CHAPTER – II

General
Experimental Procedures
MATERIALS AND METHODS

All the chemicals in these investigations used were of analytical reagent grade. Whenever necessary further purification by the way of recrystallisation or distillation was carried out. The organic compounds were purified whenever necessary and purity was checked from their reported physical constants\(^1,2\). Inorganic compounds were invariably converted to anhydrous or to the standard hydrated forms before use\(^3\).

Methods of purification, preparation of solutions and estimations of some important reagents were briefly described hereunder. The melting points (m.p) or boiling points (b.p) refer to the uncorrected and observed temperatures.

**Double distilled water:**

Tap water was distilled first over potassium permanganate and then redistilled over sulphuric acid (Qualigens, ExelaR) followed by distillation in the presence of EDTA (1.0 x 10\(^{-4}\)M) from an all glass vessel. This was followed by boiling off the dissolved carbondioxide. Doubly distilled water prepared in this manner was used through out for all the preparative and analytical procedures.

**Acetic acid:**

Acetic acid (Qualigens, ExelaR) was refluxed with chromic anhydride with the addition of small quantity of acetic anhydride\(^4,5\) corresponding to the water content of acetic acid. Any solid that separated out was filtered off and the filtrate was then distilled from all glass apparatus. The fraction distilling at 118\(^\circ\)C was collected by rejecting the large quantities of head and tail fractions.
**Buffer solutions**:  
Appropriate buffer mixtures were employed to study the kinetics at various pH values, to maintain the pH of the medium at the desired level. The stock solutions of the main constituents were prepared immediately before use by weighing out accurately the required amount of the substances in standard volumetric flask and dissolving it in doubly distilled water. Calculated amounts of these were used along with appropriate volumes of standard alkali or acid to furnish the buffer mixture of desired pH and ionic strength $\mu$ (which was adjusted with a supporting electrolyte).

**Perchloric acid:**  
Qualigens, ExcelaR 70% sample was used as such after standardization. For low acid concentration stock solutions were prepared and from this, the required volumes were used for obtaining the necessary acidity.

**Sulphuric acid:**
Sulphuric acid of Qualigens, ExcelaR grade sample was used as such. Stock solutions were prepared by appropriate dilution. The acid was standardized against a standard sodium carbonate solution using methyl orange as an indicator.

**Carbonate free sodium hydroxide solution:**
The concentrated solution of sodium hydroxide in doubly distilled water was prepared by mixing required weight of NaOH in a pyrex beaker, covered and allowed to stand for twenty four hours. The clean supernatant liquid was then rapidly filtered through a $G_4$ crucible and the filtrate was stored in a paraffin coated bottle and stoppered. From this an intermediate stock solution was prepared and used after proper dilution.
**Sodium thiosulphate:**

This solution was always freshly prepared by dissolving the requisite amount of sodium thiosulphate (AnalaR, BDH) in doubly distilled water and making up to the desired volume. The solution was standardized by the following iodometric procedure. Sodium thiosulphate is filled in burette and 5.0ml 4N sulphuric acid and 10ml of 3% potassium iodide solution (iodate free) were added and an atmosphere of CO$_2$ is created by the addition of sodium bicarbonate and titrated against thiosulphate solution till the solution turns straw yellow. The titration is further continued after addition of a few drops of freshly prepared starch solution to the disappearance of blue starch iodine end point.

**Sodium carbonate:**

Qualigens (ExcelaR) sample was used.

**Potassium dichromate:**

BDH (AnalaR) was heated at 135ºC for an hour in an air oven, cooled and preserved in desiccator.

**Potassium iodide:**

An analytical reagent grade iodate-free reagent was vacuum dried before use. The solutions of potassium iodide were freshly prepared before use by direct weighing.

**Starch:**

Analytical reagent grade (S.D fine) soluble sample was used.

**Potassium chloride:**

Qualigens, ExcelaR samples were used after drying for one and half hours at 120ºC, after cooling in a desiccator.
Preparation of Ruthenium(III) chloride:

Ruthenium(III) chloride (Johnson Mathey Co, London) analytical reagent grade sample was dissolved in water containing very dilute hydrochloric acid. The solution was standardized by the method of Horiuchi et al.\textsuperscript{7}

An aqueous solution containing 0.1 to 3.5mg of Ru(III) per 100ml was treated with an excess of EDTA, adjusted the pH 4 to 4.5 with (1N) HNO\textsubscript{3} and 20% ammonium acetate and heated to 100\degree C for ten minutes. Then it was cooled and adjusted to pH 1.8 and excess of EDTA was titrated with Bi\textsuperscript{3+} solution in the presence of xylenol orange as an indicator.

