CHAPTER IV

EXPERIMENTAL
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All the experiments were carried out in aqueous acetic acid medium in presence of sulphuric acid.

Materials:

All the chemicals used in the preparation of reagents were the purest available analar grade samples. All the preparations of the reagents and solutions were done with conductivity water.

Purification of reagents

Acetic acid

Acetic acid (Excellar qualigens-unaffected by chromic acid) was purified by refluxing with chromium trioxide and acetic anhydride (2 g of CrO₃ and 5 ml of acetic anhydride per litre of acetic acid) for 6 hours and distilled. The fraction boiling between 117⁰-118⁰c was collected and used.

Conductivity water

Conductivity water was obtained from an electrical all glass still (Tempqua-15). This ultrapure pyrogen free distilled water was used for all the experiments.

Acrylonitrile

Acrylonitrile was distilled under reduced pressure just before use.
Other Chemicals

Potassium iodide (BDH, AR), starch (AR), sodium thiosulphate (AR), sodium sulphate (BDH, AR), sodium hydroxide (AR), sulphuric acid (BDH, AR), hydroxylamine hydrochloride (AR, Qualigens) and mercuric acetate (BDH, AR) were used as such.

Preparation of oxidants

_N-Bromosaccharin_\(^3\)

Saccharin (18.3 g, 0.1 mol dm\(^{-3}\)) was dissolved in aqueous sodium hydroxide (40 ml, 10%). The solution was cooled to about 0°C in an ice-salt bath. Bromine (16 g, 0.2 mol dm\(^{-3}\)) was added to the mixture and the whole stirred for 20 minutes. The solid formed was filtered off. All residual bromine was removed by washing with sufficient amount of water followed by grinding the solid in a mortar with ice and filtering. The thoroughly drained solid was dried over sodium hydroxide in a vacuum desiccator. The yield was found to be 5 g. The melting point of the dried pure sample was 171°C (lit. m. pt. 171-3°C).

_N-Chlorosaccharin_\(^72\)

It was prepared by passing a slow stream of chlorine gas into a suspension of saccharin in water with simultaneous addition of sodium bicarbonate in small amounts for neutralising the hydrochloric acid produced. The precipitated NCSA was
filtered off and recrystallised from chloroform – hexane mixture. Melting point of the pure sample was determined as 150°C (lit. m. pt. 150 - 152°C).

Preparation of substrates

All the oximes were prepared from the respective ketones by the following procedures.

Preparation of aromatic ketoximes

Appropriate quantities of hydroxylamine hydrochloride, sodium acetate and the aromatic ketone were taken in a round-bottomed flask and enough alcohol was added to dissolve the ketone. It was then refluxed on a water bath for about three hours. The excess alcohol was distilled off and the contents of the flask were poured into ice cold water with vigorous stirring. The solid separated was filtered and recrystallized from petroleum ether (b.pt. 60-80°C) or aqueous alcohol to constant melting point. In the case of nitro derivatives, dilute ethanol was used for recrystallization. Acetophenone oxime was characterised to be the syn-isomer using nmr spectral data. (Fig. X) (P. 145 A)
<table>
<thead>
<tr>
<th>Oxime</th>
<th>Boiling point (°C)</th>
<th>Observed</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcPO</td>
<td></td>
<td>59.5</td>
<td>59</td>
</tr>
<tr>
<td>p- MeAcPO</td>
<td></td>
<td>88</td>
<td>88</td>
</tr>
<tr>
<td>p- EtAcPO</td>
<td></td>
<td>84</td>
<td>-</td>
</tr>
<tr>
<td>p- OMeAcPO</td>
<td></td>
<td>88</td>
<td>86-87</td>
</tr>
<tr>
<td>p- Cl AcPO</td>
<td></td>
<td>96</td>
<td>95</td>
</tr>
<tr>
<td>p- NO₂ AcPO</td>
<td></td>
<td>175-176</td>
<td>174</td>
</tr>
<tr>
<td>m- NO₂ AcPO</td>
<td></td>
<td>130-131</td>
<td>132</td>
</tr>
</tbody>
</table>

