CHAPTER - 2

PREPARATION OF SOLUTIONS OF REAGENTS, METHOD OF KINETIC STUDIES

AND MATERIALS EMPLOYED
2. PREPARATION OF SOLUTIONS OF REAGENTS, METHOD OF KINETIC STUDIES AND MATERIALS EMPLOYED.

The standard solution of sodium periodate (NaIO₄) was prepared by dissolving its weighed amount in double distilled water. The prepared solution was then standardized against hypo solution which was already standardized against copper sulphate (B.D.H.) solution.

The solution of perchloric acid was prepared directly by dissolving the E. Merck grade sample in double distilled water which was then standardized with standard solution of sodium hydroxide (B.D.H. or E. Merck). Perchloric acid is used as a source of hydrogen ion. Mercuric acetate (E. Merck) was dissolved in double distilled water acidified with acetic acid (10%).

Potassium chloride was prepared by dissolving calculated amount of their Analar (B.D.H.) grade sample in double distilled water. Appropriate amount of sodium thiosulphate (A.R., B.D.H.) was dissolved in double distilled water. It was standardized against standard copper sulphate solution by iodometric method.

4% of Potassium iodide (KI) (A.R. B.D.H.) was prepared by dissolving appropriate amount of sample in double distilled water. 1% starch solution of A.R. (B.D.H.) grade was used as an indicator. Both KI and starch solutions were prepared fresh each day.

Solution of substrate were prepared by dissolving weighed samples in double distilled water. One gram sample of Rhodium(III) chloride was dissolved in known strength of HCl and then solution was made up to 1000 ml.

To prevent photo-chemical reactions, the reaction stills were blackened from outside.
METHOD OF STUDY

During the course of study all the reactions were studied in black coated flasks to avoid any photochemical effect. For the prevention of any foreign ion effect, double distilled water was used throughout the course of study. The total reaction mixture was always kept at 50 ml. in each case.

The reaction mixture containing requisite amount of all the reactants i.e. substrate, Perchloric acid, Rh(III) chloride, Mercuric acetate and required volume of water were taken in a reaction bottle which was kept in an electrically operated thermostatic water bath maintained at desired temperature 35°C. In another bottle requisite volume of sodium periodate was taken and this bottle was also kept in the same thermostat to attain the desired temperature. When solutions of both bottles had attained the temperature of the thermostat, then solution of sodium periodate in its requisite volume was poured in first bottle containing other solutions and immediately a stop watch was started to record the time for beginning of the reaction. After vigorously shaking the reaction mixture for a few seconds, 5 ml. of the reaction mixture was taken out immediately and poured into acidified potassium iodide solution. The equivalent I₂ liberated was titrated with hypo standard solution using starch as an indicator. The estimation of unconsumed sodium periodate was carried out iodometrically at different intervals of time. These titrate values were used for calculation of rate constants. The above kinetic procedure was followed at different initial concentrations of various reagents used in acidic media at different temperatures viz. 30°C to 45°C.

These kinetic runs were used to ascertain the dependence of reactions on various reagents used here. The rate of the reaction i.e. (-dc/dt) in each
experiment was calculated from the slope of the curve obtained when a graph was plotted between unconsumed sodium periodate and time. The value of \((-dc/dt)\) was determined at certain fixed concentration of sodium periodate.

The value of \(k_1\) i.e. rate constant for first order is calculated from the formula

\[
k_1 = \frac{(-dc/dt)}{[\text{NaIO}_4]^*}
\]

whenever needed. The value of second order rate constant \((k_2)\) is calculated by the formula \(k_1 / [\text{reactant}]\) where reactant is one with respect to which order is to be determined.
2.1 STOICHIOMETRY AND PRODUCT ANALYSIS

For the determination of stoichiometry of the reaction, different sets of reaction mixtures containing substrate and the oxidant in the approximate molar proportions of 1:2, 1:3, 1:4 and 1:5 were allowed to stand for about 24 hours at 35°C under the experimental conditions. Corresponding blank sets were also kept in the same bath for the same time or period. After the reaction was completed, excess of the oxidant was then titrated iodometrically.

