CHAPTER - III

RUTHENIUM (III) - CATALYZED OXIDATION OF PHENYLPROPANOLAMINE WITH CHLORAMINE-B IN ACID MEDIUM: A KINETIC AND MECHANISTIC STUDY
SECTION 3.1

INTRODUCTION AND BIOLOGICAL IMPORTANCE OF PHENYLPROPA NOLAMINE

Phenylpropanolamine hydrochloride (PPA) is a sympathomimetic drug, differing from amphetamine by only a hydroxyl group on the β-carbon atom. It is a component of many decongestant and anorectic medications available without prescription. PPA is used to nasal congestion associated with the common cold, allergies, high fever, or other respiratory illness. It has been used as a non prescription diet-aid for weight loss [1]. There are four optical isomers of phenylpropanolamine: d- and l-norephedrin, and d- and l-norpseudoephedrin. D-norpseudoephedrin is also known as cathine and occurs naturally in the stimulant plant (Catha edulis). This isomer is commonly used in medications described as phenylpropanolamine. Just as ephedrine is chemically reduced into methamphetamine, phenylpropanolamine can be chemically reduced into amphetamine. Molecularly, PPA is to ephedrine, just as amphetamine is to methamphetamine, and as cathinone is to methcathinone. Thus PPA can be used in the manufacture of methamphetamine. Usually PPA can be made from cathinone. In veterinary medicine, PPA is used to control urinary incontinence in dogs.

Stability studies with a decongestant syrup formulation containing phenylpropanolamine hydrochloride in a sugar indicated a loss of PPA [2]. Vinas at al [3] studied the determination of PPA using flow injection with fluorimeter.

The review of available literature thus reveals that, there was no information available on the oxidation kinetics of phenylpropanolamine with any oxidant. There was a need for understanding the oxidation mechanism of this bio-active compound, so that the study could throw some light on the fate of the compound in biological system, and also the oxidative behavior of CAB towards PPA. The reaction of PPA with CAB in the presence of HCl medium without a catalyst was found to be sluggish, but the reaction was facile in the presence of RuCl₃ catalyst. Therefore the present chapter reports the kinetics of Ru(III)-catalyzed oxidation of PPA with CAB in HCl medium at 308 K. The objectives of the present investigations are to: (i) elucidate the reaction mechanism (ii)
put forward appropriate rate laws (iii) ascertain the reactive species of CAB and (iv) identify the products of reaction.

SECTION 3.2
RUTHENIUM (III)-CATALYSED OXIDATION OF PHENYLPROPANOLAMINE WITH CHLORAMINE-B IN HYDROCHLORICACID MEDIUM: A KINETIC AND MECHANISTIC STUDY

This section reports the kinetics of oxidation of phenylpropanolamine (PPA) with chloramine-B in presence of Ru(III)-catalyst in HCl medium at 308K. The kinetic isotopic effect and proton inventory studies have been made with D$_2$O.

Stiochiometry and product analysis

Reaction mixture containing different compositions of PPA and CAB were equilibrated in presence of HCl (0.1 mol dm$^{-3}$) and RuCl$_3$ (1×10$^{-4}$ mol dm$^{-3}$) for 48 hrs at 308 K under the condition [CAB]>> [PPA]. Determination of unreacted oxidant in the reaction mixture showed that one mole of PPA was consumed per mole of oxidant, confirming the following stoichiometry,

$$C_9H_{13}NO + RNClNa + H_2O \rightarrow C_7H_6O + C_2H_4O + RNH_2 + NaCl + NH_3 \quad \ldots\ldots(3.1)$$

where $R = C_6H_5SO_2$.

The products in the reaction mixture were extracted several times with diethylether. The combined ether extract was evaporated and subjected to column chromatography on silica gel using gradient elusion (from dichloromethane to chloroform). The reduction product of CAB, benzenesulphonamide was detected as described in Section 2.2 of Chapter II. The oxidation products of phenylpropanolamine were found to be benzaldehyde, acetaldehyde and ammonia. Formation of ammonia was quantitatively estimated by micro-Kjeldahl procedure. Benzaldehyde and acetaldehyde were detected by spot test [4]. Benzaldehyde was identified by preparing 2, 4-DNP derivative. Further it was confirmed by IR spectrum which showed a band at 1704 cm$^{-1}$ for >C=0 stretching and at 2848 cm$^{-1}$ for aldehydic -CH stretching mode. The IR spectrum is shown in Fig. 3.9.
Results

The kinetics of oxidation of phenylpropanolamine was investigated at different initial concentrations of the reactants in presence of Ru(III)-catalyst and hydrochloric acid medium at 308K.

