24.10	5.42	I	1.842
28.92	6.54		1.922
38.56	8.74	\downarrow	2.012

Table IIIEffect of Varying [Ru(III)] Catalyst Concentration on the Reaction Rate $[BAB]_{o} = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$, [DEA] = $3.5 \times 10^{-2} \text{ mol dm}^{-3}$,

energy of activation (Ea), enthalpy of activation (ΔH^{\neq}) , entropy of activation (ΔS^{\neq}) and free energy of activation (ΔG^{\neq}) were obtained from the Arrhenius plot of log k' versus 1/T, which was linear. The kinetic and activation parameters data obtained were presented in Table IV.

The reaction was also studied in the absence of Ru(III). Under pseudo-first-order conditions of $[DEA] \gg [BAB]$, a linear plot of log [BAB] time was obtained. The linearity of this plot, together with the constancy of the slope at various $[BAB]_o$, indicates a first-order dependence of the reaction rate on [BAB]. Similar results were observed for the variation of [DEA] and [HCI] as in the case of oxidation of DEA by BAB in presence of Ru(III) catalyst. The rate constants k' obtained at 303 K are listed in Tables I and II.

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 $[RuCl_5(H_2O)]^{-2}$, $[RuCl_4(H_2O)_2]^{-1}$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$, and $[RuCl(H_2O)_5]^{+2}$ 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].

$$[\operatorname{RuCl}_6]^{3-} + \operatorname{H}_2O \Longrightarrow [\operatorname{RuCl}_5(\operatorname{H}_2O)]^{2-} + \operatorname{Cl}^{-} (2)$$

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 Nbromoacetamide in $HClO_4$ medium. In the present study, however, the chloride ion has no effect on the rate which indicates that the complex ion $[RuCl_6]^{3-}$, 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-haloary1-sulphonamides. 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).

$$PhSO_2NBrNa \Longrightarrow PhSO_2NBr^- + Na^+ \qquad (3)$$

$$PhSO_2NBr^- + H^+ \Longrightarrow PhSO_2NHBr$$
 (4)

 $PhSO_2NHBr + H_2O \Longrightarrow PhSO_2NH_2 + HOBr$ (5)

$$2PhSO_2NHBr \Longrightarrow PhSO_2NH_2 + PhSO_2NBr_2 \quad (6)$$

$$HOBr + H^{+} \rightleftharpoons H_{2}OBr^{+}$$
(7)

In acidic solution, the probable oxidizing species are the free acid (PhSO₂NHBr), dibromamine-B (PhSO₂NBr₂), HOBr, and H_2OBr^+ .

The involvement of $PhSO_2NBr_2$ 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 HOBr were the primary oxidizing species, a first-order retardation of the rate by the added $PhSO_2NH_2$ would be expected, contrary to the experimental results. Hardy and Johnston [22], who have studied the pH-dependence of rel-



Figure 2 Plot of logk' versus log[Ru(III)]. [BAB]₀ = 6.0×10^{-4} mol dm⁻³; [DEA] = 3.5×10^{-2} mol dm⁻³; [H⁺] = 6.0×10^{-2} mol dm⁻³; $\mu = 0.3$ mol dm⁻³; Temp = 303 K.

ative concentrations of the species present in acidified chloramine-T solution of comparable molarities, have shown that $PhSO_2NHBr$ is the likely oxidizing species in acid medium. Narayanan and Rao [23] and Subhashini et al. [24] have reported that monohaloamines can be further protonated at $pH \ll 2$ as shown in the

Table IVTemperature Dependence of the ReactionRate and Activation Parameters of the Oxidation ofDiethylamine by Bromamine-B

 $\begin{array}{l} [\text{BAB}]_{o} = 6.0 \times 10^{4} \text{ mol } \text{dm}^{-3}, \ [\text{DEA}] = 3.5 \times 10^{-2} \\ \text{mol } \text{dm}^{-3} \\ [\text{H}^{+}] = 6.0 \times 10^{-2} \text{ mol } \text{dm}^{-3}, \ [\text{Ru}(\text{III})] = 19.28 \times 10^{-5} \\ \text{mol } \text{dm}^{-3} \end{array}$

μ = 0.3 mol dm ⁻³ , Temp = 30	13	К
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Temperature (K)	$k imes 10^4 (\mathrm{S}^{-1})$	Activation Parameters
298	2.71	$Ea = 56.8 \text{ kJ mol}^{-1}$
303	4.35	$\Delta H^{\neq} = 54.2 \text{ kJ mol}^{-1}$
308	6.62	$\Delta S^{\neq} = -130 \text{ JK}^{-1} \text{ mol}^{-1}$
313	10.23	$\Delta G^{\neq} = 94.0 \text{ kJ mol}^{-1}$

following Eqs. (8) and (9) for chloramine-T (p-Me- $C_6H_4SO_2NHCl$) and chloramine-B ($C_6H_4SO_2NHCl$), respectively.

