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CHAPTER - I

INTRODUCTION

Chemical kinetics concerns itself with the study of the rates of chemical reactions, of the factors upon which they depend and of the mechanism by which they proceed.

The energy relations between the reactants and the products are considered in thermodynamics. An important question which is not touched by thermodynamics is the rate of reaction and the mechanism of reaction i.e. the stages through which the reactants pass to reach the final products are not indicated by thermodynamics. It makes no attempt to consider the rate at which the equilibrium is attained. Thus, chemical kinetics compliments thermodynamics by supplying information about the rates of reactions and the mechanism by which reactants are converted to products.

The study of chemical kinetics reveals the effect of change in environment on the rate of a reaction. This is highly useful in chemical engineering applications. Most of the chemists are greatly interested in chemical kinetics because it provides the most general method to determine the mechanism of reactions. To suggest the mechanism of given chemical process with the help of kinetic study, we should obtain additional information such as the products of reaction, stereochemical evidences, use of isotopes, determination of short lived intermediates and refinement of kinetic methods.

To investigate the chemical reactions, various experimental techniques have been used. The reactions in gas phase, liquid phase and solid-gas interphase have been studied kinetically. A wide variety of these reactions are studied by conventional techniques which are broadly divided into two categories, namely chemical and physical. It is found that physical methods are more convenient than chemical methods. Some of the physical methods used in kinetics studies are

- (a) Pressure measurements in gaseous reactions
- (b) Dilatometry or measurements of volume changes
- (c) Optical methods such as Refractometry, Polarimetry, Colorimetry and Spectrophotometry
- (d) Electrical methods such as conductometry, Potentiometry, Polarography and Mass spectrometry.

In general, any property which changes sufficiently as a result of chemical reaction, can be used to follow the course of reactions.

Any kinetic investigation generally comprises of two parts : First to establish the relationship between the rate of the reaction and various factors such as concentrations of reactants, temperature and hydrostatic pressure (for gaseous reactions). Some other factors may be added to these such as primary and secondary salt effects, dielectric constant of the

medium and catalysis, identification of products of reaction, detection of free radicals and intermediates. The second part of the investigation is to arrive at a suitable mechanism which can account for the results obtained in velocity measurements.

1.1 OXIDATION REACTIONS AND OXIDANTS :

The greatest kinetic study has been done in liquid phase reactions because organic as well as in-organic chemists are keenly interested in these reactions. In the realm of organic reactions in solution, oxidation reactions are the most important. This is because the oxidation reactions of organic compounds have vital importance in synthetic biological fields. A variety of organic compounds like olefins, phenols, aldehydes, esters, alcohols, carboxylic acids, amines and many more have been studied with different oxidising agents like nitric acid, chromic acid, permanganate, ceric sulphate, potassium persulphate, potassium periodate, potassium bromate, lead tetraacetate, chromium (VI) oxide, vanadium(V) hexacyanoferrate, chloramine T etc.

Oxidation process is essentially a transfer of electrons from reductant to oxidant. By considering number of electrons transferred to the oxidant during oxidation, the oxidation reactions as well as the oxidants¹ are classified as follow :

- (a) One electron transfer reactions by one electron oxidants e.g. Ag(II), Mn(III), Cu(II) etc.
- (b) Two electrons transfer reactions by two electrons oxidants e.g. oxidation of 3-ethyl pentane with sodium dichromate²,
- (c) Four electrons transfer reactions by four electrons oxidants e.g. oxidation of aromatic compounds with methyl group by chromic acid in acetic anhydride.

The important and ideal one electron oxidant is Mn(III). The use of Mn(III) as an oxidant is comparatively more recent. Hence, it is proposed here to take brief review of the work done on oxidation of organic compounds by Mn(III).