Effect of varying reactant concentration on the rate

The reaction was performed in presence of Ru(III)-catalyst and HCl under pseudo-first-order conditions ([PPA]>>[CAB]). Plots of log [CAB] versus time were linear (Table 3.1; Fig. 3.1). The linearity of these plots together with the constancy of the slope for various [CAB]₀ indicates a first-order dependence of the reaction rate on [CAB]. The pseudo-first-order rate constants, k' obtained at 308 K are listed in Table 3.2. The reaction rate increased with increase in [PPA], and a plot of log k' versus log [PPA] was linear (Table 3.3; Fig.3.2) with a slope of 0.4 indicating a fractional-order dependence on [PPA]₀.

Effect of varying concentration of HCl on the rate

At constant [CAB], [PPA], [Ru(III)], ionic strength and temperature, the rate of reaction increased with increase in [HCl] (Table 3.4). A plot of log k' versus log [HCl] was linear (Fig. 3.3), with unit slope indicating a first-order dependence on [HCl].

Effect of added [Cl⁻] on the rate

The addition of [Cl⁻] in the form of NaCl, keeping [H⁺] constant did not affect the rate of reaction (Table 3.5). Hence, the dependence of the rate on [HCl] reflected the effect of [H⁺] only on the reaction.

Effect of varying [Ru(III)] on the rate

The reaction rate increased with increase in [Ru(III)] (Table 3.6), and a plot of log k' versus log[Ru(III)] was linear (Fig. 3.4) with a slope of 0.24 indicating a fractional-order dependence on [Ru(III)].

Effect of varying benzenesulfonamide

Addition of the reduction product, benzenesulfonamide (2 × 10⁻⁴ to 8 × 10⁻⁴ mol dm⁻³) to the reaction mixture had no effect on the rate (Table 3.7).
**Effect of ionic strength on the rate**

The ionic strength of the reaction mixture was varied by using the solution of NaClO₄ (Table 3.8) which had no effect on the rate.

**Effect of relative permittivity on the reaction rate**

The effect of relative permittivity (D) of the medium on the rate has been studied by using the CH₃CN – H₂O content in the reaction mixture with all other conditions kept constant. The values of relative permittivity were computed from the values of the pure liquids [5]. The rate constant, k’ increases with decreasing relative permittivity of the medium (Table 3.9). Plot of log k’ versus 1/D gave a straight line (Fig. 3.5) with a positive slope. Blank experiments performed showed that CAB did not oxidize CH₃CN under the experimental conditions employed.

**Effect of solvent isotope on the rate**

As the rate is dependent on [H⁺], solvent isotope study in D₂O medium was made. The value of k’ (H₂O) is 4.37 × 10⁻⁴ s⁻¹ and that of k’ (D₂O) is 1.83 × 10⁻⁴ s⁻¹ leading to solvent isotope effect, k'(H₂O) / k'(D₂O) = 2.39. Proton inventory studies were made in H₂O-D₂O mixtures, and the results are shown in Table 3.10. The corresponding proton inventory plot for the rate constant Kⁿobs in a solvent mixture containing Deuterium atom fraction (n) is given in Fig. 3.6.

**Effect of temperature on the rate**

The reaction was studied at different temperatures (303.4 – 321 K) keeping other experimental conditions constant (Table 3.11). From the linear Arrhenius plot of log k’ versus 1/T (Fig. 3.7) activation parameters namely energy of activation, enthalpy of activation, entropy of activation and Gibb’s free energy of activation were calculated. The activation parameters obtained are presented in Table 3.12.

