CHAPTER-2
EXPERIMENTAL METHODS

2.1 PURIFICATION OF MATERIALS

**Acetic acid:**

The procedure followed to purify acetic acid was essentially similar to that of Weissberger and Prabhakar\(^{177}\). Glacial acetic acid (2 litre) was partially frozen and about 1 litre of the liquid was removed. The residue was melted and refluxed with chromium trioxide (10g) and fractionally distilled. The portion distilling between 116-118\(^\circ\) C was collected, partially frozen and out of that, half of the acid was discarded as liquid. The remaining residue was melted and fractionalized again after treating with chromium trioxide. The fraction (at 117\(^\circ\)-118\(^\circ\)C) was collected and kept in brown bottle.

**Conductivity Water:**

Conductivity water used in all experiments was obtained by purifying water with a permutit ion exchanger and then distilling with alkaline permanganate from all glass apparatus.
**Aromatic alcohols:**

Benzyl alcohol and other substituted benzyl alcohols were the purest samples available from M/s Fluka Chemical Industries, Switzerland. They were used as such.

**Aliphatic alcohols:**

Analar grade (E-merk) methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol were purchased and used as such.

**Benzimidazole:**

Benzimidazole (BDH,AR) was used as such without purification.

**Other Chemicals:**

Analytically pure compounds such as sodium perchlorate (Germany), mercury(II)acetate, perchloric acid (BDH, AR), 1,4-dioxane and cyclohexane were used. Perchloric acid was standardized using standard sodium hydroxide solution.

**2.2 Acetic Acid-water mixture**

Acetic acid-water mixture was prepared by mixing known volumes of these solvents. Table A gives the molality of the organic solvents \( C_{\text{org,mol.dm}^{-3}} \), the molality of water \( C_{\text{w,mol.dm}^{-3}} \), the mole fraction of water in the mixture \( X_{w} \) and the dielectric constant of the binary mixture at 40°C
### Table A

<table>
<thead>
<tr>
<th>Solvent mixture % Acetic acid</th>
<th>$C_{\text{org}}$ mol.dm$^{-3}$</th>
<th>$C_{w}$ mol.dm$^{-3}$</th>
<th>$X_{w}$</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>8.64</td>
<td>27.65</td>
<td>0.7625</td>
<td>45.00</td>
</tr>
<tr>
<td>60</td>
<td>10.37</td>
<td>22.12</td>
<td>0.6810</td>
<td>34.50</td>
</tr>
<tr>
<td>70</td>
<td>12.10</td>
<td>16.59</td>
<td>0.5199</td>
<td>27.00</td>
</tr>
<tr>
<td>80</td>
<td>13.82</td>
<td>11.06</td>
<td>0.4434</td>
<td>20.00</td>
</tr>
<tr>
<td>90</td>
<td>15.55</td>
<td>05.03</td>
<td>0.2944</td>
<td>12.80</td>
</tr>
</tbody>
</table>

### 2.3 Preparation of 1-bromobenzimidazole (BBI)$^{178}$

1-Bromobenzimidazole was prepared by the bromination of benzimidazole. Benzimidazole (10g, 0.08mol) was dissolved in aqueous NaOH(40ml, 10%). The solution was cooled to 0 °C. Bromine was added to the mixture (20ml) and the reaction mixture was stirred for 15 minutes. The solid formed as a pale yellow precipitate was filtered off. Any residual bromine was removed by washing with sufficient amount of water followed by grinding the solid in a mortar and filtering. The thoroughly drained solid was dried over CaCl$_2$ in a
desicator. It was recrystallized from ethanol. Yield 11.7g(75%), melting point 197-199 ºC.

2.3.1 Stability:

Approximately (0.015 mol dm$^{-3}$) stock solutions were prepared by dissolving 1.47g of BBI in 500ml of glacial acetic acid, kept in amber colored bottles and standardized iodometrically. This stock solution did not show any noticeable change in concentration over a period of three months.

2.4 Kinetic method:

All the standard flasks and the reaction bottles were of pyrex glass with ground joint stoppers. The volumetric apparatus, the pipettes, burettes and standard flasks were standardized by usual methods.