1.2 Mn(III) AS AN OXIDANT :

Mn(III)³ is an ideal one electron oxidant. Even then its use in oxidation process has been somewhat neglected. This is probably because Mn(III) has a tendency to disproportionate as



This takes place particularly in aqueous solutions. However, this disproportionation can be suppressed nearly to completion by using large excess of Mn(II) or high acidity. Thus Mn(III) is stable in glacial acetic acid, 5 M sulphuric acid, pyrophosphoric acid etc. Another way of stabilization is to

use strongly complexing media which form stable complexes with Mn(III). Many complexes of Mn(III) such as sulphates⁴, malonates⁵, oxalates⁶, α -polycarboxylates^{7,8}, acetates^{9,10} and pyrophosphates¹¹ etc. have been prepared and studied.

Complexes of Mn(III) as acetates, sulphates and pyrophosphates have been largely used as an oxidant. These Mn(III) compounds have been prepared by oxidation of Mn(II) salts^{11,12,13} with KMnO_4 . The Mn(III) oxidises variety of organic compounds. In most of these oxidation processes, an intermediate complex is formed between Mn(III) and the substrate. If this complex is unstable, it is further oxidised and kinetic study of the oxidation process can be done. Mn(III) sulphate is found to be most stable in 5 to 7 M sulphuric acid.^{14,15}

However, it is observed that decomposition of Mn(III) sulphate is not more than 5 % per hour even at high temperatures.^{16,17}

1.3 OXIDATION BY Mn(III) PYROPHOSPHATE :

The kinetics of several oxidation reduction reactions involving Mn(III) pyrophosphate has been studied. The mechanism of oxidation of numerous organic compounds by Mn(III) pyrophosphate has been suggested by Waters and his coworkers.¹⁸ Oxidation of mandelic esters¹⁹, malonic acid²⁰, dimethyl malonate²¹, diethyl malonate²², hydroxy acids²³ and variety of other compounds²⁴ has been studied by using Mn(III) pyrophosphate as an oxidant. Waters and Leverley²³ reported that oxidation of α - hydroxy acids by Mn(III) pyrophosphate

involves the reversible formation of cyclic complex which then breaks down with loss of CO_2 to form free radical. Kinetics of oxidation of dl-glycolic acid²⁵ by Mn(III) pyrophosphate has been reported by B. Madhava Rao and P.K. Gandhi.

1.4 OXIDATION BY Mn(III) PERCHLORATE :

Oxidation of acetamide, formamide, N-methyl formamide²⁶ by Mn(III) in aqueous acid perchlorate medium has been studied by Firoz Ahmad and Vikram Baswani. Oxidation of benzamide by Mn(III) ions in aqueous perchlorate medium has also been studied by them.

1.5 OXIDATION BY Mn(III) ACETATE²⁷ :

Mn(III) acetate has been extensively used for the oxidation of large number of organic compounds.

1.5 a OXIDATION ADDITION OF CARBOXYLIC ACIDS TO OLEFINS :

One of the most outstanding reactions initiated by Mn(III) acetate is the oxidation addition of carboxylic acids to olefins leading to γ - butyrolactones, found by Bush and Finkbeiner²⁸ and by Heiba Dessau Koehl.²⁹ The course of the reaction and the formation of other major products depends largely on the nature of the substrate, reacting acid and the reaction conditions. There is no general agreement on the mechanism of this reaction together with the side reactions. The major reaction is given as follow³⁰

The rate determining step, in this reaction reported, is the formation of the aromatic radical. Simple phenols are oxidised to diphenoquinones or polymerised to polyphenylene ethers depending on the reaction conditions.^{34,35} The primary product may be phenoxy radical which can undergo variety of reactions.