**Test for free radicals**

The addition of the reaction mixture to an aqueous acrylamide monomer solution did not initiate polymerization indicating the absence of free radical species *in situ* in the reaction sequence.
Table 3.1
Effect of [CAB] on the rate of oxidation of PPA at 308 K
(Representative Run)

[CAB] = 5 \times 10^{-4} \text{ mol dm}^{-3}, [PPA] = 8 \times 10^{-3} \text{ mol dm}^{-3}, [HCl] = 10 \times 10^{-2} \text{ mol dm}^{-3},

[Ru(III)] = 1 \times 10^{-4} \text{ mol dm}^{-3}, \mu = 0.2 \text{ mol dm}^{-3}

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>( V_t ) (ml)</th>
<th>\log V_t</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.8</td>
<td>1.033</td>
</tr>
<tr>
<td>5</td>
<td>9.9</td>
<td>0.996</td>
</tr>
<tr>
<td>10</td>
<td>8.7</td>
<td>0.939</td>
</tr>
<tr>
<td>20</td>
<td>6.5</td>
<td>0.813</td>
</tr>
<tr>
<td>30</td>
<td>4.6</td>
<td>0.663</td>
</tr>
<tr>
<td>40</td>
<td>3.7</td>
<td>0.568</td>
</tr>
<tr>
<td>55</td>
<td>2.6</td>
<td>0.415</td>
</tr>
</tbody>
</table>

\[ r = 0.996 \]
\[ k' = 4.37 \times 10^{-4} (\text{s}^{-1}) \]

\( V_t \) = Titre volume of Na\(_2\)S\(_2\)O\(_3\)

**Fig. 3.1**: Plot of \( \log V_t \) versus time (min)
Table 3.2
Effect of varying the [CAB]₀ on the rate of oxidation of PPA

[PEA] = 8 x 10⁻³ mol dm⁻³,  [HCl] = 10 x 10⁻² mol dm⁻³,  
[Ru(III)] = 1 x 10⁻⁴ mol dm⁻³,  T = 308 K,  μ = 0.2 mol dm⁻³

<table>
<thead>
<tr>
<th>[CAB] x 10⁴ (mol dm⁻³)</th>
<th>k x 10⁴ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>4.39</td>
</tr>
<tr>
<td>5.0</td>
<td>4.37</td>
</tr>
<tr>
<td>7.0</td>
<td>4.36</td>
</tr>
<tr>
<td>9.0</td>
<td>4.40</td>
</tr>
<tr>
<td>11.0</td>
<td>4.42</td>
</tr>
</tbody>
</table>

Table 3.3
Effect of varying the [PPA]₀ on the rate

[CAB] = 5 x 10⁻⁴ mol dm⁻³,  [HCl] = 10 x 10⁻² mol dm⁻³,  
[Ru(III)] = 1 x 10⁻⁴ mol dm⁻³,  T = 308 K,  μ = 0.2 mol dm⁻³

<table>
<thead>
<tr>
<th>[PPA] x 10⁴ (mol dm⁻³)</th>
<th>k x 10⁴ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>3.55</td>
</tr>
<tr>
<td>6.0</td>
<td>4.02</td>
</tr>
<tr>
<td>8.0</td>
<td>4.37</td>
</tr>
<tr>
<td>10.0</td>
<td>4.70</td>
</tr>
<tr>
<td>12.0</td>
<td>5.30</td>
</tr>
</tbody>
</table>

r = 0.988

Fig. 3.2: Plot of 4+log k' versus 3+log [PEA]
Fig. 3.2

\[ 3 + \log [\text{PPA}] \]

\[ 4 + \log k' \]
Table 3.4

Effect of varying [HCl] on the reaction rate

\[ \text{[CAB]} = 5 \times 10^{-4} \text{ mol dm}^{-3}, \quad \text{[PPA]} = 8 \times 10^{-3} \text{ mol dm}^{-3}, \]

\[ \text{[Ru(III)]} = 1 \times 10^{-4} \text{ mol dm}^{-3}, \quad T = 308 \text{ K}, \mu = 0.2 \text{ mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>[HCl] x 10^2 (mol dm^{-3})</th>
<th>k x 10^4 (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>3.76</td>
</tr>
<tr>
<td>10</td>
<td>4.37</td>
</tr>
<tr>
<td>12</td>
<td>5.45</td>
</tr>
<tr>
<td>14</td>
<td>6.26</td>
</tr>
<tr>
<td>16</td>
<td>6.95</td>
</tr>
</tbody>
</table>

\[ r = 0.997 \]