$$C_6H_5SO_2NHCl + H^+ \rightleftharpoons [C_6H_5SO_2NH_2Cl]^+ \quad (9)$$

The second protonation constant for chloramine-T (p-CH₃-C₆H₄SO₂NHCl) and chloramine-B (C₆H₅-SO₂NHCl) are 102 M⁻¹ and 61 \pm 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 PhSO₂NH₂Br results in the formation of PhSO₂NHBr, species 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 λ_{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.

$$PhSO_2NH_2Br \xrightarrow{K_1} PhSO_2NHBr + H^+ \quad (i) \text{ fast}$$

$$S + Ru(III) \xrightarrow{K_2} X$$
 (ii) fast complex

 $PhSO_2NHBr + X \xrightarrow{k_3} X' complex + Ru(III) (iii) slow$

$$X' \longrightarrow X'' + PhSO_2NH_2$$
 (iv) fast
complex

$$X'' + H_2O \longrightarrow Products$$
 (v) fast

Scheme I

From the slow step of the preceding Scheme I

rate =
$$\frac{-d[BAB]_t}{dt} = k_3[PhSO_2NHBr] [X]$$
 (10)

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

$$[BAB]_{t} = [PhSO_{2}^{+}NH_{2}Br] + [PhSO_{2}NHBr] \quad (11)$$

By substituting for [PhSO₂NH₂Br] from equilibrium (i) into Eq. (11) and solving for [PhSO₂NHBr], one gets

$$[PhSO_2NHBr] = \frac{K_1[BAB]_t}{[H^+] + K_1}$$
(12)

From Scheme 1 step (ii)

$$[X] = K_2[S] [Ru(III)]$$
(13)

Substituting [PhSO₂NHBr] and [X] in Eq. (10) we get the rate law Eq. (14).

rate =
$$\frac{-d[BAB]_{t}}{dt}$$
$$= \frac{K_{1}K_{2}k_{3}[BAB]_{t}[S][Ru(III)]}{[H^{+}] + K_{1}}$$
(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 PhSO₂NH₂Br forming the active oxidizing species of BAB, PhSO₂NHBr (step (i) in Scheme I, but not shown in Scheme II). In the next fast preequilibrium, the nitrogen atom of the amine coordinates to the metal center of the active catalyst species, [RuCl₆]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 PhSO₂NHBr at the amino nitrogen of X displaces $[RuCl_6]^{3-}$ to form the next intermediate species X¹ [step (ii) of Scheme II]. In step (iii) the intermediate X' undergoes fast intramolecular rearrangements forming an intermediate X" and PhSO₂NH₂. In step (iv), a nucleophilic attack by H₂O on the α -C^{δ +} atom of the C-N bond of the neutral species X" and intramolecular rearrangements results in the formation of an α -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 CH₃CHO and NH₃. Overall, one molecule of diethylamine consumes two molecules of BAB for complete oxidation, liberating two molecules of CH₃CHO and one molecule of NH₃.

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

$$\frac{1}{k_{\rm obs}} = \frac{[{\rm H}^+] + K_1}{K_1 K_2 k_3 \,[{\rm S}] \,[{\rm Ru}({\rm III})]}$$
(15)

$$\frac{1}{k_{\rm obs}} = \frac{[{\rm H}^+]}{K_1 K_2 k_3 \,[{\rm S}] \,[{\rm Ru}({\rm III})]} + \frac{1}{K_2 k_3 \,[{\rm S}] \,[{\rm Ru}({\rm III})]} \quad (16)$$

From the plot of $1/k_{obs}$ versus [H⁺] (Fig. 3) the value of $K_2k_3 = 193.2$ and $K_1 = 3.1 \times 10^{-2}$ mol dm⁻³ or protonation constant ($1/K_1 = \text{Kp}$) is 32.3 for the spe-











cies PhSO₂NHBr 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

$$k_1 = k_0 + K_c [\text{catalyst}]^{\times}$$

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

$$k_1 = k_0 + K_c \left[\text{Ru(III)} \right]$$

Where k_1 is observed pseudo-first-order rate constant in the presence of the catalyst Ru(III), k_0 is the



Figure 3 Plot of 1/k' versus [H⁺] [BAB]₀ = 6.0×10^{-4} mol dm⁻³; [DEA] = 3.5×10^{-2} mol dm⁻³; [Ru(III)] = 19.28×10^{-5} 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

$$Kc = \frac{k_1 - k_o}{[Ru(III)]}$$
 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.

Ink' = Ink_∞ + 3/8kT (2/D-1)
$$\mu_A^2/r_A^3$$

+ $\mu_B^2/r_B^3 - \mu_{\neq}^3/r_{\neq}^3$ (17)

In Eq. (17) k_{∞} is the rate constant in a medium of infinite dielectric constant and μ 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 $r_{\mu}{}^3 > r_A{}^3 + r_B{}^3$ indicating that the extent of charge dispersal in the transition state is different. On the other hand $r_{\mu}{}^3 \approx r_A{}^3 + r_B{}^3$ implies the absence of dielectric effect of the solvent on rate as was observed in the present investigation.

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