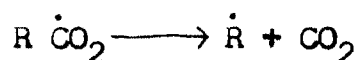
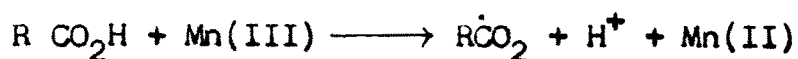
1.5 c OXIDATION OF AMINO COMPOUNDS :

The oxidation of n-substituted anilines has been reported by Bronsdijk,³⁶ Dewar³⁷ and Rindone.³⁸ At room temperature, in acetic acid, N-N-dimethyl aniline on oxidation gives N-methyl acetamide as main product. The formation of acridones from substituted 2-aminobenzophenones has been reported by Bowen.³⁹ Takaaki Aratani, Michael and Dewar have reported the reactions between Mn(III) acetate and anisole, phenetole, 1,2, 1,3 and 1,4 dimethoxybenzene, 1 and 2 methoxynaphthalein, N-N dimethylaniline, n-n diethylaniline etc.

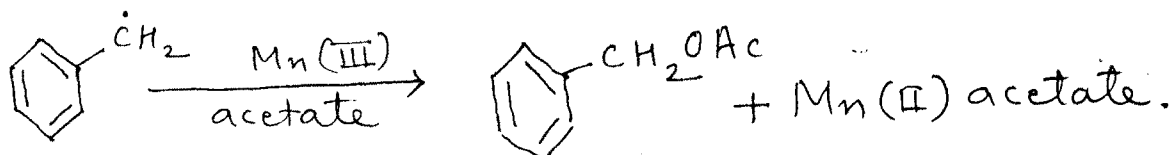
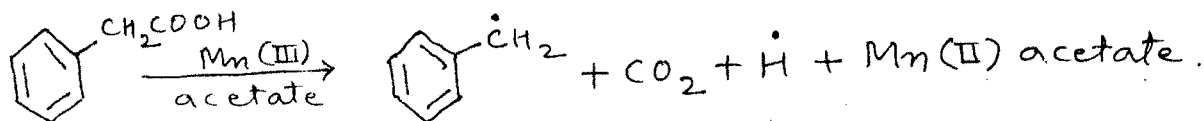
1.5 d OXIDATION OF CARBOXYLIC ACIDS :

Oxidation of carboxylic acids by Mn(III) acetate can follow two distinct pathways depending on the substrate carboxylic acid. Acetic acid and other alkyl carboxylic acids containing α - hydrogen atom are oxidised by loss of an α - hydrogen atom. Thus carboxymethyl radicals are generated. However, many carboxylic acids undergo decarboxylative

oxidation with Mn(III) acetate. The primary step is inner sphere oxidation of the carboxylate group to the carboxy radical.



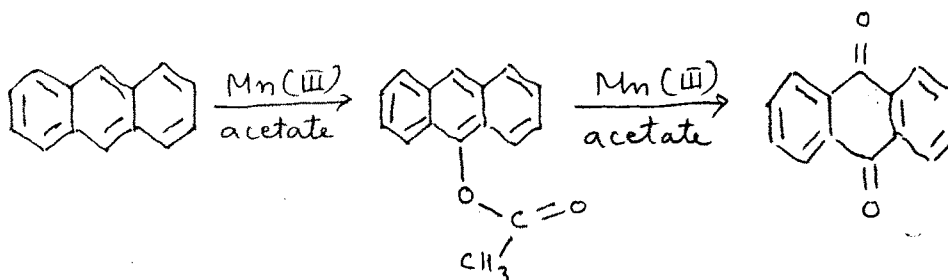
A number of common free radical reactions can occur depending on the structure of R and the reaction conditions such as dimerization, further oxidation to alkenes or esters etc. Decarboxylation with Mn(III) acetate is typically non-chain process. Thus phenyl acetic acid yields mainly benzylacetate.³⁶



The later reaction is probably ligand transfer oxidation. Similar mechanisms have been proposed for the oxidation of hydroxy acids, keto acids, amino acids⁴⁰ and N-butyric acid.⁴¹

1.5 e OXIDATION OF AROMATIC HYDROCARBONS :