An electrically operated thermostat with a jumo contact thermometer (West Germany) working in conjunction with an electronic relay which maintained temperature accurately with fluctuations not more than 0.1 ºC was used. The bath liquid was water and it was covered with a layer of thermocole bits to minimize heat and water loss due to radiation.
2.4.1 Preparation of standard solution:

The standard solution of BBI was prepared by dissolving the required quantity of it in glacial acetic acid and standardized by titrating against sodiumthiosulphate solution iodometrically. This BBI solution was found to be invariant in its strength over a period of three months.

The solution of aromatic and aliphatic alcohols was prepared by dissolving the required quantity of these in 80% acetic acid and 20% water mixture (v/v).

2.4.2 Rate Measurement:

All the kinetic reactions were carried out under pseudo-firstorder conditions, keeping [substrate] >> [BBI] in solvent system 80% (V/V) acetic acid-water medium at 308 K and the courses the reaction were followed potentiometrically.

In a typical experiment, the required quantities of the alcohol solutions, perchloric acid, acetic acid-water mixture and mercury(II)acetate solution were pipetted out in a double walled beaker provided with an inlet and outlet for circulating water from the thermostat set at the designed temperature and the solution were
kept in the beaker for nearly an hour to attain the desired temperature. The reaction was started by pipetting out the required quantity of BBI solution which had also been thermostated for nearly half an hour. The total volume of the reaction mixture was always 25ml.

A stop-watch was started when half the amount of oxidant was added. The reaction was followed by setting up a cell

\[
\text{[Pt|BI}^{(+)\text{—BBI}}|^{(+)\text{SCE}}\]
\]

made up of the reaction mixture into which the platinum electrode and reference electrode(SCE) were dipped. The emf of the cell was measured periodically using Equip-Tronics Digital potentiometer while the reaction mixture was continuously stirred using a magnetic stirrer.

The following precautions were taken:

i) When the reaction was followed potentiometrically and iodometrically both the methods gave the same values.

ii) Duplicate experiments were conducted in an atmosphere of nitrogen and without nitrogen. But there was no difference in the results obtained. All experiments reported in this thesis were done in air.
iii) All reactions were carried out under pseudo-first order conditions with substrate concentration in large excess. The rate constants were computed from linear plots of \( \log (E_t - E_0) \) versus time by least square method using linear regression method \( (r>0.99) \).

All experiment was carried out in duplicate and the velocity constants were reproducible within \( +2\% \) error. All pseudo first order rate constant \( (k_{obs}) \) are expressed in \( s^{-1} \).

2.5 Product analysis and stoichiometry:

2.5.1 Oxidation of benzyl alcohol by BBI:

Benzyl alcohol \( (0.2M) \) and BBI \( (0.6M) \) were mixed together with \( \text{HClO}_4 \) \( (1N) \) in 80% acetic acid (total volume 100ml).

The reaction mixture was kept for 48 hours to ensure the completion of the reaction. The solution was extracted with chloroform and the organic layer was washed with water, dried over anhydrous sodium sulphate. Benzaldehyde was formed as the main product under this kinetic conditions and it was identified by the formation of 2,4-dinitrophenylhydrazone derivative \( (m.p 234-236 ^\circ C, \text{lit 237} ^\circ C) \). The estimation of unreacted oxidant indicated that one mole...
of the oxidant was consumed by one mole of alcohol. Further the product benzaldehyde has also been confirmed by its IR Spectral data (Fig-A).

(absorption band appears at 1687 cm\(^{-1}\) is due to \(>\equiv\)Ostretching and the weak absorption band appears at 2829 and 2673 cm\(^{-1}\) are due to the symmetric and asymmetric stretching vibrations of c-11 bands).

\[
\text{R-} \text{C}_6\text{H}_4\text{CH}_2\text{OH} + \text{BBI} \rightarrow \text{RC}_6\text{H}_4\text{CHO} + \text{BI} + \text{HBr}
\]

2.5.2 Oxidation of primary alcohol by BBI:

Methanol (0.3M) and BBI(0.9M) were mixed together with HClO\(_4\)(1m) in 80% acetic acid(total volume 100ml)

The reaction mixture was kept for 48 hours to ensure the completion of the reaction. The solution was extracted with ether, washed with water and dried over anhydrous sodium sulphate. Formaldehyde was formed as the main product. It was identified formaldehyde in water of formalin was treated with semicarbazide. The semicarbazone derivative was formed (mp164-165\(^\circ\)C, lit-167 \(^\circ\)C).