From the above standard stock solution of Ru(III), exact volumes were taken with standard micro-pipette so that desired concentrations could be maintained in the reaction mixture.

Preparation of osmium tetroxide solution:

Os(VIII) solution was prepared from osmium tetroxide (Johnson Mathey Co, London) in 0.5M NaOH to minimize the volatility of the metal ion\textsuperscript{8}. The Os(VIII) was determined iodometrically to the starch end point\textsuperscript{9}. Necessary dilutions were made from this stock solution of Os(VIII) for the kinetic runs. Due allowance was given to already present alkalinity.

Manganese(II) chloride tetrahydrate:

Qualigens, ExcelaR sample was used as such.

Ceric Ammonium Nitrate:

Qualigens, ExcelaR sample was used as such.
Ammonium meta Vanadate:
Qualigens, ExcelaR sample was used as such.

Ferrous ammonium sulphate:
Qualigens, ExcelaR sample was used as such.

N-phenyl anthranilic acid:
Qualigens, ExcelaR sample was used as such.

Potassium permanganate:
Qualigens, ExcelaR sample was used as such.

Iodine:
Qualigens, ExcelaR sample was used as such.

Acetonitrile:
Qualigens, ExcelaR sample was used as such.

Potassium dihydrogen phosphate and Disodium hydrogen phosphate:
Qualigens, ExcelaR grade was used.

Chloramine-T (CAT):
Analytical reagent grade of May and Baker sample was used as such.

Trichloro isocyanuric acid (TCICA):
The stock solutions of Fluka purum TCICA were prepared by weighing appropriate amount of compound and dissolving it in glacial acetic acid. The required solutions for kinetic runs were prepared by diluting calculated amount with water.
Dichloro dimethyl hydantoin (M.P. 132°C): Lancaster sample was used as such.
D-Glucose (M.P. 83°C): Qualigens (ExcelaR) grade was used as such.
D-Fructose (M.P. 104°C): Qualigens (ExcelaR) grade was used as such.
dl-Camphor (M.P 179.8°C): CDH (AR) sample was used as such.
Deoxybenzoin (M.P 59°C): Sigma-Aldrich sample was used as such.
Diacetyl (B.P 88°C): Sigma-Aldrich sample was used as such.
Benzil (M.P 95°C): Sigma-Aldrich sample was used as such.
L-Cysteine (M.P 176°C): S D fine sample was used as such.
L-Cystine (M.P 261°C): S D fine sample was used as such.
ANALYTICAL METHODS

The pH measurements:

A systronics digital pH meter equipped with a glass and a reference standard calomel electrode was used for pH measurements. pH meter is standardized using standard buffers like potassium and sodium hydrogen phthalate and borax. pH of the reaction mixture is measured before and after the reaction and the average was found not to differ by more than ±0.01 pH units from measured values. The concentrations of hydrogen ion were computed from the mean of two recorded pH’s after the necessary corrections had been made for the ionic strength of the medium. The following equation was used for this purpose.

\[
[H^+] = \log^{-1}\{0.511F(\mu) - \text{pH}\} \quad \text{.........(1)}
\]

\[
F(\mu) = \left(\frac{\mu^{1/2}}{1 + 1.5\mu^{1/2} + 0.2\mu}\right)Z^2 \quad \text{.........(1a)}
\]

\[Z_i = \text{charge of the electrolyte species}\]
\[\mu = \text{ionic strength of the medium.}\]

However, for high acidic solutions of pH < 2, the concentration of H⁺ in a solution was determined directly by titrating against standard alkali (NaOH) solution using phenolphthalein as indicator. The sodium hydroxide solutions were standardized against a solution of succinic acid (primary standard).

Preparation of solvent mixtures:

The solvent mixtures were prepared by taking appropriate volumes of pure solvents. A large batch of solvent mixture thus prepared was enough to permit all kinetic runs to be performed and thus error due to possible variations in compositions was avoided. The dielectric constants of various binary solvent mixtures were calculated.
assuming linearity in the range of the solvent compositions of the present work. Such assumptions were followed earlier by workers like Wiberg and Evans\textsuperscript{10}. For acetic acid water mixtures, values reported by Smyth and Rogers\textsuperscript{11} were used.