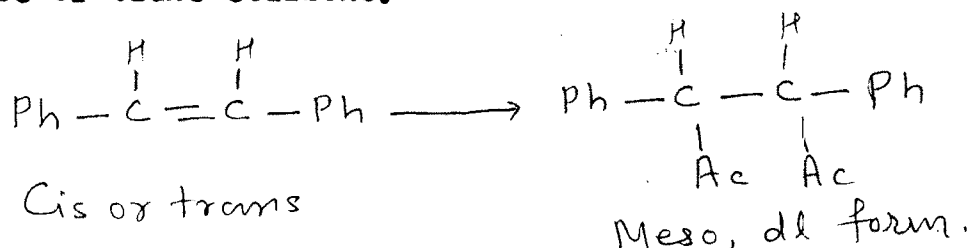
The reaction conditions and structure of the substrate highly affects the course of oxidation of aromatic hydrocarbons by Mn(III). Basically, the course of oxidation depends upon the temperature, oxidation potential of the substrate and concentration of Mn(III) acetate e.g. simple polynuclear aromatic hydrocarbons with relative low oxidation potential can be oxidised to acetates, quinones or dimeric products probably via electron transfer leading to the cation radical as a first step. Thus with excess of Mn(III) acetate anthracene is oxidised to anthraquinone or 9 - acetoxyanthracene when equimolar amounts are used.⁴²



With unsaturated hydrocarbons, several reactions have been distinguished. The common addition of carboxymethyl radicals generated by Mn(III) acetate takes place. Further lactonisation or formation of unsaturated carboxylic acids or acetoxy acids takes place.

Olefins with low oxidation potential are found to be preferentially oxidised at the double bond to a cation radical at a temperature of 100°C or below. In substituted cyclohexanones, the double bond remains unaffected and oxidation

occurs at the position α to the ketonic group. Olefins with low oxidation potential or when sterically hindered are preferentially oxidised at the double bond to a cation radical. The main products found are vicinal diol diacetates or unsaturated acetates e.g. the oxidation of cis or trans stilbene.⁴³



1.5 f OXIDATION OF ESTERS :

Oxidation of aliphatic esters viz ethyl, n-propyl, isobutyl, n-butyl acetates in 90 % acids⁴⁴ are of first order with respect to Mn(III) and ester and of inverse first order with respect to Mn(II). The products obtained were identified as formaldehyde, CO₂ and corresponding aldehydes or ketones. Kinetics and mechanism of oxidation of malonic acid and its esters viz dimethyl malonate and trimethyl malonate has been studied.⁴⁵ It was reported that the order of the reaction with respect to the substrate is one in all the cases. It is one with respect to Mn(III) in case of malonic acid. But it is zero in case of the two esters.

1.6 OXIDATION BY Mn(III) SULPHATE :

Mn(III) sulphate is also a typical one electron oxidant. It can be prepared as 0.07 M solution as well as in crystalline

state in closed containers. The 0.07 M solution of Mn(III) sulphate can be conveniently prepared by oxidation of Mn(II)¹³ sulphate $4\text{H}_2\text{O}$ with KMnO_4 . It is stable in 5 to 7 M sulphuric acid.

Kinetics of the oxidation of phenyl phosphorous acid by Mn(III) in sulphuric acid has been studied.¹⁶ The reaction is first order with respect to both phenylphosphorous acid and Mn(III). Hydrogen ions retard the reaction. The addition of sodium sulphate and increase in dielectric constant enhance the rate of reaction. The kinetics of oxidation of hypophosphorous acid and phosphorous acid has been studied spectrophotometrically by K.K. Sen Gupta et al.⁴⁶ The reaction is first order with respect to the substrate and Mn(III) and inverse first order with respect to hydrogen ions. The energy and entropy of activation have been calculated.