Fig. 3.3: Plot of 4+log k' versus 2+log [HCl]
Table 3.5
Effect of varying [Cl\(^{-}\)] on the reaction rate

\[ \text{[CAB]} = 5 \times 10^{-4} \text{ mol dm}^{-3}, \ \text{[PPA]} = 8 \times 10^{-3} \text{ mol dm}^{-3}, \ \text{[H}^{+}\text{]} = 0.1 \text{ mol dm}^{-3} \]
\[ \text{[Ru(III)]} = 1 \times 10^{-4} \text{ mol dm}^{-3}, \ T = 308 \text{ K}, \ \mu = 0.2 \text{ mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>[Cl(^{-})] x 10(^{2}) (mol dm(^{-3}))</th>
<th>k x 10(^{4}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>4.41</td>
</tr>
<tr>
<td>14</td>
<td>4.37</td>
</tr>
<tr>
<td>17</td>
<td>4.35</td>
</tr>
<tr>
<td>20</td>
<td>4.36</td>
</tr>
<tr>
<td>25</td>
<td>4.33</td>
</tr>
</tbody>
</table>

Table 3.6
Effect of varying [Ru(III)] on the reaction rate

\[ \text{[CAB]} = 5 \times 10^{-4} \text{ mol dm}^{-3}, \ \text{[PPA]} = 8 \times 10^{-3} \text{ mol dm}^{-3} \]
\[ \text{[HCl]} = 10 \times 10^{-2} \text{ mol dm}^{-3}, \ T = 308 \text{ K}, \ \mu = 0.2 \text{ mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>[Ru(III)] x 10(^{4}) (mol dm(^{-3}))</th>
<th>k x 10(^{4}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.71</td>
</tr>
<tr>
<td>0.8</td>
<td>4.16</td>
</tr>
<tr>
<td>1.0</td>
<td>4.37</td>
</tr>
<tr>
<td>2.0</td>
<td>5.25</td>
</tr>
<tr>
<td>3.0</td>
<td>5.85</td>
</tr>
</tbody>
</table>

\[ r = 0.999 \]

**Fig. 3.4:** Plot of 4+log k\(^{'}\) versus 5+log [Ru(III)]

112
Fig. 3.4

$4 + \log k'$ versus $5 + \log [\text{Ru(III)}]$
Table 3.7
Effect of added benzenesulfonamide (BSA) on the rate

\[ [\text{CAB}] = 5 \times 10^{-4} \text{ mol dm}^{-3}, \quad [\text{PPA}] = 8 \times 10^{-3} \text{ mol dm}^{-3}, \quad [\text{HCl}] = 10 \times 10^{-2} \text{ mol dm}^{-3}, \quad [\text{Ru(III)}] = 1 \times 10^{-4} \text{ mol dm}^{-3}, \quad T = 308 \text{ K}, \quad \mu = 0.2 \text{ mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>[BSA] x 10^4 (mol dm^3)</th>
<th>k x 10^4 (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>4.35</td>
</tr>
<tr>
<td>4.0</td>
<td>4.37</td>
</tr>
<tr>
<td>6.0</td>
<td>4.39</td>
</tr>
<tr>
<td>8.0</td>
<td>4.40</td>
</tr>
</tbody>
</table>

Table 3.8
Effect of ionic strength on the rate

\[ [\text{CAB}] = 5 \times 10^{-4} \text{ mol dm}^{-3}, \quad [\text{PPA}] = 8 \times 10^{-3} \text{ mol dm}^{-3}, \quad [\text{HCl}] = 10 \times 10^{-2} \text{ mol dm}^{-3}, \quad [\text{Ru(III)}] = 1 \times 10^{-4} \text{ mol dm}^{-3}, \quad T = 308 \text{ K} \]

<table>
<thead>
<tr>
<th>[NaClO_4] x 10^2 (mol dm^3)</th>
<th>k x 10^4 (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.41</td>
</tr>
<tr>
<td>15</td>
<td>4.39</td>
</tr>
<tr>
<td>20</td>
<td>4.37</td>
</tr>
<tr>
<td>25</td>
<td>4.36</td>
</tr>
</tbody>
</table>
Table 3.9