Molecularity of the reaction was calculated with the help of the following equation:

\[
W = \frac{(B - A) \times N \times M}{2 \times m}
\]

where,

- \( W \) = amount of the sample taken in the system in mg.
- \( B \) = Titre value of the blank set.
- \( A \) = Titre value of the set with sample.
- \( M \) = Molecular weight of the sample (substrate).
- \( m \) = Number of moles of NaIO\(_4\) (oxidant) consumed.
- \( N \) = Normality of the hypo solution being used as titrant.
2.1(a) STOICHIOMETRY AND PRODUCT ANALYSIS OF CYCLIC KETONES

Various experiments with different concentration of sodium periodate and substrates ([NaIO₄] : [substrate]) ratio under the experimental conditions were carried out for 48 hours in acidic medium.

Estimation of unconsumed [NaIO₄] revealed that, in acidic medium for the oxidation of each one mole of substrate three moles of periodate were consumed (Table 2.1). Accordingly the stoichiometric equation may be given as below:

1) Stoichiometric equation for cyclopentanone in acidic medium.

\[
\text{CH}_2\text{CH} = \text{CH} - \text{CH}_2 \text{C}=\text{O} + 3\text{HIO}_4 \rightarrow \text{CH}_2\text{CH} = \text{CH} - \text{CH}_2 \text{CH}_2\text{COOH} + 3\text{HIO}_3
\]

(cyclopentanone) Glutaric acid

2) Stoichiometric equation for cyclohexanone in acidic medium.

\[
\text{CH}_2\text{CH} = \text{CH} - \text{CH}_2 \text{C}=\text{O} + 3\text{HIO}_4 \rightarrow \text{CH}_2\text{CH} = \text{CH} - \text{CH}_2 \text{CH}_2\text{COOH} + 3\text{HIO}_3
\]

(cyclohexanone) Adipic acid

3) Stoichiometric equation for cycloheptanone in acidic medium

\[
\text{CH}_2\text{CH} = \text{CH} - \text{CH}_2 \text{C}=\text{O} + 3\text{HIO}_4 \rightarrow \text{CH}_2\text{CH} = \text{CH} - \text{CH}_2 \text{CH}_2\text{COOH} + 3\text{HIO}_3
\]

(cycloheptanone) Pimelic acid
Identification of the end products formed in the above reactions i.e. Glutaric acid, adipic acid and Pimelic acid respectively were carried out as follows:

Took a small amount of reaction mixture in a test tube and added to it twice its amount of resorcinol then added 1 ml. conc. H₂SO₄ to this mixture. Heated till the mixture becomes red brown in colour. Cooled and poured in 200 ml. water which had been made alkaline with NaOH. A violet red coloured fluorescence is obtained in case of Adipic acid and Pimelic acid. A yellow green fluorescence is obtained in case of Glutaric acid.

The end products were also identified by the spot test analysis.
2.1(b) STOICHIOMETRY AND PRODUCT ANALYSIS OF SUGARS:

Estimation of unconsumed sodium periodate revealed that in acidic medium for the oxidation of each one mole of substrate two moles of periodate were consumed in case of maltose, dextrose and three moles of periodate were consumed in case of sucrose (Table 2.2). Accordingly the stoichiometric equation may be given as below:-

1) Stoichiometric equation for maltose in acidic medium.