Kinetics of oxidation of Te(IV) by Mn(III) sulphate has been studied in 2M dm^{-3} sulphuric acid medium by Rambabu, Vani and Dikshitalu.⁴⁷ The order in Te(IV) is found to be unity and in Mn(III) it lies between one and two. Added Te(IV) does not have any effect on the rate but the other product Mn(II) retards the reaction considerably. A mechanism consistent with the kinetic data has been proposed wherein both Mn(III) and MnOH^{+2} are presumed to be the reactive species of Mn(II). Kinetics of ^{oxidation of} oxalic acid and citric acid mixture with Mn(III) sulphate was studied by

Barek Jiri, Berka Antonin et. al,⁴⁸ to varify the applicability of the logarithmic extrapolation method for second order reactions that involve the transfer of different number of electrons. Kinetics and mechanism of the oxidation of benzamide by Ag(II), Co(III) and Mn(III) ions in aqueous perchlorate medium was studied by Ahmed, Firoz Sabir ~~et. al.~~⁴⁹ The reaction was found to be first order with respect to benzamide. Activation parameters were also determined. The reaction was found to be accelerated by increasing $[H^+]$ but unaffected by $NaClO_4$. A radical mechanism was postulated. Oxidation of diethylamine and triethylamine has been studied.⁵⁰ The reaction is first order with respect to both Mn(III) and triethylamine. In case of diethylamine the reaction is first order with respect to Mn(III) and it is second order with respect to diethylamine.

1.7 OXIDATION OF FORMALDEHYDE :

The oxidation of formaldehyde by various oxidants like nessler's reagent, ammonium nitrate, Co(III), bromamine-T, chloramine-T etc. have been studied.

1.7 a OXIDATION BY NESSLER'S REAGENT⁵¹ :

The reaction is first order with respect to formaldehyde and Hg(II). The rate is inversely proportional to $][I^-]$ and directly proportional to $[OH^-]^2$. A general mechanism

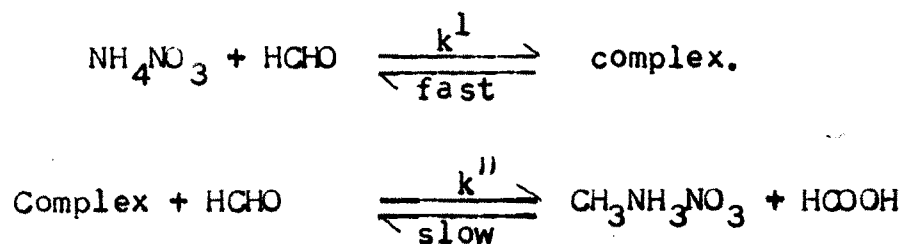
involving two electron transfer in the rate determining step has been proposed taking HgI_3^- as the reacting species.

1.7 b OXIDATION BY AMMONIUM NITRATE⁵² :

Kinetics of the reaction of ammonium nitrate with formaldehyde to give methylammonium nitrate and formic acid under the condition $[\text{NH}_4\text{NO}_3] \gg [\text{HCHO}]$ are reported. The rate law has been found to be of the form

$$\text{Rate} = k [\text{HCHO}]^2 [\text{NH}_4\text{NO}_3]^{0.6}$$

It has been explained by assuming the formation of 1:1 complex between HCHO and NH_4NO_3 in an initial fast step which later reacts with another molecule of HCHO in a slow step to give the products.



Werner has suggested that the complex formed might be methyleneimine ($\text{CH}_2 = \text{NH}$) which is a very weak base and whose salt is probably completely dissociated in aqueous solution. The formation constant K of the complex and bimolecular rate constant k of the slow step have been evaluated at different temperatures. Various thermodynamic parameters for both the steps are also presented and discussed.

1.7 c OXIDATION BY COBALTIC ION⁵³ :

Kinetic study of oxidation of formaldehyde by Co(III) in aqueous 5N and 10N H_2SO_4 has been reported. The rate equation has been determined. The reaction was of a variable order with respect to Co(III) ion. The overall reaction is second order at low concentrations. It is first order at high concentrations. The order at intermediate concentrations is variable as found experimentally. Since formaldehyde reacts very rapidly with the cobaltic ion and its oxidation product formic acid reacts some 100 or more times, slowly, it is very likely that in the presence of excess of formaldehyde the main product of oxidation is formic acid.