Effect of dielectric permittivity of the medium on the rate

\[ [\text{CAB}] = 5 \times 10^{-4} \text{ mol dm}^{-3}, \quad [\text{PPA}] = 8 \times 10^{-3} \text{ mol dm}^{-3}, \quad [\text{HCl}] = 10 \times 10^{-2} \text{ mol dm}^{-3}, \]
\[ [\text{Ru(III)}] = 1 \times 10^{-4} \text{ mol dm}^{-3}, \quad T = 308 \text{ K}, \quad \mu = 0.2 \text{ mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>CH$_3$CN (%)</th>
<th>D</th>
<th>$k' \times 10^{-4}$ (s$^{-1}$)</th>
<th>$10^2 / D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>73.6</td>
<td>4.37</td>
<td>1.359</td>
</tr>
<tr>
<td>5</td>
<td>71.8</td>
<td>4.46</td>
<td>1.393</td>
</tr>
<tr>
<td>10</td>
<td>70.0</td>
<td>4.76</td>
<td>1.428</td>
</tr>
<tr>
<td>15</td>
<td>68.2</td>
<td>4.95</td>
<td>1.466</td>
</tr>
<tr>
<td>20</td>
<td>66.5</td>
<td>5.15</td>
<td>1.504</td>
</tr>
</tbody>
</table>

r = 0.999

**Fig. 3.5:** Plot of 4+$\log k'$ versus $10^2 / D$

![Graph showing the relationship between 4+$\log k'$ and $10^2 / D$ with a regression line and data points.](image)
Table 3.10
Proton inventory studies for the oxidation of PPA in H₂O-D₂O mixture at 308K

<table>
<thead>
<tr>
<th>Atom fraction of D₂O (n)</th>
<th>k \times 10^4 (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>4.375</td>
</tr>
<tr>
<td>0.25</td>
<td>4.202</td>
</tr>
<tr>
<td>0.50</td>
<td>3.916</td>
</tr>
<tr>
<td>0.75</td>
<td>3.302</td>
</tr>
<tr>
<td>0.95</td>
<td>1.829</td>
</tr>
</tbody>
</table>

**Fig. 3.6**: Plot of k' versus n

![Graph of k' versus n](image-url)
### Table 3.11

**Effect of temperature on the reaction rate**

\[ [\text{CAB}] = 5 \times 10^{-4} \text{ mol dm}^{-3}, \quad [\text{PPA}] = 8 \times 10^{-3} \text{ mol dm}^{-3}, \]
\[ [\text{HCl}] = 10 \times 10^{-2} \text{ mol dm}^{-3}, [\text{Ru(III)}] = 1 \times 10^{-4} \text{ mol dm}^{-3}, \mu = 0.2 \text{ mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( k \times 10^4 ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.4</td>
<td>2.57</td>
</tr>
<tr>
<td>308</td>
<td>4.37</td>
</tr>
<tr>
<td>313</td>
<td>8.02</td>
</tr>
<tr>
<td>318</td>
<td>13.32</td>
</tr>
<tr>
<td>321</td>
<td>18.47</td>
</tr>
</tbody>
</table>

\( r = 0.999 \)

**Fig. 3.7**: Plot of \( 4+\log k' \) versus \( 10^3/T \)

![Graph](image.png)
Table 3.12
Kinetic and thermodynamic parameters for the oxidation of PPA with CAB in the presence of HCl and Ru(III) catalyst

<table>
<thead>
<tr>
<th>Activation parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a = 86.29 , \text{kJ mol}^{-1}$</td>
</tr>
<tr>
<td>$\Delta H^\circ = 83.70 , \text{kJ mol}^{-1}$</td>
</tr>
<tr>
<td>$\Delta S^\circ = -37.46 , \text{JK}^{-1} , \text{mol}^{-1}$</td>
</tr>
<tr>
<td>$\Delta G^\circ = 71.99 , \text{kJ mol}^{-1}$</td>
</tr>
</tbody>
</table>

Table 3.13
Double reciprocal plot of $1/k'$ versus $1/[S]$ at constant [Ru(III)] and [H$^+$]

<table>
<thead>
<tr>
<th>1/ [S]</th>
<th>1/k'</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>2817</td>
</tr>
<tr>
<td>167</td>
<td>2487</td>
</tr>
<tr>
<td>125</td>
<td>2288</td>
</tr>
<tr>
<td>100</td>
<td>2128</td>
</tr>
<tr>
<td>83</td>
<td>1887</td>
</tr>
</tbody>
</table>