\[
\text{CHOH} \quad \text{H-C-OH} \quad \text{HO-C-H} \quad \text{H-C-OH} + 2\text{HIO}_4 + 2\text{H}^+ \quad \rightarrow \\
\text{HO-C-H} \quad \text{H-C-OH} \quad \text{H-C} \quad \text{H-C-OH} \\
\text{H-C} \quad \text{H-C} \quad \text{CH}_2\text{OH} \quad \text{maltose} \quad \text{CH}_2\text{OH} \\
\text{H-C} \quad \text{H-C} \quad \text{H-C} \quad \text{H-C} \quad \text{HO-C-H} \quad \text{H-C-OH} \quad \text{H-C-OH} \\
\text{H-C-OH} \quad \text{H-C-OH} \quad \text{H-C} \quad \text{H-C} \quad \text{CH}_2\text{OH} \quad \text{maltobionic acid} \quad \text{CH}_2\text{OH}
\]
2. Stoichiometric equation for dextrose in acidic medium.

\[
\begin{align*}
\text{CHO} & \quad \text{COOH} \\
\text{H-C-OH} & \quad \text{H-C-OH} \\
\text{HO-C-H} & \quad \text{HO-C-H} \\
\text{H-C-OH} & \quad \text{H-C-OH} \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} \\
\text{(Dextrose)} & \quad \text{(Gluconic acid)} \\
\end{align*}
\]

\[\text{HO-C-H + 2HIO}_4 \rightarrow \text{HO-C-H + 2HIO}_3 + \text{H}_2\text{O}\]

3) Stoichiometric equation for sucrose in acidic medium.

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} \\
\text{H-C-OH} & \quad \text{H-C-OH} \\
\text{HO-C-H} & \quad \text{HO-C-H} \\
\text{H-C-OH} & \quad \text{H-C-OH} \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} \\
\text{(sucrose)} & \quad \text{(formic acid)} \\
\end{align*}
\]

\[\text{HO-C-H + 3HIO}_4 \rightarrow \text{HCOOH}\]
The end products formed in the above reactions i.e., maltobionic acid, gluconic acid, formic acid and tetraldehyde respectively for maltose, dextrose and sucrose were identified by conventional method.$^2$
Table 2.1

Stoichiometric results for oxidation of cyclopentanone, cyclohexanone, and cycloheptanone

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<td>4.96</td>
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[Rh(III)] = $5.72 \times 10^{-5}$ M  
[HClO₄] = $1.00 \times 10^{-3}$ M  
[KCl] = $1.00 \times 10^{-3}$ M  
Temp. = 35°C  
[Hg(OAc)₂] = $1.25 \times 10^{-3}$ M  
$[IO₄]⁺ = [IO₄]$ left unconsumed after 48 h.  
$[IO₄]⁻ = [IO₄] - [IO₄]⁺$ i.e. oxidant consumed during the reaction.
### Table 2.2

Stoichiometric results for oxidation of Maltose, Dextrose and Sucrose

<table>
<thead>
<tr>
<th>$10^2$ [IO$_4^-$] M</th>
<th>$10^3$ [Substrate] M</th>
<th>$10^3$ [IO$_4^-$]* M (residual)</th>
<th>[IO$_4^-$]/[substrate]</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Maltose</td>
<td>Dextrose</td>
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<td>12.50</td>
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<tr>
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<td>5.00</td>
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<td>2.60</td>
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$[\text{Rh(III)}] = 5.72 \times 10^{-5}$ M, $[\text{KCl}] = 1.00 \times 10^{-3}$ M

$[\text{HClO}_4] = 1.00 \times 10^{-3}$ M (maltose), $2.5 \times 10^{-3}$ M (dextrose) & $5.00 \times 10^{-3}$ M (sucrose)

$[\text{Hg(OAc)}_2] = 1.25 \times 10^{-3}$ M (maltose & dextrose), $1.67 \times 10^{-3}$ M (sucrose)

Temp. = 35°C.

$[\text{IO}_4^-]^* = [\text{IO}_4^-]$ left unconsumed after 48 h.

$[\text{IO}_4^-]^2 = [\text{IO}_4^-] - [\text{IO}_4^-]^*$ i.e. oxidant consumed during the reaction.
References