1.7 d OXIDATION BY BROMAMINE I⁵⁴ :

Kinetics of oxidation of formaldehyde and formic acid by bromamine-I has been investigated in perchloric acid medium. The rate followed first order kinetics each in [Bromamine-I] and [Substrate] with both the substrates. The rate was zero order in $[H^+]$ with formaldehyde. Effect of added reaction products, variations in ionic strength and dielectric constant of the medium have also been investigated. The rate constants for the rate limiting steps have been computed. The latter constants have been used to predict the rate constants for the variation of $[H^+]$ and $[HCOOH]$. At constant $[HCHO]$ and $[bromamine-I]$, the rate decreased with increase in $[H^+]$.

1.7 e OXIDATION BY CHLORAMINE-T⁵⁵ :

The Os(VIII) catalysed oxidation of formaldehyde by chloramine-T in alkaline medium has been investigated. The reaction is first order with respect to chloramine-T and Os(VIII). It is inverse first order with respect to alkali and zero order with respect to aldehyde. Variation in the ionic strength does not have any effect on reaction rates. The energy and entropy of activation for the oxidation reactions are 15.2 K cal/mole and -16.9 ^{e.u.} ~~ev.~~ for formaldehyde and 16.0 k cal/mole and -14.7 ^{e.u.} ~~ev.~~ for acetaldehyde respectively. The mechanism suggested involves the formation of an intermediate complex between N-chlorotoluene-p-sulphonamide and Os(VIII) in the slow rate controlling step which abstracts hydride ion from the aldehyde in the fast step. The rates of oxidation of formaldehyde and acetaldehyde decreased linearly with increase in $[\text{OH}^-]$. Addition of Os(VIII) showed a positive catalytic effect on the first order reaction rate.

1.7 f OXIDATION BY PEROXYDISULPHATE

Kinetics of oxidation of formaldehyde by $\text{K}_2\text{S}_2\text{O}_8$ or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was studied in aqueous media. The oxidation was a free radical reaction, second order with respect to persulphate when $[\text{persulphate}]$ is in excess to $[\text{HCHO}]$. It was zero order with $[\text{HCHO}]$ when $[\text{HCHO}]$ is excess to (persulphate).

1.8 OXIDATION OF BENZALDEHYDE :

For the oxidation of benzaldehyde, various oxidants have been used. They are permanganate in water-acetic acid mixture, permanganate in buffer medium, permanganate in sulphuric acid-acetic acid mixture, vanadium(V), sodium periodate, chloramine-T etc.

1.8 a OXIDATION BY PERMANGANATE IN WATER-ACETIC ACID MIXTURE⁵⁷ :

Permanganate oxidation of benzaldehyde and its derivatives has been studied in water-acetic acid mixtures. The rate constants are found to increase with increasing [acetic acid] but less rapidly at higher concentrations. Arrhenius parameters have also been evaluated. The bimolecular rate constant increases with increasing proportion of acetic acid in the solvent mixture. The graphs of k values against [acetic acid] show that the increase is linear up to about 50 % concentration of acetic acid beyond which the slope value decreases and the plot is no longer linear.

The oxidation of benzaldehyde by acid permanganate has been studied in acetic acid - sulphuric acid mixture. The reaction is first order each in substrate and oxidant. The rate of reaction increases with the increase in sulphuric acid concentration and that the order with respect to H^+ was unity. The solvent effect has been studied at $30^{\circ}C$ by various acetic acid contents of the medium at constant sulphuric acid

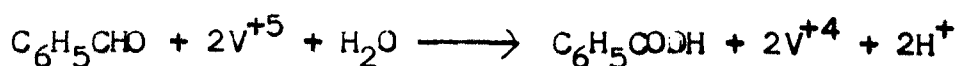
concentration. A linear plot of $\log k$ against $D-1/2D + 1$ showed that the reaction is of dipole-dipole nature. The reaction was found to be first order in aldehyde and permanganate. The acrylamide test showed absence of any free radicals. There was slight decrease in rate with increasing ionic strength from 0.5M to 2.0 M.

