SUMMARY

Chemical kinetics is a dynamic chapter of physical chemistry which deals with the study of rate of reactions with all the factors which influence the rate of reaction\(^1\) and with explanation of rate in terms of the reaction mechanism through which chemical reactions occur. The rate (i.e. \(-dc/dt\)) of the reaction can be derived either in terms of consumption of reactant or product formation of reaction with time. Several factors such as temperature, concentration of reactants and products, catalyst, medium (i.e. H\(^+\) or OH\(^-\)), ionic strength of the medium (used for deciding the nature of reacting species of the reactants involved in the reaction), total pressure of the system (in case of gaseous reactions), viscosity of the system, the dielectric constant of reaction mixture, pH and so on influence the rate of chemical reaction. Kinetic investigation gives an idea about the quantitative relationship between the rate of reaction and all those factors which influence it. The term order of reaction, in fact gives the relationship between rate of the reaction and concentration of a particular reactant. For multi steps reactions the kinetics is governed by the slowest step, which is also called rate determining step or rate controlling step. There are many reactions in which orders are not simple power functions of the concentration of the reactant but zero or positive fractional and negative fractional. The elucidation of the exact rate law then requires carefully planned experiments in which influence of products and reactants are studied systematically. Although a number of mechanisms can be derived on the basis of observed kinetic results but out of all the mechanisms, only one mechanism conforming to the experimentally observed kinetic data would be correct. Comparison of an experimentally observed rate law with the derived rate law allows one to make some choice among apparently reasonable mechanisms. Thus only that mechanism, which gives the rate law of the form determined by experiments, may be considered as plausible mechanism for the reaction.
However, the proposed mechanism may no longer remain valid, if some new information's are uncovered. Reaction mechanism is derived concept which can be changed or modified if some new concepts or new facts are observed\textsuperscript{2}.

Kinetic investigation gives the insight of the reaction mechanism by which chemical changes occur. Kinetic investigation is solely concerned to establish the series of steps by which the reactants are converted into products. In other cases where the reaction mechanism is known, studies of kinetics of reaction may be employed to shed light on the details of the interaction among the reactant molecules. This objective demands that the experimental data be summarized in equations of the same form as those which appear in theoretical treatment of reaction kinetics\textsuperscript{1}. A clue to the reality of reaction mechanism can be obtained by use of isotopic tracers\textsuperscript{3}, detection of short lived intermediates, variation of ionic strength\textsuperscript{4}, catalyst and change of solvents\textsuperscript{5}, the product identification etc. on the rate of reaction.

**Bharat Singh, Ashish et al**\textsuperscript{43} have studied oxidation of crotonic acid(CA) by chloramine-T in presence of Pd(II) and Os(VIII) as homogenous catalysts. The reactions are zero order in [chloramine-T] and first order each in both [Pd(II)] and [Os(VIII)] while first order in [CA] at lower concentrations tending towards zero order at its higher concentrations has been observed. Positive effect of added [Cl\textsuperscript{-}] and zero effect of added p-toluenesulphonamide (PTS) have been observed in Pd(II) catalysed reaction while in Os(VIII) catalysed reaction negative effect of PTS on rate of reaction has been observed. Negligible effect of change in [H\textsuperscript{+}] and ionic strength of the medium and decrease in rate with decrease in dielectric constant of the medium have been observed in both Pd(II) and Os(VIII) catalysed reactions. The catalytic efficiency is in the order of Pd(III) > Os(VIII). The products of oxidation in both reactions are acetaldehyde and glyoxylic acid. Activation parameters have been computed and mechanistic
steps consistent with the kinetic results, reaction stoichiometry and product analysis for both of the catalysed reactions have been discussed.

Bharat Singh, Anamika Singh et al\textsuperscript{44} have studied Environmentally Benign Mechanistic Studies of Aquachlororhodium (III) Complex Catalysis in Oxidation of D-threonine by aqueous alkaline Chloramine-T: A Kinetic Approach.

Further, Bharat Singh and Anirudhh K. Singh et al\textsuperscript{45} have also published a paper Mechanistic aspect of osmium (VIII) catalysed oxidation of crotonic acid by aqueous alkaline solution of chloramine-T: A kinetic modeling.

Ashok Kumar Singh and Bharat Singh et al\textsuperscript{13} have published a paper entitled Kinetics and mechanism of Pd(II) catalysed oxidation of D-arabinose, D-xylose and D-galactose by N-bromosuccinimide in acidic solution.

A paper, A kinetic and fluorimetric investigation of papain modified at tryptophan-69 and -177 by N-bromosuccinimide has been reported by Gordon Lowe and Alan S. Whitworth\textsuperscript{14}.

N. Venkatasubramanian and V. Thiagarajan have reported\textsuperscript{15} Mechanism of oxidation of alcohols with N-bromo succinimide.

Kameshwar Singh, J. N. Tiwari and S. P. Mushran have published a paper on Kinetics and mechanism of oxidation of diethyl ketone by N-bromosuccinimide.

Ashok Kumar Singh and Bharat Singh et al\textsuperscript{16} have published a paper on N-Bromosuccinimide oxidation of maltose and D-galactose using chloro-complex of Rh(III) in its nano-concentration range as homogeneous catalyst: A kinetic and mechanistic study.

