CHAPTER-II
EXPERIMENTAL

REAGENTS USED AND PREPARATION OF THEIR STOCK SOLUTIONS, METHOD OF INVESTIGATION, STOICHIOMETRY OF THE REACTIONS AND PRODUCT ANALYSIS
2. 1: Reagents used and preparation of their stock solutions

Prior to kinetic study of reaction, several solutions of reagents were prepared which are described below-

(1) Oxalic acid (H$_2$C$_2$O$_4$. 2H$_2$O): E. Merck grade of oxalic acid was used for preparing standard solution of its required strength and it was used for standardizing sodium hydroxide solution using phenolphthalein as an indicator.

(2) Sodium hydroxide (NaOH): E. Merck grade of sodium hydroxide was used. Since sodium hydroxide is deliquescent. Therefore its stock solution was prepared by dissolving approximate amount for its required strength in double distilled water. The stock solution so prepared was, further, standardized against oxalic acid standard solution using Phenolphthalein as indicator. NaOH is used as source of hydroxide ion in present kinetic investigation.

(3) Copper sulphate (CuSO$_4$. 5H$_2$O): E. Merck sample of copper sulphate was used for preparing its standard solution. While preparing its standard solution, about 25ml of 0.2M acetic acid was added to known volume of distilled water in which weighed amount of copper sulphate was dissolved. Acetic acid was added to copper sulphate solution at preparation stage to avoid hydrolysis of copper sulphate.

(4) Sodium thiosulphate (Na$_2$S$_2$O$_3$.5H$_2$O): Appropriate amount of sodium thiosulphate (E. Merck) for required strength was dissolved in double distilled water. The solution so prepared was kept as such for 2 to 3 days for its stabilization. This stock solution was standardized against copper sulphate standard solution iodometrically. Sodium
thiosulphate (Hypo) solution was used to estimate the concentration of remaining oxidant in reaction mixture at different time intervals iodometrically during kinetic investigation of reactions.

(5) Potassium iodide (KI): About 4% (by weight) freshly prepared solution of potassium iodide of E. Merck is used in Iodometric titration.

(6) Starch: Freshly prepared 1% starch (E. Merck) solution was used in iodometric titration.

(7) Potassium iodate (KIO₃): The solution of potassium iodate (E. Merck) was prepared by dissolving appropriate amount of potassium iodate for its required strength in double distilled water. The solution so prepared was standardized against copper sulphate solution iodometrically. It was used as oxidant in present kinetic investigation.

(8) Perchloric acid (HClO₄): The solution of Perchloric acid (E. Merck) was prepared directly by dissolving appropriate volume of sample for its required strength in double distilled water which was further standarised against standard solution of sodium hydroxide using Phenolphthalein as an indicator. Perchloric acid is used as source of hydrogen ion (H₃O⁺) in present investigations.

(9) Chloramine - T (CAT): The solution of chloramine - T (E. Merck) was prepared by dissolving appropriate amount for its required strength in double distilled water. The strength of prepared chloramine -T (CAT) was checked iodometrically for active chlorine by standardizing it against sodium thiosulphate (Hypo) which was already standarised against copper sulphate solution. The prepared solution of chloramine - T
(CAT) was always stored in blackened flask to prevent its photochemical decomposition. It was used as oxidant in present kinetic investigation.

(10) **Crotonic acid (CA):** The solution of crotonic acid (Koch-light lab) was prepared by dissolving appropriate amount of crotonic acid for its required strength in double distilled water. It was used as reducing substrate in kinetic study.

(11) **L-methionine (Met):** The solution of L-methionine (Senn chemicals) was prepared by dissolving appropriate amount of sample for its required strength in double distilled water. It was used as reducing substrate in kinetic study.

(12) **Potassium chloride (KCl):** Desired and weighed quantity of KCl (E. Merck) was dissolved in known volume of double distilled water to prepare its standard solution.

(13) **Sodium perchlorate (NaClO₄):** E. Merck sample of sodium perchlorate is used for preparing its solution for the study of effect of ionic strength of medium on the reaction rate. Its weighed quantity was dissolved in known volume of distilled water.

(14) **Iridium (III) chloride [Ir(III)Cl₃]:** The solution of Ir(III) chloride (S.D. fine chem.) was prepared by dissolving one gram sample in 200ml of 0.01M solution of hydrochloric acid and the solution so prepared was diluted to 1000 ml with double distilled water. The strength of the prepared Ir(III) chloride solution was $3.349 \times 10^{-3}$ M. It was used as homogeneous catalyst in present kinetic investigation.

(15) **Osmium tetroxide (OsO₄):** The solution of osmium tetroxide (Matthey and Johnson) was prepared by dissolving its one gm of sample in 200 ml of 0.1M NaOH and the solution so prepared was diluted to 1000 ml with double distilled water. The
strength of so prepared O₃O₄ solution was 3.39×10⁻³M. It was used as homogeneous catalyst in present kinetic investigation.

(16) **Rhodium (III) chloride:** The solution of rhodium (III) chloride (Matthey and Johnson) was prepared by dissolving its 1 gm sample in 200 ml of 3.6M hydrochloric acid and the solution so prepared was diluted to 500 ml with double distilled water. The strength of so prepared rhodium(III) chloride solution was 7.60×10⁻³M. It was used as homogeneous catalyst in present investigation.

(17) **Mercuric acetate (Hg (OAc)₂):** Mercuric acetate (E. Merck) was dissolved firstly in glacial acetic acid (AR) and then made up to its required volume with double distilled water. Acetic acid strength in Hg(OAc)₂ solution should not be more than 20%. It was used as scavenger in redox reaction.

(18) **Para-toluene sulphonamide (PTS):** Para-toluene sulphonamide (E. Merck) was firstly dissolved in acetic acid and then made up to its required volume with double distilled water.
2. 2: METHOD OF INVESTIGATION

During course of kinetic study black coated glass wares (conical) have been used as reaction mixture vessel to avoid any photochemical reaction. Double distilled water has been used throughout the investigation to eliminate any foreign ion effect. All the reagents used were of highest purity percentage available. Kinetic investigations have been carried out titrimetrically.

The actual progress of reaction has been monitored by estimating the concentration of unconsumed oxidant (CAT /or KIO₃ in present investigation) in the reaction mixture at regular time intervals against standard solution of sodium thiosulphate (Hypo) iodometrically.

The reaction mixture containing requisite amounts of all other reactants of redox reaction, except oxidant, was taken in a reaction vessel (blackened from outside) which was kept in an electrically operated thermostatic waterbath set at desired temperature (± 0.1°C). The requisite volume of oxidant was also taken in another black coated vessel which too was placed in the same thermostat for thermal equilibrium.

After half an hour when solutions of both vessels had acquired the temperature of bath then required volume of oxidant was sucked out by a pipette and poured in reaction vessel which was already containing mixture of all other reactants to initiate redox reaction. Immediately this mixed solution was vigorously shaken and the stop watch was started to record time. Thereafter an aliquot (5ml) was at once taken out at
zero time from this reaction vessel and quickly transferred to 5ml of KI (4%) solution acidified by 5ml HClO₄ (0.5M) solution. The function of KI solution is to check the reaction. The remaining (i.e. unconsumed) amount of oxidant in aliquot of reaction mixture reacts with KI and liberates an equivalent amount of iodine from KI solution. This liberated I₂ was titrated against standard solution of hypo using starch as an indicator.

The progress of the reaction was monitored by measuring the remaining oxidant concentration at different time intervals. The readings noted at different time intervals were used to calculate the rate constant (k) of reaction with help of initial rate (i.e. -dc/dt). These results were used for kinetic studies of redox reactions undertaken in the present thesis.
2.3: Stoichiometry of the reactions and products analysis

(1) In oxidation of crotonic acid by chloramine-T (RNNaCl) in the presence of Rh(III)chloride as homogeneous catalyst in alkaline medium:

Varying [CA]: [RNNaCl] ratios were equilibrated at 35°C for 72 hours under the experimental condition [CA] << [RNNaCl]. Estimation of remaining [RNNaCl] in different sets indicated that one mole of CA consumes two moles of chloramine-T. Accordingly, the following stoichiometric equation can be formulated as given below:

\[
\begin{align*}
\text{CH}_3\text{C} = \text{CHCOOH} + 2 \text{RNNaCl} + 2 \text{H}_2\text{O} & \xrightarrow{\text{Rh(III)}\text{OH}^-} \text{CHO} \text{COOH} + \text{CH}_3\text{CHO} + 2 \text{RNH}_2 + 2 \text{NaCl}
\end{align*}
\]

Where R = CH₃C₆H₄SO₂ —

The aforesaid products were analysed by NUCON gas chromatography [1] using porapak-Q 101 column and programmed oven temperature having F. I. D. detector. The major products were identified as glyoxylic acid and acetaldehyde by comparison of retention time with the retention time of their standard solutions. The products were found to be identical under both stoichiometric and kinetic conditions and also by a spot test [2]. The reduction product of CAT, p-toluene sulphonamide (RNH₂) was detected by paper chromatography [3]. [Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl solution in ethanol as spray reagent (Rf 0.905).]
(2) In oxidation of crotonic acid by chloramine-T [RNNaCl] in the presence of osmium(VIII) as homogeneous catalyst in alkaline medium:

Varying [CA]: [RNNaCl] ratios were equilibrated at 35°C for 72 hours under the experimental condition [CA] << [RNNaCl]. Estimation of remaining [RNNaCl] in different sets indicated that one mole of CA consumes four moles of chloramine-T. Accordingly, the following stoichiometric equation can be formulated as given below:

\[
\text{CH}_3\text{CH}=\text{CHCOOH} + 4 \text{RNCNa} + 4 \text{H}_2\text{O} \xrightarrow{\text{OsO}_4/\text{OH}^-} \text{CH}_3\text{COOH} + \text{COOH} + 4 \text{RNH}_2 + 4 \text{NaCl}
\]

Acetic acid was identified as the product by thin layer chromatography (TLC) technique [4] using n-butanol-dimethylamine-water in the ratio of 85:1:14 as the developing solvent was used to verify the presence of acetic acid in oxidation of CA. The R\text{f} value was found to be 0.44 which is very close to the reported R\text{f} value, 0.45 for acetic acid in the aforesaid solvent system. The aforesaid products were analysed by NUCON gas chromatography using porapak-Q 101 column and programmed oven temperature having F. I. D.detector. The major products were identified as oxalic acid and acetic acid in the Os(VIII) catalysed oxidation of CA by CAT in alkaline medium, by comparing the retention time of identified products with the retention time of their standard solutions. The reduction product of CAT, p-toluene sulphonamide (RNH\text{2}) was detected by paper chromatography [3]. [Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl solution in ethanol as spray reagent (R\text{f} 0.905).]
(3) In oxidation of L-methionine by chloramine-T in the presence of Ir(III)chloride as homogeneous catalyst in alkaline medium:

Varying [L-methionine]: [RNNaCl] ratios in the presence of NaOH were equilibrated at 308K for 24 hours under the experimental condition [L-methionine] << [RNNaCl]. The unchanged [RNNaCl] in the reaction mixtures was determined by iodometric titrations. The analysis showed that one mole of L-methionine consumed two moles of chloramine-T. Accordingly, the following stoichiometric equation can be formulated as given below:

\[
\begin{align*}
\begin{array}{c}
R'\text{S}^-\text{CH}_3 + 2\text{RNHCl} & \xrightarrow{\text{Ir(III)/OH}^-} R'\text{S}^-\text{CH}_3 + 2\text{RNH}_2 + 2\text{HCl}
\end{array}
\end{align*}
\]

Methionine sulphone

The reaction mixture in the stoichiometric ratio in presence of NaOH and Ir(III) catalyst under stirred condition was allowed to progress for 24 h at 308 K. After completion of the reaction, the reaction mixture was neutralized with dilute HCl and the products were extracted with ethyl acetate. The organic products were identified by using TLC technique and separated by column chromatography. The purified compounds were recrystalized by methanol. The reduction product of CAT, p-toluene sulphonamide was identified [5] by paper chromatography using PhCH\_2OH saturated with H\_2O as the solvent with 0.5% vanillin in 1% HCl solution in ethanol as the spray reagent (R\_f = 0.905). Identification of methionine sulphone was also made through paper
chromatography [6]. [The solvent employed was n-butanol–glacial acetic acid–water (4:1:5 v/v), and a 0.2% solution of ninhydrin in butanol, water, and acetic acid (95:4:0.5) was used as the spray reagent (Rf 0.17).]

(4) In oxidation of L-methionine by potassium iodate in the presence of Rh(III) chloride as homogeneous catalyst in acidic medium:

Varying [L-methionine]: [KIO₃] ratios were equilibrated at 308K for 24 hours under the experimental condition [L-methionine] << [KIO₃]. Estimation of remaining [KIO₃] in different sets indicated that 3 moles of L-methionine consumed 2 moles of KIO₃. Accordingly, the following stoichiometric equation can be formulated as given below:

\[
3 \text{R-S-CH}_3 + 2 \text{IO}_3^- \xrightarrow{[\text{Rh(III)]/H}^+} 3 \text{R-S-CH}_3 + 2 \text{I}^-
\]

Identification of methionine sulphone was also made through paper chromatography [6]. [The solvent employed was n-butanol–glacial acetic acid–water (4:1:5 v/v), and a 0.2% solution of ninhydrin in butanol, water, and acetic acid (95:4:0.5) was used as the spray reagent (Rf 0.17).]

(5) In oxidation of L-methionine by potassium iodate in the presence of Rh(III) chloride as homogeneous catalyst in alkaline medium:

Varying [L-methionine]: [KIO₃] ratios were equilibrated at 308K for 24 hours under the experimental condition [L-methionine] << [KIO₃]. Estimation of remaining [KIO₃] in different sets indicated that 3 moles of L-methionine consumed 2 moles of KIO₃. Accordingly, the following stoichiometric equation can be formulated as given below:
Identification of methionine sulphone was also made through paper chromatography [6]. [The solvent employed was n-butanol–glacial acetic acid–water (4:1:5 v/v), and a 0.2% solution of ninhydrin in butanol, water, and acetic acid (95:4:0.5) was used as the spray reagent (Rf 0.17).]

\[
3 \text{R-S-CH}_3 + 2 \text{IO}_3^- \xrightarrow{[\text{Rh(II)}]/\text{OH}^-} 3 \text{R-S-CH}_3 + 2 \text{I}^-
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REFERENCES