Preparation of aliphatic ketoximes

Preparation of acetoxime

About 10 g of hydroxylamine hydrochloride was dissolved in 20 ml of water in a round-bottomed flask and to this 20 ml of 30% sodium hydroxide solution was added. The mixture was cooled in ice and 15.2 ml of acetone was added slowly. The flask was shaken well and the solid separated was filtered and dried. This was recrystallized form petroleum ether (b.pt. 40-60°C) to constant melting point (59.5°C).
Preparation of other aliphatic ketoximes.\textsuperscript{76}

The procedure for the preparation of these oximes was the same as that for acetoxime with a slight change. After vigorous shaking of the mixture, the flask was left overnight. The reaction mixture was extracted with ether and the ether extract was evaporated. The pure ketoximes were obtained by distilling the liquid after ether evaporation and collecting the fraction distilling between appropriate temperatures. \textit{n}-Butyl methyl ketoxime was distilled under reduced pressure.

<table>
<thead>
<tr>
<th>Oximes</th>
<th>Boiling point ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
</tr>
<tr>
<td>EMKO</td>
<td>150 – 151</td>
</tr>
<tr>
<td>MnPKO</td>
<td>166 – 168</td>
</tr>
<tr>
<td>M/PKO</td>
<td>157 – 159</td>
</tr>
<tr>
<td>NBMKO</td>
<td>115 /35 mm</td>
</tr>
<tr>
<td>/BMKO</td>
<td>170</td>
</tr>
</tbody>
</table>

Preparation of Alicyclic ketoximes\textsuperscript{76}

10g of hydroxylamine hydrochloride and 16 g of sodium acetate were dissolved in 40 ml of water in a round-bottomed flask. The flask was heated to $40^\circ$C and then to the hot solution 10g of the ketone was added and shaken well. The oxime separated was filtered and recrystallised with petroleum ether (60-80$^\circ$C) to constant melting point.
In the case of cycloheptanone oxime the organic layer was separated from the aqueous layer, dried over anhydrous sodium sulphate and distilled under reduced pressure. The fraction collected at 151°C /20 mm was collected.

<table>
<thead>
<tr>
<th>Oxime</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
</tr>
<tr>
<td>Cyclopentanone oxime</td>
<td>57</td>
</tr>
<tr>
<td>Cyclohexanone oxime</td>
<td>90</td>
</tr>
</tbody>
</table>

**Preparation of stock solutions**

**Sulphuric acid**:

2.5 mol dm$^{-3}$ of sulphuric acid solution was prepared using conductivity water.

**Mercuric acetate**

It was prepared in 50% acetic acid with strength 0.05 mol dm$^{-3}$.

**Substrate**

0.1 mol dm$^{-3}$ of substrate solution was prepared in acetic acid.
Oxidants

A stock solution of NBSA and NCSA of strength $1 \times 10^{-2} \text{ mol dm}^{-3}$ were prepared afresh in 80% aqueous acetic acid. Their strengths were ascertained by iodometric titrations.

Estimation of oxidants

5 ml of the stock solution of NBSA or NCSA was pipetted out into a clean conical flask. About 5 ml of 20% potassium iodide were added. The liberated iodine was titrated against standardised sodium thiosulphate solution using freshly prepared starch as an indicator. From the volume and strength of the sodium thiosulphate solution, the strength of NBSA or NCSA solution was calculated using the relation,

$$\text{strength of oxidant} = \frac{\text{volume of sodium thiosulphate} \times \text{strength of sodium thio sulphate}}{5 \times 2}$$

(61)

$$\text{C}_7\text{H}_4\text{SO}_3\text{NX} + 2 \text{H}^+ + 2\text{I}^- \rightarrow \text{C}_7\text{H}_4\text{SO}_3\text{NH} + \text{HBr} + \text{I}_2$$