The product was also identified by IR (Fig-B)

\[
\text{R-} \text{CH}_2\text{OH} + \text{BBI} \rightarrow \text{RCHO} + \text{BI} + \text{HBr}
\]
Spectra page
Spectra page
2.5.2 Polymerization test with acrylonitrile.

The following test was performed to check whether any intermediate radicals were formed during Oxidation of aromatic and aliphatic alcohols by BBI in acetic acid medium.

To a solution of 0.1g alcohol in 10ml of acetic acid a few drops of acrylonitrile was added and shaken well. 5ml of 0.01 mol⁻³ BBI in glacial acetic acid was added and stirred well. The solution was kept under nitrogen atmosphere for an hour in a thermostat. No polymer formation was observed.

2.6 THE THERMODYNAMIC FUNCTIONS OF ACTIVATION

In kinetics the variations of reaction rate are usually expressed by Arrhenius equation, which in its integrated form is

\[ \log k = \log A - \frac{E_a}{2.303 RT} \]

where \( k \) is the reaction rate constant.
A is pre-exponential factor and

Ea is Arrhenius activation energy

This equation is in accord with the exponential fact that for most reactions a plot of log k versus 1/T is a straight line. The slope of this line is \(-\text{Ea}/2.303\ \text{R}\). \Ea\ calculated in this way is known as Arrhenius activation energy.

According to the theory of absolute reaction rates due to Glasstone, Laidler and Eyring the expression for the rate constant ‘k’ of a reaction is given as

\[
k = \frac{kT}{h} K^# = \frac{kT}{h} e^{-\Delta G^# /RT} = \frac{kT}{h} e^{-\Delta H^# /RT} e^{-\Delta S^# /RT}
\]

-----(2)

Where \(k\) is the Boltzmann constant, \(h\) is the Planck’s constant, \(K^#\) is the constant for the equilibrium between the reactants and the activated complex and \(\Delta G^#\) is the standard free energy of activation, \(\Delta H^#\) and \(\Delta S^#\) are the enthalpy and entropy of activation respectively.

\[
\ln k = \ln \left(\frac{k}{h}\right) + \ln T - \frac{\Delta H^#}{RT} + \frac{\Delta S^#}{R} \ 
\]

---(3)
Differentiating

\[
\frac{d(\ln k)}{dt} = \frac{1}{T} + \frac{\Delta H^\#}{RT^2} = \frac{RT + \Delta H^\#}{RT} \quad \text{---(4)}
\]

The differential form of Arrhenius equation given by

\[
\frac{d(\ln k)}{dt} = \frac{\Delta H^\#}{RT^2} \quad \text{-------(5)}
\]

Comparing (4) and (5)

\[
E_a = \Delta H^\# + RT \quad \text{-------(6)}
\]

It follows that \(\Delta H^\#\) can be obtained from the Arrhenius activation energy subtracting RT. Although \(\Delta H^\#\) is usually reckoned from the Arrhenius activation energy by means of equation (4) a fastidious calculation makes use of a rearranged form of equation (3). A plot of ln(k/T) versus 1/T has slope \(-\Delta H^\#/R\). \(\Delta H^\#\) is \(-1.987\) times the slope. For most solution kinetics data there is little practical difference between the two methods of calculations. With reference to equation (6), equation (2) can be written as
\[ K = \left[ e^{\frac{kT}{h}} \right] e^{\frac{E_a}{RT}} e^{\frac{\Delta S^\#}{R}} \tag{7} \]

Taking common logarithms and rearranging

\[ \frac{\Delta S^\#}{4.576} = \log k - 10753 - \log T - \frac{E_a}{4.57T} \tag{8} \]

Equation (8) is valid only if the rate constant is based on second as the unit of time. In the present work, the thermodynamic parameters have been determined by making use of equations (6) and (8).