$r = 0.985$

Fig. 3.8: Plot of $1/k'$ versus 1/[S]
Fig. 3.8
Discussion and mechanism

Chloramine-B acts as a mild oxidant in both acidic and alkaline media. In general CAB undergoes a two-electron change in its reactions forming the reduction products, benzenesulfonamide (BSA) and NaCl. The oxidation potential of CAB-BSA redox couple varies \[6\] with pH of the medium (0.619 V - 1.289 V over the pH range of 9.25 - 0.65). Aqueous solution of CAB behaves as a strong electrolyte and depending on the pH, CAB furnishes different types of reactive species \[6 - 8\]. The possible oxidizing species in acidified CAB solutions are dichloramine-B (RNCl\(_2\)), the conjugate acid (RNHCl), HOCl and H\(_2\)O\(^+\)Cl. If RNCl\(_2\) were to be the reactive species, then the rate law predicts the second-order dependence on \([\text{CAB}]_0\) and negative effect of BSA, which is not in agreement with the experimental observation. If HOCl acts as a reactive oxidant species a first-order retardation of rate on added BSA (RNH\(_2\)) was expected. However, there was no such effect is seen. Hardy and Johnston \[9\] studied the pH dependent relative concentrations of the species present in acidified bromamine-B solutions of comparable molaritites, have shown that RNHBr is the likely oxidizing species in acid medium. Narayanan and Rao\[10\] and Subhashini et al \[11\] have reported that monohaloamines can be further protonated at pH 2 as shown in the following equations (3.2) and (3.3) for monochloramine-T (CH\(_3\)C\(_6\)H\(_4\)SO\(_2\)NHCl) and monochloramine-B (C\(_6\)H\(_5\)SO\(_2\)NHCl), respectively.

\[
\begin{align*}
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHCl} + \text{H}^+ & \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}^+\text{HCl} \quad \ldots.. (3.2) \\
\text{C}_6\text{H}_5\text{SO}_2\text{NHCl} + \text{H}^+ & \rightarrow \text{C}_6\text{H}_5\text{SO}_2\text{N}^+\text{HCl} \quad \ldots.. (3.3)
\end{align*}
\]

The second protonation constants for chloramine-T and chloramine-B are 102 M\(^{-1}\) and 61 ± 5 M\(^{-1}\) respectively at 25 °C.

Cady and Connick\[12\] and Connick and Fine \[13\] based on the ion exchange properties and UV-spectral studies have shown that octahedral complexes such as [RuCl\(_5\)(H\(_2\)O)]\(^2-\), [RuCl\(_4\)(H\(_2\)O)\(_2\)]\(^+\), [RuCl\(_3\)(H\(_2\)O)\(_3\)], [RuCl\(_2\)(H\(_2\)O)\(_4\)]\(^+\) and [RuCl(H\(_2\)O)\(_5\)]\(^2+\) cannot exist in aqueous solution of RuCl\(_3\). However other studies \[14 - 16\] have shown that the following ligand substitution equilibrium in acidic solution,

\[
\begin{align*}
\text{RuCl}_3 \cdot x \text{H}_2\text{O} + \text{HCl} & \rightarrow [\text{RuCl}_6]^{3-} + x \text{H}_2\text{O} \\
[\text{RuCl}_6]^{3-} + \text{H}_2\text{O} & \leftrightarrow [\text{RuCl}_5(\text{H}_2\text{O})]^{2-} + \text{Cl}^- \quad \ldots.. (3.4)
\end{align*}
\]
Singh et al. [17, 18] have used the above equilibrium in Ru(III)-catalyzed oxidation of primary alcohols by bromamine-T and ethylene glycols by N-bromoacetamide in HClO₄ medium. In the present study, however, the absence of effect of chloride ion on the rate indicates that equilibrium (3.4) does not play a role in the reaction and hence the complex ion, [(RuCl₅(H₂O))²⁻] is assumed to be the reactive catalyzing species. Similar results were observed in the Ru(III)-catalyzed oxidations of chloroacetic acid[19], ethanol[20] and aliphatic primary amines[21] by bromamine-T.

Ultraviolet spectral measurements showed that a sharp absorption band was noticed at 216 nm for Ru(III), 226.5 nm for CAB and around 220 nm for PPA in presence of 0.1 mol dm⁻³ HCl. A mixture of CAB and Ru(III) solutions in the presence of HCl showed an absorption band at 265 nm, while for a mixture of PPA and Ru(III) solutions an absorption band was noticed at 220 nm. The spectral evidence showed that complex formation takes place only between Ru(III) and CAB.

Based on the preceding discussion, a detailed mechanistic interpretation (Scheme 3.1) for the Ru(III)-catalyzed CAB-PPA reaction in acid medium has been proposed to substantiate the observed kinetics.

\[
\begin{align*}
\text{RNHCl} + \text{Ru(III)} & \overset{K_1}{\longrightarrow} X \quad \text{fast} \quad \ldots \ldots \text{(i)} \\
X + S & \overset{K_2}{\longrightarrow} X' \quad \text{fast} \quad \ldots \ldots \text{(ii)} \\
X' + H^+ & \overset{k_3}{\longrightarrow} X'' \quad \text{slow and r.d.s} \quad \ldots \ldots \text{(iii)} \\
X'' + H_2O & \overset{k_4}{\longrightarrow} \text{Products} \quad \text{fast} \quad \ldots \ldots \text{(iv)}
\end{align*}
\]

Scheme 3.1

Step (iii) of Scheme 3.1 determines over all rate law,

\[
\text{rate} = -d[CAB]/dt = k_3[X'][H^+] \quad \ldots \ldots \text{(3.5)}
\]

If [CAB] represents total [CAB] in solution, then

\[
[CAB] = [\text{RNHCl}] + [X] + [X'] \quad \ldots \ldots \text{(3.6)}
\]
From, steps (i) and (ii) of Scheme 3.1

\[
[\text{RNHCl}] = \frac{[\text{X}]}{K_1[\text{Ru(III)}]}
\]

and

\[
[X] = \frac{[\text{X}']}{K_2[S]}
\]

Substituting these in equation (3.6) and solving for \([\text{X}']\) we get

\[
[\text{X}'] = \frac{K_1K_2[\text{CAB}][S][\text{Ru(III)}]}{1 + K_1[\text{Ru(III)}] + K_1K_2[S][\text{Ru(III)}]}
\]

…… (3.7)

By substituting for \([\text{X}']\) from equation (3.7) in equation (3.5), the following rate law (3.8) is obtained,

\[
\text{rate} = \frac{K_1K_2k_3[\text{CAB}][S][\text{Ru(III)}][\text{H}^+]}{1 + K_1[\text{Ru(III)}] + K_1K_2[S][\text{Ru(III)}]}
\]

…… (3.8)

The rate law (3.8) is in good agreement with all experimental results. Since \(\text{rate} = k'[\text{CAB}]\), rate law (3.8) can be transformed into equations (3.9) to (3.11).

\[
k' = \frac{K_1K_2k_3[S][\text{Ru(III)}][\text{H}^+]}{1 + K_1[\text{Ru(III)}] + K_1K_2[S][\text{Ru(III)}]}
\]

…… (3.9)

\[
\frac{1}{k'} = \frac{1}{K_1K_2k_3[S][\text{Ru(III)}][\text{H}^+]} + \frac{1}{K_1k_3[S][\text{H}^+]} + \frac{1}{k_3[\text{H}^+]}
\]

…… (3.10)

\[
\frac{1}{k'} = \frac{1}{K_2k_3[S]} \left\{ \frac{1}{K_1[\text{Ru(III)}][\text{H}^+]} + \frac{1}{[\text{H}^+]} \right\} + \frac{1}{k_3[\text{H}^+]}
\]

…… (3.11)

Based on equation (3.11), plot of \(1/k'\) versus \(1/[S]\) at constant \([\text{Ru(III)}]\), \([\text{H}^+]\) and temperature has been found to be linear. The decomposition constant \(k_3\) was calculated \((k_3 = 6.06 \times 10^{-3} \text{ s}^{-1})\) from the intercept of the plot.