X=Br or Cl

(62)
Experimental conditions

Oxidation by NBSA

All the rate measurements were carried out in 50% (v/v) aqueous acetic acid medium in the temperature range 278K – 308K in the presence of sulphuric acid (0.10 mol dm$^{-3}$) and 2.00 x $10^{-3}$ mol dm$^{-3}$ of mercuric acetate. The kinetic runs were followed under pseudo-first order condition keeping the concentration of substrate in considerable excess over that of the oxidant. Ionic strength of the medium was maintained by adding calculated quantities of sodium sulphate. The concentration of NBSA was varied in the range 1.00 - 1.40 x $10^{-3}$ mol dm$^{-3}$ and those of substrates from 1.00 - 3.00 x $10^{-2}$ mol dm$^{-3}$ in order to evaluate the rate dependence on the oxidant and substrate respectively. The order with respect to acid was determined by varying the concentration of sulphuric acid at constant ionic strength. The influence of ionic strength on the rates of oxidation was investigated by performing the reaction in the presence of added sodium sulphate with concentrations ranging from 0.10 - 0.40 mol dm$^{-3}$ maintaining the constant acid concentration. By varying the percentage of acetic acid in the range 50-80% (v/v), the effect of dielectric constant on the rate was studied. In order to compute activation parameters, kinetic runs were carried out at different temperatures. Effect of added saccharin and mercuric acetate on the rate of the reaction were studied by varying the concentration of corresponding reagents.
Oxidation by NCSA

All the kinetic runs were carried out in 50% (v/v) aqueous acetic acid under pseudo-first order condition, ([subs] >> [NCSA]), in presence of sulphuric acid. The order with respect to NCSA and substrates were determined by varying the concentration of oxidant and substrate as in the case of NCSA oxidation.

The effect of $[H^+]$ ($2.50 \times 10^{-2} - 10.00 \times 10^{-2} \text{ mol dm}^{-3}$) at constant ionic strength (0.10 mol dm$^{-3}$) and the effect of ionic strength ($2.50 - 10.00 \times 10^{-2} \text{ mol dm}^{-3}$) were also investigated. The percentage of acetic acid was varied from 50-80% (v/v) to study the effect of dielectric constant. Reaction was followed at different temperatures (278 – 293K) to evaluate the activation parameters.

Typical measurements

In all the experiments, calculated quantities of substrate, acetic acid, mercuric acetate (in the case of NCSA oxidation, mercuric acetate is not used), Sulphuric acid and conductivity water were first pipetted out into the reaction vessel so that the total volume of the reaction mixture was 50ml after the addition of the oxidant. The reaction mixture was thermally equilibrated at the desired temperature ($\pm 1^\circ\text{C}$). Calculated volume of the oxidant from the thermostated stock solution was pipetted out into the reaction mixture, starting a stop watch simultaneously at the time of half addition of oxidant. Aliquot portions (5ml) of the reaction mixture were withdrawn at known intervals of time and transferred quantitatively into a conical flask containing approximately 5 ml of 20%. Potassium iodide solution. The liberated iodine was
titrated against standardised sodium thio sulphate solution using starch as an indicator.

From the amount of oxidant unreacted, [oxidant], was determined iodometrically for each kinetic run. The pseudo-first order rate constant, \( k' \, s^{-1} \) was evaluated from the slopes of the plots of \( \log([\text{oxidant}] \) Vs time (min)

\[
k_i(s^{-1}) = \frac{\text{Slope} \times 2303}{60}
\]  

(63)

**Test for free radicals**

The reaction mixture was tested with monomer acrylonitrile – a free radical trap in nitrogen atmosphere.

**Stoichiometry**

The stoichiometry of the reactions between the substrate and oxidant was determined by taking excess of [NBSA] over [substrate] and allowing the reaction to go for completion. Since the concentration of the substrate taken is less compared to that of oxidant, all the substrate taken would have completely reacted leaving behind the unreacted oxidant. The concentration of remaining oxidant was estimated iodometrically. From the amount of substrate reacted and the amount of oxidant (NBSA or NCSA) consumed, the stoichiometry \([\text{substrate}]:[\text{oxidant}]\) was estimated

**Product analysis**

A reaction mixture containing a slight excess of oxidant, substrate and acetic acid- water mixture was kept aside at room temperature for a day, so that the substrate completely converted into product. This reaction mixture was analysed for the
products using spot tests. Further the mixture was neutralised with sodium bicarbonate and extracted with ether. The ether extract was dried with anhydrous sodium sulphate, concentrated and then it was analysed by spot test. The product was also confirmed by thin layer chromatography. It was found that the parent ketones were obtained as products.

**Accuracy of results**

The pseudo-first order rate constants $k_i(s^{-1})$ were evaluated by the method of least squares. Duplicate experiments were carried out to estimate the experimental error. It was observed that the rate constants could be reproduced with an accuracy of $\pm 3\%$. 