**Preparation of solutions for kinetic runs:**

The solutions for each run are prepared using doubly distilled water or any other required solvent mixture. The calculated volumes or weights of standard compounds were taken in two separate volumetric flasks. Standard aqueous buffers were used to fix the pH of the medium wherever necessary. The flasks were then filled up to the mark with the appropriate solvent or solvent mixtures. Titrimetric and spectrophotometric methods were used to standardize solutions. The general formula (Eq.2) was made use of in spectrophotometric determinations.

\[ A = \varepsilon cl \]  

\text{Where A is the absorbance, } \varepsilon = \text{molar extinction coefficient, } c = \text{concentration and } l = \text{optical path length (usually 1cm). Beer-Lambert’s law was found to be obeyed in the concentration ranges employed for the experiments.}

**Kinetic measurements:**

All standard flasks and reaction bottles were of pyrex or corning glass with well ground and air tight stoppers. To prevent any photochemical reaction, the outside surfaces of reaction bottles were painted black. The loss due to the evaporation was considered negligible. The volumetric flasks, the pipettes, burettes and the standard flasks were standardized by the usual methods.
Velocity measurements:

The required amount of any substrate was weighed accurately in a standard volumetric flask and made up with water or the required solvent mixture. The oxidant solution was also prepared by same method by mixing appropriate amount of acid and catalyst wherever necessary. Sufficient time was allowed to compensate for any change of heat during dilution. The solution flasks of two main reactants and the reaction bottle were thermostated for a considerably long period of equilibration before mixing (An electrically operated thermostatic water bath maintained by a Jumo mercury switch relay and a Jumo contact thermometer was used for the purpose) The substrate solution was first pipetted out into reagent bottle by means of a pipette. After allowing a little more time to compensate for any slight temperature variation, an equal volume of other reactant (oxidant) solution, which has been standardized just before use was transferred with a rapid delivery pipette. The instant of half delivery being noted as zero time. The reaction bottle was then stoppered and thoroughly shaken. The progress of the reaction was followed by withdrawing 5.0ml aliquots of the reaction mixture at different time intervals and discharging into proper freezing mixtures and they were later analysed by standard procedures.

The following rate equation was used to determine pseudo first order rate constants expressed as min$^{-1}$ or sec$^{-1}$.

$$k_1 = \frac{2.303}{t} \log \left( \frac{a}{a-x} \right) \quad \text{...........}(3)$$

Where \( t = \) time, \((a-x)\) and \(a\) are the concentrations of the disappearing reactant at time \(t\) and zero respectively.
For zero order reactions in the oxidant, the zero order rate constants \((k_0)\) are expressed as mole \(\text{lit}^{-1} \text{min}^{-1}\) or moles \(\text{lit}^{-1} \text{sec}^{-1}\) which were computed from
\[
k_0 = \frac{x}{t} \tag{4}
\]
where ‘\(x\)’ is the concentration reacted at time ‘\(t\)’.

All the experiments were carried out in duplicate and the velocity constants were reproducible within \(\pm 3\%\) error. Solvent oxidation was routinely checked and corrections were made whenever necessary. For fast reactions each run was performed thrice and the mean of these three values has been recorded.

**ESTIMATION METHODS**

**Titrimetric method:**

**Estimation of N-halo compounds like Trichloro isocyanuric acid (TCICA), Chloramine-T (CAT) and Dichloro dimethyl hydantoin (DCDMH):**

The solution of N-halo compound and the aliquots from reaction mixture are well estimated iodometrically. 5.0 ml of N-halo compound is dumped into an iodine flask containing 5.0ml of 5N sulphuric acid and 5.0ml of 5% potassium iodide solution and kept in dark for 3 minutes. Then the solution is titrated against standard thiosulphate taken in a burette to the disappearance of starch iodine blue end point.

**Estimation of Iodine:**

The stock solution was prepared by dissolving a known weight of iodate free potassium iodide in known volume of doubly distilled water in a 100ml measuring flask with stopper which was wrapped
with black paper. Pure sample of iodine was weighed out and transferred quickly into the measuring flask by using dry funnel and was dissolved by gentle shaking. This operation was carried out in the cold till all the iodine had gone into solution. Then the volume was made up. The exact strength of the total iodine can be determined by titrating against a freshly standardized sodium thiosulphate solution using starch as an indicator. The end point is indicated by disappearance of the blue colour. However the exact strength of iodine in solution can also determined spectrophotometrically as reported earlier12.

**Estimation of permanganate:**

The method employed by Tompkins13 was used: 5.0 ml aliquots of the reaction solution to 5% KI solution acidified with 2N H₂SO₄ and the liberated iodine was titrated with standard thiosulphate solution. To reduce aerial oxidation of the acidified iodide solution, the acid concentration was kept low. When possible, the aliquot was titrated immediately after the withdrawl. In fast runs they were titrated in random order. In all the cases the titrations were completed with in 10 minutes of the liberation of iodine. The low concentration of the thiosulphate employed necessitated its standardization frequently with standard dichromate.