In Scheme 3.1 \(S\) represents substrate, \(X\) and \(X'\) represent complex intermediate species whose structures are shown in Scheme 3.2, where a detailed mechanistic interpretation of Ru(III)-catalyzed PPA oxidation by CAB in HCl medium is proposed. PPA with one mole of CAB gets oxidized to acetaldehyde, formaldehyde and Ammonia. The oxygen atom of the oxidant is coordinated to the metal center of the active catalyst.
species, \([\text{RuCl}_3(\text{H}_2\text{O})]^2-\) to form a loosely bound metal complex X. [step (i) of Scheme 3.2]. Then the NH\(_2\) group of the substrate readily reacts with the complex, X to give an another intermediate complex, X', RNH\(_2\) and releasing \([\text{RuCl}_3(\text{H}_2\text{O})]^2-\) [step (ii) of Scheme 3.2]. This intermediate X' undergo intermolecular rearrangements [steps (iii) and (iv)] forming acetaldehyde and formaldehyde.

A change in solvent composition by varying the CH\(_3\)CN content in CH\(_3\)CN – H\(_2\)O affects the reaction rate. The general equation relating to the effect of dielectric constant to the reaction rate in a bimolecular reaction has been derived by Landskroener and Laidler[22]. For the limiting case of zero angle of approach between two dipoles, Amis [23] has shown that,

\[
\ln k'_{D} = \ln k'_{D_{\infty}} - \frac{2\mu_1\mu_2}{DkT^3} \quad \text{……..(3.12)}
\]

Where \(k'_{D}\) is a function of dielectric constant D, \(\mu_1\) and \(\mu_2\) are the dipole moments of reactions, \(r\) is the distance of approach for two dipoles, k is the Boltzmann constant and \(T\) is the absolute temperature. Equation (3.12) predicts a linear relation between \(\log k'\) versus \(1/D\). The slope of the line should be negative for a reaction between two dipole molecules and positive for ion-dipole reactions. In the present case, the plot of \(\log k'\) versus \(1/D\) is linear with a positive slope, thus supporting the participation of ion-dipole species in the rate determining step.

The observed solvent isotope effect supports the proposed mechanism and the derived rate law. For a reaction involving a fast equilibrium H\(^+\) or OH\(^-\) ion transfer, the rate increases in D\(_2\)O medium, since D\(_3\)O\(^+\) and OD\(^-\) which are stronger acid and stronger base respectively than H\(_3\)O\(^+\) and OH\(^-\) ions [24,25]. In the present case, the observed solvent isotope effect of \(k'(\text{H}_2\text{O}) / k'(\text{D}_2\text{O}) > 1\) is due to the protonation step followed by hydrolysis involving the OH bond scission. The retardation of rate in D\(_2\)O is due to the hydrolysis step which tends to make the normal kinetic isotope effect. The proton inventory studies made in H\(_2\)O–D\(_2\)O mixture could throw light on the nature of the transition state. The dependence of the rate constant, \(k'_{\text{obs}}\) on the deuterium atom fraction ‘n’ in the solvent mixture is given by the following form of Gross-Butler equation [26, 27].
Where $\phi_i$ and $\phi_j$ are isotope fractionation factor for isotopically exchangeable hydrogen sites in the transition state (TS) and in the ground/reactant state (RS), respectively. The Gross-Butler equation permits the evaluation of $\phi_i$ when the value of $\phi_j$ is known. However, the curvature of proton inventory plot could reflect the number of exchangeable proton in the reaction [26]. Plot of $k_{\text{obs}}^n$ versus $n$ (Fig.3.6) is a curve in the present case, and this in comparison with the standard curves, indicate the involvement of a single proton or H-D exchange in the reaction sequence [28]. This proton exchange is indicative of the participation of hydrogen ion in the formation of transition state.

The mechanism is further supported by the value of energy of activation and other thermodynamic parameters. The fairly high positive values of free energy of activation and enthalpy of activation indicates that, the transition state is highly solvated, while the negative entropy of activation suggests the formation of the compact activated complex with fewer degrees of freedom. The reduction product (RNH₂) did not influence the rate, showing that it is not involved in pre-equilibrium. Addition of Cl⁻ ion has no effect on the rate indicating that no free chlorine is formed in the reaction. All these observations also confirm the proposed mechanism and derived rate law.
\[
\text{Scheme 3.2}
\]
References


