CHAPTER IX

KINETICS OF OXIDATION OF EPHEDRINE BY BROMAMINE-T IN HClO₄ AND NaOH MEDIA: A MECHANISTIC STUDY
Section 9.1

OXIDATION OF Ephedrine: A REVIEW

Ephedrine (EPH) is a sympathomemetic amine used as stimulant, appetite suppressant, and concentration aid, and to treat hypertension associated with regional anesthesia\(^1,2\). It is also useful as a pressor agent in hypotensive states following sympathectomy. Because of its importance, several analytical procedures are reported in the literature for the determination of EPH in pharmaceuticals\(^3^6\).

Fujita Toshiki and Hayakari Makoto\(^7\) have investigated the mixture of ephedrine and methamphetamine was treated with metaperiodate. Ephedrine hydrochloride alone was specifically oxidized to benzaldehyde, and the decrease in metaperiodate was determined by iodometry.

Walash M I et al\(^8\) have reported the determination of ephedrine, norephedrine, and methylidopa by new oxidimetric titrants, bromamine T, dibromohydantoin, N-bromophthalimide, and N-bromosuccinimide.

Colorimetric determination of ephedrine with periodic acid has reported by Chang, Yu-hung\(^9\). The oxidation product of ephedrine hydrochloride with periodate at pH 7.2 was absorbed in concentrated H\(_2\)SO\(_4\) and the color developed with p-hydroxybiphenyl.

Popov, D. M. et al\(^10\) have reported the chromato spectrophotometric determination of ephedrine hydrochloride.

Quantitative determination and photo degradation of ephedrine in aqueous solution has reported by Usmanghani, K. et al\(^11\). It is reported that photo degradation of ephedrine hydrochloride at pH 7 gave benzaldehyde, 2, 5-diphenyl-3, 4-dimethyltetrahydrooxazole and some unknown compounds. The reaction which is pseudo-1st order was followed by non aqueous titration with HClO\(_4\) and by an ion-exchange method.

Survey of literature reveals that, there was no information on the oxidation kinetics of EPH with any oxidant. In the light of the available information, the present paper reports for the first time a detailed kinetics of oxidation of EPH with BAT in acidic and alkaline media.
Section 9.2

KINETICS OF OXIDATION OF EPHEDRINE BY BROMAMINE-T IN HClO₄ AND NaOH MEDIA

The kinetics and mechanism of oxidation of ephedrine by BAT in the presence of HCl and NaOH media at 313K and 303K respectively is reported in this section.

The details about the preparation of reagents and experimental procedures are reported in Section 1.8 of Chapter 1.

Stoichiometry

Varying ratios of BAT to EPH reaction mixture in presence of $5 \times 10^{-2}$ mol dm$^{-3}$ HClO$_4$ and $4 \times 10^{-4}$ mol dm$^{-3}$ of NaOH at 313 K and at 303 K respectively were equilibrated for 48 hrs. Estimation of unreacted BAT in the reaction mixture showed that one mole of EPH consumed one mole of oxidant in both media confirming the following stoichiometry:

$$C_{10}H_{15}NO + RNBrNa + H_2O \rightarrow C_7H_6O + C_2H_4O + CH_3NH_2 + RNH_2 + Na^+ + Br^-$$ (9.1)

Where R= p-CH$_3$C$_6$H$_4$SO$_2$.

Product analysis

After the completion of reaction, the reaction products were neutralized with acid/alkali and extracted with diethyl ether. The oxidation products were purified by brine solution and recrystallized. Then these were isolated and subjected to spot tests and chromatographic analysis (TLC technique). The products were identified as benzaldehyde, acetaldehyde, methyl amine and $p$-toluenesulfonamide.

The reduction product of the oxidant $p$-toluenesulfonamide (PTS) was detected by paper chromatography. Benzyl alcohol saturated with water was used as solvent with 0.5 % vanillin in 1 % HCl solution in ethanol as spray reagent. Presence of PTS was also confirmed by its IR stretching bands at 3365 cm$^{-1}$ and 3275 cm$^{-1}$ for N-H bands and at 1310 cm$^{-1}$ and 1160 cm$^{-1}$ for S=O bands.
The aldehyde was detected by 2, 4-DNP derivative and by conventional spot tests. Furthermore the presence of aldehyde was confirmed by IR and $^1$H NMR spectral data. The IR spectra showed a band at 1696 cm$^{-1}$ for aldehyde (C=O) group, 3073 cm$^{-1}$ for alkyl C-H stretch and 2745 and 2827 cm$^{-1}$ for aldehyde C-H stretches confirms the presence of benzaldehyde. It was further confirmed by $^1$H NMR spectral studies. $^1$H NMR (CDCl$_3$): $\delta$ 9.87 (s, 1H), 7.81 (d, 2H), 7.45(dd, 2H), 7.54 (dd, 1H). $^1$H NMR spectra was recorded using AMX-400 NMR spectrometer. The other oxidation products, acetaldehyde was identified by iodoform and nitroprusside test$^{13}$ and methylamine was confirmed by spot tests.

RESULTS

The kinetics of oxidation of EPH with BAT has been kinetically investigated at different initial concentrations of reactants in the presence of HClO$_4$ at 313K or NaOH at 303K. For the sake of convenience the salient features obtained in these two media is discussed separately.

KINETICS OF OXIDATION IN ACID MEDIUM

Effects of EPH and BAT

With the [EPH] in excess at constant [HClO$_4$], [NaClO$_4$] and temperature, the [BAT]$_0$ was varied. Plots of log [BAT]$_0$ versus time were linear ($r > 0.994$) indicating a first-order dependence of the rate on [BAT]$_0$. The pseudo-first-order rate constants ($k$) calculated from the slopes of the above plots are given in Table 9.1. Further the values of $k$ are unaltered with variation of [BAT]$_0$ confirming the first-order dependence of the rate on [BAT]$_0$. Under the similar experimental conditions an increase in [EPH]$_0$ increased the $k$ values (Table 9.1). Plots of log $k$ versus log [EPH] was linear (Fig.9.1; $r = 0.994$) with a slope of 0.70 indicating a fractional-order dependence on [EPH]$_0$.

Effect of varying [HClO$_4$]

The rate increased with increasing [HClO$_4$] (Table 9.1), and a plot of log $k$ versus log [HClO$_4$] was linear (Fig.9.2; $r = 0.995$) with a slope of 0.43 indicating a fractional-order dependence of the rate on [H$^+$].
Effect of added p-toluene sulfonamide (PTS) and halide ions

Addition of the reduction product of BAT, p-toluene sulfonamide (PTS) had no effect on the rate, indicating that the PTS do not involve in a pre-equilibrium step prior to the rate determining step. (Table 9.2). Addition of chloride or bromide ions in the form of NaCl or NaBr ($2 \times 10^{-3} - 1 \times 10^{-2}$ mol dm$^{-3}$) has negligible effect on the rate of the reaction (Table 9.2).

Effect of varying ionic strength and dielectric permittivity

The reaction rate remained unchanged by varying ionic strength of the medium through addition of NaClO$_4$ (0.1–1.0 mol dm$^{-3}$) (Table 9.3). The dielectric permittivity of the medium was varied by adding different proportions (0 – 40 % v/v) of CH$_3$OH to the reaction mixture. The rate increased with increasing methanol content (Table 9.3). A plot of log $k'$ versus $1/D$, where $D$ is the dielectric permittivity of the medium, gave a straight line (Fig. 9.3; $r = 0.998$) with a positive slope. (The $D$ values are obtained from the literature). Blank experiments showed that CH$_3$OH was oxidized slightly (<3%) by the oxidants under the present experimental conditions. This was corrected for the calculation of net reaction rate constant for the oxidation of EPH by BAT.

Effect of Temperature and test for free radicals

The reaction was studied at different temperatures (303K - 323K) (Table 9.4), keeping other experimental conditions constant. From the linear Arrhenius plot of log $k'$ versus $1/T$ (Fig. 9.4; $r = 0.991$), activation energy and other thermodynamic parameters for the composite reaction were computed. The results are compiled in Table 9.4. Addition of aqueous acrylonitrile monomer solution to the reaction mixture in an inert atmosphere did not initiate polymerization indicating the absence of free radical species in the reaction sequence.
KINETICS OF OXIDATION IN ALKALINE MEDIUM

Effect of EPH and BAT

Under pseudo-first-order condition, at constant [OH⁻], [NaClO₄] and temperature, the [BAT]₀ was varied. Plots of log [BAT]₀ versus time were found linear (r > 0.997) indicating a first-order dependence of the rate on [BAT]₀. The pseudo-first-order rate constants (k') calculated from the slopes are given in Table 9.5. The values of k' are unaltered with variation of [BAT]₀ confirming the first-order dependence of the rate on [BAT]₀. Under similar experimental conditions an increase in [EPH]₀ increased the rate (Table 9.5). Plot of log k' versus log [EPH] was linear (Fig. 9.1; r = 0.998) with a slope of 0.38 indicating a fractional-order dependence on [EPH].

Effect of varying [OH⁻]

The rate increased with increasing [OH⁻] (Table 9.5), and a plot of log k' versus log [OH⁻] was linear (Fig. 9.5; r = 0.996) with a slope of 0.77 indicating a fractional-order dependence of the rate on [OH⁻].

Effect of added p-toluene sulfonamide (PTS) and halide ions

Addition of reduced product of BAT, PTS (1 × 10⁻³ – 1 × 10⁻² mol dm⁻³) to the reaction mixture had no effect on the rate (Table 9.2) indicating that it is not involved in any pre-equilibrium step. Addition of NaCl or NaBr (2 × 10⁻³ - 1 × 10⁻² mol dm⁻³) has negligible effect on the rate of the reaction (Table 9.2).

Effect of varying ionic strength and dielectric permittivity

The reaction rate was not affected by varying the ionic strength of the medium (0.1 – 1.0 mol dm⁻³) (Table 9.3). The rate increased with increasing CH₃OH (0 – 40 %) content of the reaction mixture (Table 9.3). A plot of log k' versus 1/D was linear (Fig. 9.3; r = 0.997) with a positive slope. Under the present experimental conditions, methanol was oxidized slightly (<3%) by the oxidants. This was corrected for the calculation of net reaction rate constant for the oxidation of EPH by BAT.
Effect of Temperature and test for free radicals

Kinetic and thermodynamic parameters were calculated by studying the reaction at different temperatures (293 – 313 K) (Table 9.4). A plot of log \( k' \) versus \( 1/T \) was linear (Fig.9.4; \( r = 0.998 \)), and the results are given in Table 9.4. Addition of the reaction mixture to an acrylamide monomer did not initiate polymerization indicating the absence of free radicals.
### Table 9.1

Effect of varying concentrations of BAT, EPH and HClO₄ concentrations on rate

<table>
<thead>
<tr>
<th>10⁴[BAT] (mol dm⁻³)</th>
<th>10³[EPH] (mol dm⁻³)</th>
<th>10³[HClO₄] (mol dm⁻³)</th>
<th>k '10⁴ (s⁻¹)</th>
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</thead>
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<td>5.0</td>
<td>50.0</td>
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μ = 0.8 mol dm⁻³; T = 313K

### Table 9.2

Effect of varying concentrations of p-toluenesulfonamide, NaCl and NaBr on rate

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<th>[PTS]x10³ mol dm⁻³</th>
<th>10⁴k¹(s⁻¹) *Acid</th>
<th>10³[NaCl] mol dm⁻³</th>
<th>10⁴k²(s⁻¹) *Acid</th>
<th>10³[NaBr] mol dm⁻³</th>
<th>10⁴k³(s⁻¹) *Acid</th>
<th>10³[NaOH] mol dm⁻³</th>
<th>10⁴k₄(s⁻¹) *Acid</th>
<th>10³[NaOH] mol dm⁻³</th>
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<td>1.56</td>
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* [BAT]₀ = 5×10⁻⁴ mol dm⁻³, [EPH]₀ = 5×10⁻³ mol dm⁻³, [HClO₄] = 5×10⁻² mol dm⁻³, μ = 0.8 mol dm⁻³; T = 313K; # [BAT]₀ = 1×10⁻³ mol dm⁻³, [EPH]₀ = 1×10⁻² mol dm⁻³, [NaOH] = 4×10⁻⁴ mol dm⁻³, μ = 0.8 mol dm⁻³, T = 303K.
Table 9.3

Effect of Solvent composition on the reaction rate

<table>
<thead>
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<th>CH₃OH (%, v/v)</th>
<th>D</th>
<th>10⁴ (k'(s^{-1})) *Acid</th>
<th>#Alkaline</th>
<th>(\mu)</th>
<th>10⁴ (k'(s^{-1})) *Acid</th>
<th>#Alkaline</th>
</tr>
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<tr>
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<td>1.0</td>
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<td>4.39</td>
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* \([\text{BAT}]_0 = 5 \times 10^{-4} \text{mol dm}^{-3}, [\text{EPH}]_0 = 5 \times 10^{-3} \text{mol dm}^{-3}, [\text{HClO}_4] = 5 \times 10^{-2} \text{mol dm}^{-3}, T = 313 \text{K}.*

# \([\text{BAT}]_0 = 1 \times 10^{-3} \text{mol dm}^{-3}, [\text{EPH}]_0 = 1 \times 10^{-2} \text{mol dm}^{-3}, [\text{NaOH}] = 4 \times 10^{-4} \text{mol dm}^{-3}, T = 303 \text{K}.*
Table 9.4

Effect of varying temperature on the reaction rate constant and activation parameters for the oxidation of EPH with BAT

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>Acid</th>
<th>Temperature(K)</th>
<th>Alkaline</th>
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Activation Parameters

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<td>ΔS^o (JK^-1 mol^-1)</td>
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* [BAT] = 5 × 10^-4 mol dm^-3; [EPH] = 5 × 10^-3 mol dm^-3; [HClO₄] = 5 × 10^-2 mol dm^-3; μ = 0.8 mol dm^-3.
# [BAT] = 1 × 10^-3 mol dm^-3; [EPH] = 1 × 10^-2 mol dm^-3; [NaOH] = 4 × 10^-4 mol dm^-3; μ = 0.8 mol dm^-3.
Table 9.5

Effect of varying concentrations of BAT, EPH and NaOH concentrations on the reaction rate

<table>
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<tr>
<th>$10^3$ [BAT] (mol dm$^{-3}$)</th>
<th>$10^3$ [EPH] (mol dm$^{-3}$)</th>
<th>$10^4$ [NaOH] (mol dm$^{-3}$)</th>
<th>$\kappa 10^4$ (s$^{-1}$)</th>
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$\mu = 0.8$ mol dm$^{-3}$; $T = 303$K.
Table 9.6

Effect of varying [EPH] at different temperatures in acidic and alkaline media

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<tr>
<th>$10^3$[EPH] mol dm$^{-3}$</th>
<th>*Acidic $10^4 k'(s)^{-1}$</th>
<th>#Alkaline $10^4 k'(s)^{-1}$</th>
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* [BAT] = $5 \times 10^{-4}$ mol dm$^{-3}$, [HClO$_4$] = $5 \times 10^{-2}$ mol dm$^{-3}$; $\mu = 0.8$ mol dm$^{-3}$.

# [BAT] = $1 \times 10^{-3}$ mol dm$^{-3}$, [NaOH] = $4 \times 10^{-4}$ mol dm$^{-3}$; $\mu = 0.8$ mol dm$^{-3}$. 
Table 9.7

Values of $k_3$ and $k_7$ at different temperatures and values of thermodynamic and activation parameters for rate determining step in acidic and alkaline reactions

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<td></td>
<td>318</td>
</tr>
</tbody>
</table>

* $[\text{BAT}] = 5 \times 10^{-4}$ mol dm$^{-3}$; $[\text{HClO}_4] = 5 \times 10^{-2}$ mol dm$^{-3}$; $\mu = 0.8$ mol dm$^{-3}$.

# $[\text{BAT}] = 1 \times 10^{-3}$ mol dm$^{-3}$; $[\text{NaOH}] = 4 \times 10^{-4}$ mol dm$^{-3}$; $\mu = 0.8$ mol dm$^{-3}$.
Fig. 9.1 Plot of log$k'$ versus log[PEH] + log[EPH]

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Fig. 9.2 Plot of log$k'$ versus log[NaOH]

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Fig. 9.2 Plot of log$k'$ versus log[HCIO₄]
Fig. 9.3 Plot of log$k'$ versus $1/D$  $10^2/D$

Fig. 9.4 Plot of log$k'$ versus $1/T$  $10^3/T$
Fig. 9.5 Plot of log$k'$ versus log[OH$^-$] $+$ log[OH$^+$]

Fig. 9.6 Plot of $1/k'$ versus $1/[EPh]$ 

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Fig. 9.7 Plot of $1/k'$ versus $1/[H^+]$.

Fig. 9.8 Plot of $\log k_j$ and $\log k_\alpha$ versus $1/T$.
Fig. 9.9 Plot of $1/k'$ versus $1/[EPH]$

Fig. 9.10 Plot of $1/k'$ versus $1/[EPH]$
DISCUSSION

The reactive species of BAT responsible for oxidizing character depend on the pH of the medium\(^{17}\). The work of Pryde and Soper\(^{18}\), Morris et al\(^{19}\), Bishop and Jennings\(^{20}\) and conductometric and pH titrations of CAT with HCl and H\(_2\)SO\(_4\) solutions\(^{21,22}\) indicated the existence of the many equilibria in acid and alkaline solutions of CAT and it can be extended to BAT since it is identical with that of CAT.

*Mechanism and rate law in acid medium*

The possible oxidizing species in acidified BAT solutions are RNHBr, RNBr\(_2\), HOBr and possibly H\(_2\)OBr\(^{+}\). RNBr\(_2\) can be ruled out as the reactive species, since it predicts the second-order dependence on [BAT]\(_0\), which is not in agreement with the experimental results, since a first-order with respect to [BAT]\(_0\) was noticed. If HOBr acts as a reactive oxidant species, a first-order retardation of the rate on added PTS was expected. However, no such effect was noticed. Based on the equilibrium, disproportionation and hydrolysis constants of reactions, Bishop and Jennings\(^{20}\), as a first approximation, have calculated the concentrations of different species in 0.05 mol dm\(^{-3}\) of CAT solution at different pH. The acid form of CAT (CH\(_3\)C\(_6\)H\(_4\)SO\(_2\)NHCl) was found to be the predominant species under acidic conditions. In view of similarity in properties of CAT and BAT, similar argument can be extended to BAT solutions. Further, the rate of reaction was accelerated by H\(^+\) ions and therefore RNHBr can be assumed to be the active oxidizing species of BAT under the present experimental conditions. Based on the experimental results and preceding discussion, a suitable scheme 9.1 has been proposed for the oxidation of EPH with BAT in acid medium,

\[
\begin{align*}
\text{RNBr}^- + \text{H}^+ & \overset{k_1}{\rightleftharpoons} \text{RNHBr} & \text{fast (i)} \\
\text{RNHBr} + \text{EPH} & \overset{k_2}{\rightarrow} \text{X} & \text{fast (ii)} \\
\text{X} & \overset{k_3}{\rightarrow} \text{X}' & \text{slow and r.d.s (iii)} \\
\text{X}' + \text{H}_2\text{O} & \overset{k_4}{\rightarrow} \text{products} & \text{fast (iv)}
\end{align*}
\]

*Scheme 9.1*
In Scheme 9.1, EPH is the substrate, X and X' are the complex intermediate species whose structures are shown in Scheme 9.3.

From the slow step of Scheme 1,

\[
rate = \frac{-d[BAT]}{dt} = k_3[X]
\]  
\hspace*{1cm} (9.2)

If \([BAT]_t\) represents the total effective concentration of BAT in solution the

\[
[BAT]_t = [RNBr^-] + [RNHBr] + [X]
\]  
\hspace*{1cm} (9.3)

From which, solving for \([X]\), one obtains,

\[
[X] = \frac{K_1K_2[BAT][EPH][H^+]}{1 + K_1[H^+] + K_1K_2[EPH][H^+]} \hspace*{1cm} (9.4)
\]

Substituting Eq. (9.4) in Eq. (9.2), the following rate law can be obtained:

\[
rate = \frac{K_1K_2k_3[BAT][EPH][H^+]}{1 + K_1[H^+] + K_1K_2[EPH][H^+]} \hspace*{1cm} (9.5)
\]

Since \(rate = k'[BAT]\), Eq. (9.5) can be transformed into equations (9.6) – (9.8).

\[
k' = \frac{K_1K_2k_3[EPH][H^+]}{1 + K_1[H^+] + K_1K_2[EPH][H^+]} \hspace*{1cm} (9.6)
\]

\[
\frac{1}{k'} = \frac{1}{K_1K_2k_3[EPH][H^+]} + \frac{1}{K_2k_3[EPH]} + \frac{1}{k_3} \hspace*{1cm} (9.7)
\]

\[
\frac{1}{k'} = \frac{1}{K_2k_3[EPH]} \left( \frac{1}{K_1[H^+]} + 1 \right) + \frac{1}{k_3} \hspace*{1cm} (9.8)
\]

From the slope and intercept of the linear plots of \(1/k'\) vs \(1/[EPH]\) and \(1/k'\) vs \(1/[H+]\) (Fig. 9.6 and Fig. 9.7, \(r > 0.998\)) the values of \(K_1, K_2\) and \(k_3\) for standard run were found to be 1.08 dm³ mol⁻¹, 2.2 x 10³ dm³ mol⁻¹ and 5 x 10⁻⁴ s⁻¹, respectively.
Since the rate was fractional order with [EPH], Michaelis-Menten type of kinetics was adopted. The effect of [EPH] on the rate at different temperatures (303-323K) was studied (Table 9.6) and by plotting 1/k' vs. 1/ [EPH] (Fig. 9.6, r=0.997) values of decomposition constants k3 were calculated. Activation parameters for the rate limiting step were computed from the Arrhenius plot of log k3 vs 1/T (Fig. 9.8, r=0.988). These results are presented in Table 9.7. A comparison with the activation parameters obtained for the composite reaction shows that the values largely refer to the rate limiting step supporting the fact that reaction before the rate limiting step is fast, involving low activation energy.

The effect of varying dielectric permittivity (D) of the medium on the rate has been described in many studies. An increase in the rate with decreasing dielectric permittivity of the medium supports the proposed mechanism. Laidler and Eyrings and Amis have shown that, a plot log k' versus 1/D gives a straight line with a positive slope for a reaction involving a positive ion and dipole and a negative slope for a negative ion-dipole or dipole-dipole interactions. In the present investigations a plot of log k' versus 1/D was linear with a positive slope. This observation indicates the ion-dipole nature of the rate determining step in the reaction sequence and also points to extending of charge to the transition state.

The reduction product of the oxidant (RNH2 or PTS) does not influence the rate showing that, it is not involved in any pre-equilibrium. The change in the ionic strength of the medium does not alter the rate indicating that non-ionic species are involved in the rate limiting step.

The proposed mechanism is also supported by the moderate values of energy of activation and other thermodynamic parameters (Table 9.4 and 9.7). The moderate value of ΔH‡ and the large negative value of ΔS‡ indicate that, the transition state is more ordered than the reactants.

**Mechanism and rate law in alkaline medium**

In alkaline solutions of BAT, RNBr2 does not exist and hence the expected reactive species are RNHBr, HOBBr and RNBr'. Further, Hardy and Johnston reported the following equilibria in alkaline solutions of bromamine-B:
If $C_6H_5SO_2NHBr$ and HOBr were to be the reactive oxidizing species, according to equations (9.16) and (9.17), the retardation of rate by added $C_6H_5SO_2NH_2$ and OH would be expected. In the present investigations no such effects were observed. The rate increased with increasing OH, and hence $C_6H_5SO_2NBr^-$ is the most likely oxidizing species in alkaline medium. Since the haloamines have similar properties, the above argument can be extended to BAT also, and it is reasonable to assume that $CH_3C_6H_4SO_2NBr^-$ as the reactive oxidizing species in alkaline medium.

Considering the above facts and all the experimental data, the following Scheme 9.2 is proposed for the oxidation of EPH with BAT in alkaline medium:

\[
\begin{align*}
RNHBr + OH^- & \rightleftharpoons RNBr^- + H_2O \quad \text{fast (i)} \\
RNBr^- + EPH & \stackrel{k_6}{\longrightarrow} X \quad \text{fast (ii)} \\
X & \stackrel{k_7}{\longrightarrow} X' \quad \text{slow and r d s (iii)} \\
X' + H_2O & \stackrel{k_8}{\longrightarrow} \text{products} \quad \text{fast (iv)}
\end{align*}
\]

**Scheme 9.2**

Here X and X' are the complex intermediate species whose structures are shown in Scheme 9.4, where a detailed mechanistic interpretation of oxidative cleavage of EPH by BAT in alkaline medium is illustrated.

Step (iii) of Scheme 2 determines the overall rate,

\[
\text{rate} = \frac{-d[BAT]}{dt} = k_7[X] \quad (9.11)
\]

If $[BAT]_t$ represents the total effective concentration of BAT in solution then,

\[
[BAT]_t = [RNHBr] + [RNBr^-] + [X] \quad (9.12)
\]
Solving for \([X]\) from equilibrium steps (i) and (ii), one obtains

\[
[X] = \frac{K_s K_b [EPH][OH^-][BAT]}{[H_2O] + K_s [OH^-] + K_s K_b [EPH][OH^-]} \tag{9.13}
\]

By substituting \([X]\) from Eq. (9.13) into Eq. (9.11), the following rate law is obtained:

\[
rate = \frac{K_s K_b k_7 [EPH][OH^-][BAT]}{[H_2O] + K_s [OH^-] + K_s K_b [EPH][OH^-]} \tag{9.14}
\]

Since, \(rate = k[BAT]\),

Eq. (9.14) can be transformed into Equations (9.15) – (9.17).

\[
k' = \frac{K_s K_b k_7 [EPH][OH^-]}{[H_2O] + K_s [OH^-] + K_s K_b [EPH][OH^-]} \tag{9.15}
\]

\[
\frac{1}{k'} = \frac{[H_2O]}{K_s K_b k_7 [EPH][OH^-]} + \frac{1}{K_s K_b [EPH]} + \frac{1}{k_7} \tag{9.16}
\]

\[
\frac{1}{k'} = \frac{1}{K_s K_b k_7 [EPH]} \left( \frac{[H_2O]}{K_s [OH^-]} + 1 \right) + \frac{1}{k_7} \tag{9.17}
\]

The plots of \(1/k'\) vs \(1/[EPH]\) (Fig.9.10, \(r = 0.996\)) for the standard run has been found to be linear. The value of \(k_7\) was calculated from the intercept of the plot and is found to be \(6.67 \times 10^{-4}\text{s}^{-1}\).

Since the rate was fractional order with \([EPH]\) the effect of \([EPH]\) on the rate at different temperatures (298-318K) was studied (Table 9.6) and by plotting \(1/k'\) vs \(1/\text{[EPH]}\) (Fig. 9.11, \(r \geq 0.986\)) values of decomposition constants \(k_7\) were calculated. Activation parameters for the rate limiting step were computed from the Arrhenius plot of \(\log k_7\) vs \(1/T\) (Fig. 9.8, \(r = 0.993\)). These results are presented in Table 9.7.

The proposed mechanism is further supported by the moderate values of energy of activation and other activation parameters. The fairly high positive values of free energy of activation and enthalpy of activation indicate that the transition state is highly solvated, while
the large negative entropy of activation indicates that the transition state is highly solvated, and compact activated complex with less number of degrees of freedom.

The reduction product does not influence the rate showing that it is not involved in a pre-equilibrium. The change in ionic strength of the medium does not alter the rate indicating the involvement of the non-ionic species in the rate determining step. Addition of halide ions had no effect on the rate indicating that no interhalogen or free bromine is formed. All these observations are also in conformity with the proposed mechanism.

A comparison with the activation parameters obtained for the composite reaction both in acidic and alkaline media shows that the values largely refer to the rate limiting step supporting the fact that reaction before the rate limiting step is fast, involving low activation energy.
REFERENCES