Bharat Singh et al\textsuperscript{17,18,19} have studied oxidation of many compounds by N-bromosuccinimide.
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.

Following are kinetic observations made in the title reaction:

1. The title reaction shows first-order kinetics with respect to chloramine-T.
2. Zero -order kinetics with respect to D-threonine has been observed.
3. In case of rhodium (III) chloride used as catalyst first-order kinetics was observed.
4. Negative effect of [H+] variation on reaction rate was observed.
5. A negligible effect of p-toluene sulphonamide [PTS] was observed.
6. Negative effect of added KCl on rate of the reaction was observed.
7. Negligible effect of ionic strength of medium was observed.
8. Marked effect of rise in temperature was observed.

The above kinetic results have been used to suggest the reaction mechanism on whose basis the following rate law consistent with the above results has been proposed

\[
-\frac{d[CAT]}{dt} = \frac{k_1 k_2 [CAT][Rh(III)]_T}{k_1 K_2 + k_2 [Cl^-](k_{-1}[H^+] + k)}
\]
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

Following are kinetic observations made in the title reaction:

1. The title reaction shows first-order kinetics with respect to N-bromosuccinimide.

2. First-order kinetics with respect to Trimethylene glycol has been observed.

3. In case of ruthenium (III) chloride used as catalyst first-order kinetics was observed to tend to zero-order.

4. Negative effect of \([\text{OH}^-]\) variation on reaction rate was observed.

5. A negligible effect of mercuric acetate was observed.

6. Positive effect of added KCl on rate of the reaction was observed.

7. Negligible effect of ionic strength of medium was observed.

8. Negligible effect of added succinimide \([\text{NHS}]\) was observed

9. Marked effect of rise in temperature was observed.

The above kinetic results have been used to suggest the reaction mechanism on whose basis the following rate law consistent with the above results has been proposed

\[- \frac{d[NBS]}{dt} = \frac{3kdK_1K_2[NBS][TMG][\text{Ru(III)}][\text{Cl}^-]}{[\text{OH}^-] + K_1K_2[\text{Ru(III)}][\text{Cl}^-]}\]
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.

Following are kinetic observations made in the title reaction:

1. The title reaction shows first-order kinetics with respect to N-bromosuccinimide which tends to zero-order at its higher concentration.
2. Zero-order kinetics with respect to trimethylene glycol has been observed.
3. In case of ruthenium (III) chloride used as catalyst first-order kinetics was observed.
4. No effect of [H$^+$] variation on reaction rate was observed.
5. A negligible effect of mercuric acetate was observed.
6. Negative effect of added KCl on rate of the reaction was observed.
7. Negligible effect of ionic strength of medium was observed.
8. Negligible effect of added succinicnimide [NHS] was observed.
9. Marked effect of rise in temperature was observed.

The above kinetic results have been used to suggest the reaction mechanism on whose basis the following rate law consistent with the above results has been proposed:

The above kinetic results have been used to suggest the reaction mechanism on whose basis the following rate law consistent with the above results has been proposed:

$$\frac{d[NBS]}{dt} = \frac{K_1 k_d [NBS] [Ru(III)]_T}{K_1 + [Cl^-]}$$
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

Following are kinetic observations made in the title reaction:

1. The title reaction shows first-order kinetics with respect to N-bromosuccinimide.
2. Zero-order kinetics with respect to trimethylene glycol has been observed.
3. In case of iridium (III) chloride used as catalyst first-order kinetics was observed.
4. Positive effect of \([\text{OH}^-]\) variation on reaction rate was observed.
5. A negligible effect of mercuric acetate was observed.
6. Negative effect of added KCl on rate of the reaction was observed.
7. Negligible effect of ionic strength of medium was observed.
8. Negligible effect of added succinimide [NHS] was observed
9. Marked effect of rise in temperature was observed.

The above kinetic results have been used to suggest the reaction mechanism on whose basis the following rate law consistent with the above results has been proposed

\[
-\frac{d[NBS]}{dt} = \frac{k_d k_1[NBS][Ir(III)]_f[OH^-]}{k_{-1}[Cl^-] + k_1[OH^-]}
\]

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
Following are kinetic observations made in the title reaction:

1. The title reaction shows first-order kinetics with respect to N-bromosuccinimide.

2. Zero-order kinetics with respect to dimethyl digol has been observed.

3. In case of iridium (III) chloride used as catalyst first-order kinetics was observed.

4. Zero effect of [OH\textsuperscript{-}] variation on reaction rate was observed.

5. A negligible effect of mercuric acetate was observed.

6. Positive effect of added KCl on rate of the reaction was observed.

7. Negligible effect of ionic strength of medium was observed.

8. Negligible effect of added succinicnimide [NHS] was observed.

9. Marked effect of rise in temperature was observed.

The above kinetic results have been used to suggest the reaction mechanism on whose basis the following rate law consistent with the above results has been proposed

\[
- \frac{d[NBS]}{dt} = \frac{k_d K_i'[Ir(III)]_T[NBS][Cl^-]}{1 + K_i'[Cl^-]}
\]

The kinetic results of above reactions have been interpreted and have been used to elucidate the reaction mechanism for these reactions. The proposed mechanisms have been discussed and on their basis the corresponding rate laws conforming to the observed experimental results have been derived.