Kinetics of the Kuthenium(III) Catalyzed Oxidation of Amides by Sodium N-Bromotoluenesulfonamide in Hydrochloric Acid Solution

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KINETICS OF THE RUTHENIUM(III) CATALYZED OXIDATION OF AMIDES BY SODIUM N-BROMOTOLUENESULFONAMIDE IN HYDROCHLORIC ACID SOLUTION

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ABSTRACT

The kinetics of Ru(III) catalyzed oxidations of urea, methylurea and ethylurea by sodium N-bromo-p-toluenesulfonamide, also known as bromamine-T (BAT), in HCl solution has been studied at 30°C. The reaction rate shows a first-order dependence each on [BAT], [amide] and [Ru(III)] and fractional-order on [H⁺]. Additions of halide ions and the reaction product of BAT (p-toluenesulfonamide) and the variation of ionic strength and dielectric constant of the medium do not have any significant effect on the reaction rate. Activation parameters have been evaluated. A Taft linear free energy relationship is observed for the reaction, with $\rho^* = -0.64$ and $-2.95$ and $\delta = -0.25$, indicating that electron donating groups

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enhance the rate. An isokinetic relationship is observed with $\beta = 391K$ indicating that enthalpy factors control the rate. The existence of the relationship has been supported by the Exner criterion. The protonation constant of monobromamine-T calculated from a plot of $1/k'$ versus $1/[H']$ is 29.15. Mechanisms consistent with the observed kinetic data have been proposed.

**INTRODUCTION**

A literature survey showed that kinetic studies of reactions of amides are very scanty. To our knowledge, there is no information available in the literature on the oxidation of amides by bromamines. The present studies were undertaken to investigate the kinetic and mechanistic aspects of the oxidation of three amides, urea, methylurea and ethylurea, by bromamine-T ($p$-CH$_2$C$_6$H$_4$SO$_2$NBrNa.3H$_2$O or BAT) in HCl solution in the presence of Ru(III) as catalyst at 30°C.

**EXPERIMENTAL**

Bromamine-T was prepared by the reported procedure and its purity was checked by iodometry and by its mass spectrum, UV, IR, and $^1$H and $^{13}$C NMR spectra. An aqueous solution of BAT was prepared, standardized, and preserved in a brown bottle to prevent its photochemical deterioration.

Analar grade urea, ethylurea, and methylurea were obtained from Sisco Chem. Industries, Bombay, and their aqueous solutions were prepared. A solution of RuCl$_3$ (Arora Matthey) in 0.500 mol L$^{-1}$ HCl was used as catalyst. Allowance was made for the amount of HCl present in the catalyst solution while preparing solutions for all kinetic runs. All other chemicals used were of accepted grades of purity. Triply distilled water was used for preparing aqueous solutions. The ionic strength of the reaction mixture was kept at a high value by adding a saturated solution of NaClO$_3$. 

ANANDA ET AL.
Kinetic Measurements

Mixtures containing requisite amounts of the amide, NaClO₄, RuCl₃, and HCl were equilibrated at 30°C. To this was added a measured amount of a pre-equilibrated (30°C) aqueous solution of BAT of known concentration. The progress of the reaction was monitored iodometrically for two half-lives by withdrawing aliquots from the reaction mixture at regular time intervals. The pseudo-first-order rate constants calculated were reproducible within ± 3%. Regression analysis of the experimental data was carried out on an EC-72 statistical calculator.

RESULTS

Stoichiometry and Product Analysis

Reaction mixtures containing different compositions of the amide and BAT in the presence of 0.100 mol L⁻¹ HCl and 4.8 x 10⁻⁵ mol L⁻¹ RuCl₃ were equilibrated at 30°C for 24 hours. The iodometric determination of the unreacted BAT in the reaction mixture showed that one mole of BAT was consumed per mole of the amide substrate as represented by equation (1).

\[ \text{R-C-NH}_2 + \text{TsNBrNa} + \text{H}_2\text{O} \rightarrow \text{RNH}_2 + \text{TsNH}_2 + \text{CO}_2 + \text{Na}^- + \text{Br}^- \] (1)

where R = NH₂ for urea, CH₂NH for methylurea (Meu), and C₂H₅NH for ethylurea (Etu) and Ts = p-CH₃C₆H₄SO₂ for BAT and p-toluenesulfonamide.

The presence of hydrazines as oxidation products of the amides in the reaction mixture was detected by the salicylaldehyde test. The other product, CO₂, was detected by the conventional lime water test. Attempts to quantitate the amount of CO₂ evolved were unsuccessful. The reaction product, p-toluenesulfonamide, was detected by paper chromatography, using benzylalcohol 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).
Effect of Reactants on the Rate

With the substrate in excess, at constant [HCl], [Ru(III)], [amide], ionic strength and temperature, plots of log [BAT] versus time were linear indicating a first-order dependence of the reaction rate on [BAT]. The pseudo-first-order rate constants \( k' \) are given in Table I. The reaction rate in each case increased with increase in [amide], and the plots of log \( k' \) versus log [amide], were linear, with the slope equal to unity (Table II and Fig. 1), indicating a first-order dependence of the rate on [amide].

Effect of Varying [HCl] on the Rate

The reaction was studied with varying [HCl] and keeping the other conditions the same. The rate increased with increase in [HCl] (Table III and Fig. 2) and plots of log \( k' \) versus log [HCl] were linear with fractional slopes indicating fractional-order dependencies on [HCl].

Effect of Varying [Ru(III)] on the Rate

The reaction rate increased with an increase in [Ru(III)] and plots of log \( k' \) versus log [Ru(III)] were linear with slopes equal to unity (Table IV and Fig. 3) showing first-order dependencies on [Ru(III)].

Effect of Cl\(^-\) and Br\(^-\) Ions on the Rate

The addition of Cl\(^-\) ion in the form of NaCl (0.120 to 0.250 mol L\(^-1\)) and Br\(^-\) ion in the form of NaBr (1.00 x 10\(^{-3}\) to 5.00 x 10\(^{-3}\) mol L\(^-1\)) had no effect on the rate of reaction. Hence, the dependence of the rate on [HCl] reflected the effect of [H\(^+\)] only on the reaction.

Effect of p-Toluenesulfonamide on the Rate

The addition of the reaction product, p-toluenesulfonamide (TsNH\(_2\)) (1.00 x 10\(^{-3}\) - 4.00 x 10\(^{-3}\) mol L\(^-1\)), had no effect on the rate of reaction.
TABLE I. Effect of [BAT]₀ on the Rate of Oxidation of Amides

\[
[\text{Amide}]_0 = 0.100 \text{ mol L}^{-1}, [\text{HCl}] = 0.100 \text{ mol L}^{-1}, \\
[Ru(\text{III})] = 4.82 \times 10^{-5} \text{ mol L}^{-1}, \mu = 0.40 \text{ mol L}^{-1}, T = 303 \text{ K}.
\]

| \(10^4 [\text{BAT}]_0\) (mol L\(^{-1}\)) | \(10^4 k' \text{ (s}^{-1}\)) |
|---|---|---|
| | Urea | Meu | Etu |
| 6.0 | 1.52 | 2.26 | 4.49 |
| 8.0 | 1.54 | 2.29 | 4.51 |
| 10.0 | 1.57 | 2.31 | 4.53 |
| 12.0 | 1.60 | 2.34 | 4.55 |
| 14.0 | 1.61 | 2.39 | 4.58 |

TABLE II. Effect of [Amide]₀ on the Reaction Rate

\[
[\text{BAT}]_0 = 1.00 \times 10^{-3} \text{ mol L}^{-1}, [\text{HCl}] = 0.100 \text{ mol L}^{-1}, \\
[Ru(\text{III})] = 4.82 \times 10^{-5} \text{ mol L}^{-1}, \mu = 0.40 \text{ mol L}^{-1}, T = 303 \text{ K}.
\]

| \(10^2 [\text{Amide}]_0\) (mol L\(^{-1}\)) | \(10^4 k' \text{ (s}^{-1}\)) |
|---|---|---|
| | Urea | Meu | Etu |
| 5.0 | 0.82 | 1.23 | 2.29 |
| 7.5 | 1.20 | 1.57 | 3.38 |
| 10.0 | 1.57 | 2.31 | 4.53 |
| 15.0 | 2.29 | 3.51 | 6.76 |
| 20.0 | 3.16 | 4.60 | 9.12 |

Plots of \(\log k'\) versus \(\log [\text{amide}]_0\):

- \(r = 0.999\)
- \(\text{order} = 0.964\)
Effect of Ionic Strength on the Rate

The ionic strength of the reaction mixture, varied using a saturated solution of NaClO₄, had no effect on the rate of reaction.

Effect of Temperature on the Rate

The reaction was studied at different temperatures in the range 298-313 K and the values of k' were determined (Table V) from the pseudo-first-order plots. The energy of activation, $E_a$, was calculated from the Arrhenius plot of log k' versus 1/T. The other activation parameters, namely enthalpy of activation ($\Delta H'$),
Table III. Effect of Varying [HCl] on the Reaction Rate

\[ \text{[Amide]}_0 = 0.100 \text{ mol L}^{-1}, \text{[BAT]}_0 = 1.00 \times 10^{-3} \text{ mol L}^{-1} \]
\[ \text{[Ru(III)]} = 4.82 \times 10^{-5} \text{ mol L}^{-1}, \mu = 0.40 \text{ mol L}^{-1}, T = 303 \text{ K}. \]

<table>
<thead>
<tr>
<th>10^2 [HCl] (mol L^{-1})</th>
<th>10^4 k' (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Urea</td>
</tr>
<tr>
<td>2.00</td>
<td>0.79</td>
</tr>
<tr>
<td>5.00</td>
<td>1.28</td>
</tr>
<tr>
<td>10.0</td>
<td>1.57</td>
</tr>
<tr>
<td>15.0</td>
<td>1.74</td>
</tr>
<tr>
<td>25.0</td>
<td>1.88</td>
</tr>
</tbody>
</table>

Plots of \( \log k' \) versus \( \log [\text{HCl}] \)

\( r = 0.980 \quad 0.986 \quad 0.986 \)

\( \text{order} = 0.343 \quad 0.340 \quad 0.360 \)

entropy of activation (\( \Delta S' \)) and free energy of activation (\( \Delta G' \)), were then calculated by making use of the value of \( E_a \) (Table VI).

Test for Free Radicals

Addition of the reaction mixture to aqueous acrylamide monomer solutions did not initiate polymerization indicating the absence of \textit{in situ} formation of free radical species in the reaction sequence.

DISCUSSION AND MECHANISM

Cady and Connick\(^8\) and Connick and Fine\(^9\) have determined the formulas of aqueous ruthenium(III) complex species using ion-exchange resin properties and
UV spectral studies. These studies have shown that octahedral complex species such as \([\text{RuCl}_3(\text{H}_2\text{O})]^{2-}\), \([\text{RuCl}_4(\text{H}_2\text{O})_2^-]\), \([\text{RuCl}_6(\text{H}_2\text{O})_3]\), \([\text{RuCl}_4(\text{H}_2\text{O})_4]\) and \([\text{RuCl}(\text{H}_2\text{O})_3]^{2-}\) do not exist in aqueous solutions of RuCl₃. Other studies have shown that the following equilibrium exists for RuCl₃ in acidic solutions:

\[
[\text{RuCl}_3]+\text{H}_2\text{O}\rightleftharpoons [\text{RuCl}_4(\text{H}_2\text{O})]^{2-} + \text{Cl}^-
\] (2)

Singh et al.\(^{12,13}\) used the above equilibrium in the ruthenium(III) chloride catalyzed oxidation of primary alcohols by BAT and of ethylene glycols by N-nitrosoacetamide in HClO₄ solution. In the present study, however, the addition of
Table IV. Effect of Varying [Ru(III)] on the Reaction Rate

\[ [\text{Amide}]_0 = 0.100 \text{ mol L}^{-1}, [\text{BAT}]_0 = 1.00 \times 10^{-3} \text{ mol L}^{-1}, \]
\[ [\text{HCl}] = 0.100 \text{ mol L}^{-1}, \mu = 0.40 \text{ mol L}^{-1}, T = 303 \text{ K}. \]

| \(10^2 [\text{Ru(III)}] (\text{mol L}^{-1})\) | \(10^4 k' (s^{-1})\) |
|---|---|---|
| Urea | Meu | Etu |
| 2.89 | 1.00 | 1.35 | 2.88 |
| 3.86 | 1.32 | 1.78 | 3.71 |
| 4.82 | 1.57 | 2.31 | 4.53 |
| 6.75 | 2.18 | 3.16 | 6.61 |
| 9.64 | 3.00 | 4.46 | 9.55 |

Plots of log \(k'\) versus log [Ru(III)]

\[ r = 0.999 \quad 0.999 \quad 0.998 \]

order \(r = 0.968 \quad 0.996 \quad 1.005 \)

chloride ion in the form of NaCl at constant \([H^+]\) and ionic strength had no effect on the rate indicating that \([\text{RuCl}_n]^-\) is the most likely catalyzing species that interacts with the substrate to form a complex intermediate. Similar kinetic results were observed in the Ru(III) catalyzed oxidation of chloroacetic acids by BAT\(^7\) (bromamine-T) and BAB\(^4\) (bromamine-B or N-bromobenzencesulfonamide).

Pryde and Sopper\(^{15,16}\), Morris et al.\(^{17}\) and Bishop and Jennings\(^{18}\) have shown the existence of similar equilibria in acid and alkaline solutions of N-metallo-N-haloarylsulfonamides. BAT (TsNBrNa), like its chlorine analogue, chloramine-T, behaves as a strong electrolyte in aqueous solutions forming different species as shown in equations (3)-(7).
Fig. 3. Plots of log k' versus log [Ru(III)]: A = ethylurea, B = methylurea, C = urea. [Amide]₀ = 0.100 mol L⁻¹, [BAT]₀ = 1.00 x 10⁻³ mol L⁻¹, [HCl] = 0.100 mol L⁻¹, µ = 0.40 mol L⁻¹, T = 303 K

\[
\begin{align*}
\text{TsNBrNa} & \rightleftharpoons \text{TsBr}^- + \text{Na}^+ \quad (3) \\
\text{TsNBr}^+ + \text{H}^- & \rightleftharpoons \text{TsNHBr} \quad (4) \\
\text{TsNHBr} + \text{H}_2\text{O} & \rightleftharpoons \text{TsNH}_2^- + \text{HOBr} \quad (5) \\
2\text{TsNHBr} & \rightleftharpoons \text{TsNH}_2^+ + \text{TsNBr}_2 \quad (6) \\
\text{HOBr} + \text{H}^- & \rightleftharpoons \text{H}_2\text{OBr}^- \quad (7)
\end{align*}
\]

In acidic solutions, the probable oxidizing species are the free acid (TsNHBr), dibromamine-T (TsNBr₂), HOBr, and H₂OBr⁻. The involvement of TsNBr₂ in the
### Table V. Effect of Temperature on the Reaction Rate

[Amide]₀ = 0.100 mol L⁻¹, [BAT]₀ = 1.00 x 10⁻³ mol L⁻¹, [HCl] = 0.100 mol L⁻¹, [Ru(III)] = 4.82 x 10⁻⁵ mol L⁻¹, \( \mu = 0.40 \) mol L⁻¹.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>(10^4 k') (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Urea</td>
</tr>
<tr>
<td>298</td>
<td>1.12</td>
</tr>
<tr>
<td>303</td>
<td>1.57</td>
</tr>
<tr>
<td>308</td>
<td>2.23</td>
</tr>
<tr>
<td>313</td>
<td>3.30</td>
</tr>
</tbody>
</table>

PLOTS of log \( k' \) versus 1/T

\( r = 0.999 \)  
\( \text{slope} = -2.989 \)

### Table VI. Activation Parameters for the Oxidation of Amides by BAT in the Presence of HCl and Ru(III) Catalyst.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( \Delta H' ) (kJ mol⁻¹)</th>
<th>( \Delta S'/JK^{-1} ) mol⁻¹</th>
<th>( \Delta G' ) (kJ mol⁻¹)</th>
<th>( E_a^* ) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>54.7</td>
<td>-137</td>
<td>96.3</td>
<td>57.3</td>
</tr>
<tr>
<td>Meu</td>
<td>47.9</td>
<td>-157</td>
<td>95.7</td>
<td>50.4</td>
</tr>
<tr>
<td>Etu</td>
<td>43.4</td>
<td>-166</td>
<td>94.0</td>
<td>45.9</td>
</tr>
</tbody>
</table>
mechanism leads to a second-order rate law according to equation (6), which is contrary to the experimental observations. As equation (5) indicates a slow hydrolysis, if HIOBr were the primary oxidizing species, a first-order retardation of the rate by the added TsNH$_2$ would be expected, contrary to results. Hardy and Johnston$^{19}$ have studied the pH dependence of relative concentrations of the species present in acidified chloramine-T solutions of comparable molarities and shown that TsNHBr is the likely oxidizing species in acid solutions. Narayanan and Rao$^{20}$ and Subhashini et al.$^{21}$ have reported that monohaloamines can be further protonated at pH < 2 as shown in the following equations (8) and (9) for monochloramine-T (p-CH$_3$C$_6$H$_4$SO$_2$NHCl) and monochloramine-B (C$_6$H$_5$SO$_2$NHCl), respectively:

\[
\begin{align*}
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCl} + \text{H}^+ & \rightleftharpoons \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2\text{Cl} \\
\text{C}_6\text{H}_5\text{SO}_2\text{NHCl} + \text{H}^+ & \rightleftharpoons \text{C}_6\text{H}_5\text{SO}_2\text{NH}_2\text{Cl}
\end{align*}
\]

The second protonation constants for p-CH$_3$C$_6$H$_4$SO$_2$NHCl and C$_6$H$_5$SO$_2$NHCl are 102 M$^{-1}$ and 61.5 M$^{-1}$, respectively, at 298 K. Gupta$^{22}$ believes that the values could be lower than those reported by the above workers.$^{20,21}$ In the present case, the fractional-order in [H'] indicates that the protonation of TsNHBr results in the formation of TsNH$_2$Br which is likely to be the active oxidizing species involved in the mechanism of oxidation of the substrates. Based on the preceding discussion, the mechanism in Scheme I is proposed for the reaction.

In Scheme I, 'S' represents the amide substrate while X and X' represent the complex intermediate species whose structures are shown in Scheme II. A detailed mechanistic interpretation of the Ru(III) catalyzed amide-BAT reaction in acid solution is presented in Scheme II. An initial equilibrium involves protonation TsNHBr forming the active oxidizing species of BAT, TsNH$_2$Br (step (i) in Scheme I, but not shown in Scheme II). In the next fast pre-equilibrium, the oxygen atom of the amide coordinates to the metal center of the active catalyst species, [RuCl$_6$]$^{3+}$, to form a loosely bound metal complex anion X (step (I) of Scheme II) trapped in a solvent cage, which increases the
nucleophilicity of the amide nitrogen. This kind of loose metal ion-substrate complex formation has been involved as an intermediate in some studies with Ru(III) catalyst\textsuperscript{5,12,13}. Then an electrophilic attack by TsNII\textsubscript{2}Br at the amide nitrogen of X occurs to form N-bromamide as intermediate through a fast intramolecular rearrangement, with the elimination of TsNH\textsubscript{2} and RuCl\textsubscript{3}, respectively, (steps (II) and (III) in Scheme II). This N-bromamide undergoes Hofmann rearrangement forming alkylisocyanate with the elimination of a proton (step (IV) in Scheme II). In step (V) of Scheme II a nucleophilic attack by water on the isocyanate carbon of the intermediate results in the formation of carbamic acid (N-carboxyalkylamine), which eliminates CO\textsubscript{2} to form the corresponding alkyamine.

From the slow step in Scheme I,
\[
\text{rate} = k_3 \left[ \text{TsNH}_2\text{Br} \right] [X]
\] (10)
If [BAT]\textsubscript{t} represents the total [BAT], then
\[
[BAT]_t = [\text{TsNII}Br] + [\text{TsNH}_2\text{Br}]
\] (11)

By substituting for [TsNHBr] from equilibrium step (i) into equation (11), one obtains
where R = NH₂ for urea, CH₃NH for methylurea, and C₂H₅NH for ethylurea and Ts = p-CH₃C₆H₄SO₂ for BAT and p-toluenesulfonamide.

**Scheme II**
RU'IHENIUM(II1) CATALYZED OXIDATION

\[ [\text{BAT}]_i = \frac{[\text{TsNH}_2\text{Br}]}{K_i[\text{H}']} + [\text{TsNH}_2\text{Br}] \]

or

\[ [\text{BAT}]_i = \frac{[\text{TsNH}_2\text{Br}][K_i[\text{H}'] + 1]}{K_i[\text{H}']} \]

Or

\[ [\text{TsNH}_2\text{Br}] = \frac{K_i[\text{BAT}]_i[\text{H}']}{K_i[\text{H}'] + 1} \]  \hspace{1cm} (12)

Substituting for \([X]\) from equilibrium step (ii) of Scheme I and for \([\text{TsNH}_2\text{Br}]\)
from equation (12) into equation (10), one obtains the rate law (equation 13),

\[ \text{rate} = \frac{K_i K_j k_i [\text{BAT}]_i [\text{H}'] [S] [\text{Ru(III)}]}{K_i[\text{H}'] + 1} \]  \hspace{1cm} (13)

The rate law is in good agreement with the experimental results, such as first-order each in \([\text{BAT}]_i\), \([\text{substrate}]\) and \([\text{Ru(III)}]\) and fractional-order in \([\text{H}']\).

Since the rate = \(k' [\text{BAT}]_i\), equation (13) can be transformed into equation (14).

\[ k' = \frac{K_i K_j k_i [S] [\text{Ru(III)}][\text{H}']}{K_i[\text{H}'] + 1} \]

or

\[ \frac{1}{k'} = \frac{1}{K_i k_j [S] [\text{Ru(III)}]} + \frac{1}{K_i K_j k_i [S] [\text{Ru(III)}][\text{H}']} \]  \hspace{1cm} (14)
Table VII. Plots of $1/k'$ versus $1/[H^+]$ 

<table>
<thead>
<tr>
<th>$10^2[H^+]$ (M)</th>
<th>$1/[H^+]$ (M$^{-1}$)</th>
<th>$1/k'$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Urca</td>
</tr>
<tr>
<td>2.00</td>
<td>50.0</td>
<td>12658</td>
</tr>
<tr>
<td>5.00</td>
<td>20.0</td>
<td>7812</td>
</tr>
<tr>
<td>10.0</td>
<td>10.0</td>
<td>6369</td>
</tr>
<tr>
<td>15.0</td>
<td>6.66</td>
<td>5747</td>
</tr>
<tr>
<td>25.0</td>
<td>4.00</td>
<td>5319</td>
</tr>
</tbody>
</table>

$r = 0.999$  
slope = $1.59 \times 10^3$  
Intercept = $4.70 \times 10^3$

Based on equation (14), a plot of $1/k'$ versus $1/[H^+]$ at constant [amide]$_0$, [Ru(III)] and temperature was found to be linear for each amide (Table VII and Fig. 4). The values of $K_1$ and $(K_2k_s)$ were calculated from the slope and intercept of the plots for the standard runs with [BAT]$_0$ = $1.00 \times 10^{-3}$ mol L$^{-1}$, [amide]$_0$ = $0.100$ mol L$^{-1}$, [Ru(III)] = $4.82 \times 10^{-5}$ mol L$^{-1}$ at 303K. The values of the protonation constant $K_1$ (or $K_p$) of TsNHBr, $(K_2k_s)$, and deprotonation constant $K'_1$ are presented in Table VIII. Furthermore, the values of $K_1$ or $K'_1$ are compared with the corrected values obtained for the oxidation of primary amines by BAT$^{23}$. The constancy of the $K_1$ and $K'_1$ values is a strong indirect evidence for the formation of the reactive species TsNH$_2$Br from TsNHBr supporting the proposed mechanism of oxidation of amides by BAT (Schemes I and II).

The existence of a linear-free-energy relationship (LFER) for the oxidation of amides by BAT has been evaluated$^{24}$.
as single parameter correlations with the polar substituent constant $\sigma^*$ and steric substituent constant $E_s$ were made by plotting $\log k'$ versus $\sigma^*$, $\log k'$ versus $E_s$, and $\log k'$-$E_s$ versus $\sigma^*$. The following regression equations were found:

\[
\log k' = -0.64 \sigma^* - 3.51 \quad (r = 0.8678) \quad (15)
\]
\[
\log k' = -0.25E_s - 3.49 \quad (r = 0.8072) \quad (16)
\]
\[
(\log k' - E_s) = -2.95\sigma^* - 3.6 \quad (r = 0.9993) \quad (17)
\]
Table VIII. The Kinetic Data Calculated Using Equation (14)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$K_3k_3$ (M$^{-2}$ s$^{-1}$)</th>
<th>$K_1$ or $K_p$ (M)</th>
<th>$K'_1 = 1/K_p$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urrea</td>
<td>44.1</td>
<td>29.6</td>
<td>3.38 x 10$^{-2}$</td>
</tr>
<tr>
<td>Mceu</td>
<td>63.2</td>
<td>30.7</td>
<td>3.25 x 10$^{-2}$</td>
</tr>
<tr>
<td>Etu</td>
<td>133</td>
<td>27.2</td>
<td>3.67 x 10$^{-2}$</td>
</tr>
</tbody>
</table>

Calculated from plots of $1/k'$ versus $1/[H^+]$

Fig. 5. A plot of $\Delta H^*$ versus $\Delta S^*$ for the three amides: $[\text{Amide}]_0 = 0.100$ mol L$^{-1}$, $[\text{BAT}]_0 = 1.00 \times 10^{-3}$ mol L$^{-1}$, $[\text{HCl}]_0 = 0.100$ mol L$^{-1}$, $[\text{Ru(III)}] = 4.82 \times 10^{-5}$ mol L$^{-1}$, $\mu = 0.40$ mol L$^{-1}$
The implication of the electronic effect on the rate is less clear from equation (15). The value of $\rho^* = -0.64$ suggests that the electronic effect plays a role in the reaction. The sensitivity towards the steric effect ($\sigma = -0.25$) is not too significant as revealed by equation (16). However, an excellent correlation in equation (17) shows that both steric and electronic factors have a synergistic effect on the rate. The negative values of the reaction constant $\rho^* (-0.64$ and $-2.95$) indicate that the presence of electron donating groups in the amide substrate increases the reaction rate. The rate of oxidation of amides by BAT increases in the following order: urea $<$ methylurea $<$ ethylurea (Tables I-V).
The relative magnitudes of energies of activation for the oxidation of amides in Table VI, which support the above trend, indicate that the reactions are enthalpy-controlled. This is verified by calculating the isokinetic temperature (β) from the slope of a linear plot of $\Delta H'$ versus $\Delta S'$ (Fig. 5) for each amide. The β value at 391 K, which is higher than the experimental temperature used in the present study, implies that the substrate oxidation is enthalpy-controlled. Further confirmation of the existence of an isokinetic relationship was inferred from the Exner-criterion by plotting log $k'(313\, K)$ versus log $k'(363\, K)$ which yielded a linear plot (Fig. 6; r = 0.9984). The value of β from the Exner slope was found to be 410 K. The fairly negative value of $\Delta S'$ indicates the formation of a rigid associative transition state in each case. The constancy of the $\Delta G'$ values indicates that the three amidcs react with BAT via the same mechanism.

REFERENCES


18. E. Bishop and V. J. Jennings, Talanta, 1, 197 (1958); 8, 22, 34, 697 (1961); 2, 581, 593 (1962).


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