**Estimation of Ce(IV):**

Aliquot of 5.0ml was discharged into a known excess of ferrous ammonium sulphate solution containing dilute H₂SO₄ and the excess was titrated against standard potassium dichromate using N-phenyl anthranilic acid as indicator.
Estimation of vanadium (V) solution:

Aliquot of 5.0 ml vanadium (V) solution was dumped into excess of acidified standard ferrous ammonium sulphate solution and left over iron (II) was titrated was against standard potassium dichromate solution with N-phenyl anthranilic acid as an indicator.

Thermodynamic functions of activation:

Activation energies were obtained by Arrhenius equation
\[ k = A \cdot e^{-\frac{E}{RT}} \]
where \( k \) is the rate constant and \( A \) is the frequency factor.

According to the theory of absolute reaction rates, the following expressions may be written for the rate coefficient \( k \) of the reaction.

\[ k = \frac{KT}{h} K^\neq \]
\[ = \frac{KT}{h} e^{-\Delta F^\neq/RT} \]
\[ = \frac{KT}{h} e^{-\Delta H^\neq/RT} e^{\Delta S^\neq/R} \]

Where \( K \) is the Boltzmann constant, \( h \) is the Plank’s constant, \( K^\neq \) is the constant for the equilibrium between the reactants and the activated complex, \( \Delta H^\neq \) is the enthalpy and \( \Delta S^\neq \) the entropy of activation and \( \Delta F^\neq \) (or \( \Delta G^\neq \)) is the standard free energy of activation, and \( R \) is the universal gas constant. It has been assumed that transmission coefficient is unity. The state with respect to which thermodynamic parameters have been calculated is one mole per litre. The units of \( \Delta H^\neq, \Delta S^\neq \) are KJmol\(^{-1}\) and JK\(^{-1}\)mole\(^{-1}\) respectively. The average values of apparent activation parameters were also calculated in some cases in a similar manner by making use of appropriate rate constants.
DATA TREATMENT

Best fitting plots by linear regression:

When there are two variables like y and x for a series of data, confirming to an equation of the type: \( y = a + bx \) where ‘y’ is the dependent variable and ‘x’ is the independent variable, ‘b’ and ‘a’ are the slope and coefficient of the intercept respectively, of the curve drawn by plotting ‘y’ against ‘x’, a best curve can be obtained by the method of regression or by the least squares method of plotting.

In the present case the independent variables were time, temperature and concentration units usually, but at times functions of reaction velocity or concentration units were also used as independent variables. The dependent variables were the data connected with the velocity of reactions and the values derived there from.

The method enabled the determination of coefficients ‘a’ and ‘b’ reliably with respect to the errors of the variable ‘y’ by using the foregoing principle of maximum confidence for variables having a normal distribution. This led to the ‘regression curve’ for the regression of ‘y’ and ‘x’. The influence of random errors was compensated by minimizing the sum of the squares of the deviations of the individual points from the regression curves.

By this method the regression coefficient or the slope ‘b’ of the curve comprising ‘n’ point was calculated from the normal equations by means of the relationship.

\[
b = \frac{\Sigma xy - n\Sigma y}{(\Sigma x)^2 - n\Sigma x^2}
\]

and the shift or the intercept ‘a’ of the regression line was obtained as
\[ a = \frac{(\Sigma y - b \Sigma x)}{n} \]

Thus the regression points 'y' for the best fitting curve can be found. This method of plotting has been applied in many instances of the present investigation.

The estimate of the standard deviation of the scatter around the regression line is given by the relationship

\[ S_{y/x} = \frac{\Sigma (y_1 - \bar{Y})^2}{\sqrt{n - 2}} \]

Where \( y_1 \) is for a given value, \( x_i \) the experimental value of the dependent variable, while \( Y_1 \), is the same value but calculated from the regression equation. The estimate of the standard deviation of the regression coefficient, \( S_b \) and \( S_a \) are given by the relationships.

\[ S_b = \frac{S_{y/x}}{\sqrt{\Sigma (x_1 - \bar{x})^2}} \]

and

\[ S_a = S_{y/x} \frac{\Sigma x_1^2}{n \Sigma (x_1 - \bar{x})^2} \]

Where \( \bar{x} = \frac{\Sigma x}{n} \)

These relationships have been used to calculate the standard deviation of the slope and intercept of the regression line and from these values standard deviations of the various parameters have been estimated.
References:


