CHAPTER-II

EXPERIMENTAL
2. A: REAGENTS USED AND PREPARATION OF THEIR STOCK SOLUTIONS

Prior to kinetic study of reaction, solutions of several reagents were prepared as 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 stock solution was prepared by dissolving its 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 also used as source of hydroxide ion (OH⁻) 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 is added to known volume of distilled water in which weighed amount of copper sulphate is dissolved. Acetic acid is 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 reaction.

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 as an indicator.

7. Perchloric acid (HClO₄): The standard solution of perchloric acid (E. Merck, 70%) was prepared directly by dissolving its appropriate volume of sample for its required strength in double distilled water which was further standardised against standard solution of sodium hydroxide using phenolphthalein as an indicator. Perchloric acid is used as source of hydrogen ion in present investigations.

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

9. N-bromosuccinimide (NBS): The solution of N-bromosuccinimide (E. Merck) was prepared by dissolving its
appropriate amount for its required strength in the double distilled water. The strength of prepared N-bromosuccinimide (NBS) solution was checked iodometrically for active bromine by standardizing it against standard sodium thiosulphate (Hypo) which was already standardized against copper sulphate solution. The prepared solution of N-bromosuccinimide (NBS) was stored in flask blackened from outside to prevent its photochemical decomposition. It was used as oxidant in present kinetic investigation.

10. **D-Threonine**: The solution of D-threonine of required strength was prepared by dissolving its weighed quantity in known volume of double distilled water. It was used as reducing substrate in kinetic study.

11. **Trimethylene glycol**: The solution of trimethylene glycol (E. Merck) was prepared by dissolving its appropriate amount of trimethylene glycol for its required strength in double distilled water. It was used as reducing substrate in kinetic study.

12. **Dimethyl digol (DMD)**: The solution of dimethyl digol (E. Merck) was prepared by dissolving its appropriate volume for its required strength in double distilled water. It was used as reducing substrate in kinetic study.

13. **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.

14. **Sodium perchlorate (NaClO₄)**: E. Merck sample of sodium perchlorate was 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.
15. **Rhodium (III) chloride**: The solution of Rhodium (III) chloride was prepared by dissolving its one gm sample in 200 ml of 3.6 M hydrochloric acid and the solution so prepared was diluted to 500 ml with double distilled water. The strength of so prepared Rh(III) chloride solution was $7.60 \times 10^{-3}$ M. It was used as homogeneous catalyst in present investigation.

16. **Ruthenium (III) chloride**: The solution of Ruthenium (III) chloride was prepared by dissolving its one gm sample in 200 ml of 3.6 M hydrochloric acid and the solution so prepared was diluted to 500 ml with double distilled water. The strength of so prepared Ru(III) chloride solution was $3.60 \times 10^{-3}$ M. It was used as homogeneous catalyst in present investigation.

17. **Iridium (III) chloride**: The solution of Ir(III) chloride (S.D. fine chem.) was prepared by dissolving one gram sample in 200 ml 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.

18. **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 for bromide ion in present investigation.

19. **Succinimide (NHS)**: Succinimide (NHS) was firstly dissolved in acetic acid and then made up to its required volume with double distilled water.
2.B: METHOD OF INVESTIGATION

During the 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. Preliminary investigation shows negligible effect of ionic strength on the reaction rate, therefore all the experiments have been carried out without keeping ionic strength of the medium constant.

The actual progress of reaction has been monitored by estimating the concentration of unconsumed oxidants CAT or NBS (whichever is used) 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, were taken in a reaction vessel (conical flask blackened from outside) which was kept in an electrically operated thermostatic water bath set at desired temperature (± 0.1°C). The requisite volume of oxidant was taken in another black coated vessel which was also placed in the same thermostat for thermal equilibrium. After half an hour, when solutions of both vessels had acquired the temperature of water bath, then required volume of oxidant solution was sucked out by a pipette and poured in the reaction vessel which was already containing mixture of all other reactants to initiate redox reaction and immediately this mixed solution was vigorously shaken and the stop watch was started to record time. Thereafter an aliquot (5ml) of this reaction mixture was at once taken out at zero time and quickly transferred to a conical flask
containing 5ml of KI (4%) solution and 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 and thereafter 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 (-dc/dt) i.e. initial rate. The initial rates obtained at different [oxidant] were used for kinetic studies of redox reactions undertaken in the present thesis.

2.C: PRESENT INVESTIGATION

The present thesis consists of two parts: Part A and Part B.

Part A: This part contains study of the reaction given below and described in detail in 3rd chapter.

    Kinetic and mechanistic study of Rh (III) chloride catalysed oxidation of D-threonine by chloramine - T in acidic medium.

Part B: This part contains the following four reactions given below and have been studied in detail in 4th, 5th, 6th and 7th chapters respectively.

(I) Kinetic and mechanistic study of N-bromosuccinimide oxidation of trimethylene glycol in aqueous alkaline solution in the presence of aquachloro-complex of ruthenium (iii) used as homogeneous catalyst

(II) Kinetic and mechanistic study of n-bromosuccinimide oxidation of trimethylene glycol in aqueous acidic solution in the presence
of aquachloro-complex of ruthenium (iii) used as homogeneous catalyst.

(III) Kinetic and mechanistic study of n-bromosuccinimide oxidation of trimethylene glycol in aqueous alkaline solution in the presence of aquachloro-complex of iridium (iii) used as homogeneous catalyst

(IV) Kinetic and mechanistic study of n-bromosuccinimide oxidation of dimethyl digol in aqueous alkaline solution in the presence of aquachloro-complex of iridium (iii) used as homogeneous catalyst