The rate of oxidation of eight aromatic aldehydes by KMnO_4 has been determined from pH 5 to 13. A general acid catalysed and a specific hydroxyl ion catalysed reaction was observed. The aldehydes in which the aldehyde H has been replaced by deuterium were found to be oxidised at a much slower rate than the unlabelled compounds in neutral solutions. This deuterium isotope effect was observed to decrease with increasing pH. In neutral solution, the oxidising agent appears to be the source of the oxygen introduced into the aldehyde whereas in basic solution, the solvent contributed a major part of this oxygen. The reaction in neutral solution probably involves the formation of permanganate ester of the hydrate of the aldehyde, followed by a rate determining loss of the aldehyde hydrogen as a proton. A free radical mechanism is suggested for the reaction in basic solution.

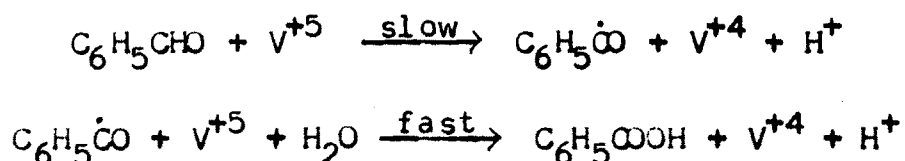
1.8 b OXIDATION BY VANADIUM (V)⁵⁸ :

The reaction between benzaldehyde and vanadium(V) in sulphuric acid-acetic acid mixtures in nitrogen atmosphere is found to obey a second order rate law. There is no

evidence for complex formation between benzaldehyde and vanadium(V). The stoichiometry was calculated to be two moles of vanadium(V) for one mole of benzaldehyde as follow.



Under the conditions of $[\text{aldehyde}] \gg [\text{V}^{+5}]$ the reaction followed first order kinetics. The pseudo-first order rate constants increased with increase in [benzaldehyde] and the order with respect to [benzaldehyde] was found to be one. The rate of oxidation increased with increase in percentage of acetic acid. The oxidation of benzaldehyde to benzoic acid may be represented as follow



The increase in rate with decrease in dielectric constant which indicates the reaction to be ion dipole type, also supports the mechanism suggested.

1.8 c OXIDATION BY SODIUM PERIODATE⁵⁹ :

Benzaldehyde and substituted benzaldehydes are oxidised by sodium periodate in alkaline medium in presence of OsO_4 . The rate of oxidation exhibits zero order dependence on $[\text{IO}_4^-]$ and first order dependence each on [substrate] and $[\text{OsO}_4]$. The data suggests that the oxidation of benzaldehyde proceeds via the rapid formation of a complex between the aldehyde hydrate

mono-anion and Os(VIII) which decomposes slowly with loss of H^+ followed by a fast reaction between the reduced Os(VI) species and periodate. The zero order rate constants increased with increasing initial [aldehyde]. It is observed that the reaction rate is not affected by change in ionic strength.

1.8 d OXIDATION BY CHLORAMINE-T⁶⁰ :

The kinetics of OsO_4 catalysed oxidation of benzaldehyde and substituted benzaldehydes by chloramine-T in aqueous and aqueous-t-butanol under alkaline conditions has been investigated. The reaction shows zero order dependence on the substrate. The order with respect to chloramine-T is one. The reaction shows first order dependence on $[OsO_4]$ and inverse first order dependence on $[OH^-]$.

1.8 e OXIDATION BY ACID BROMATE⁶¹ :

The kinetics of oxidation of benzaldehyde and some substituted benzaldehydes have been investigated in aqueous acetic acid medium in presence of sulphuric acid. The reaction exhibits first order both in substrate and oxidant and second order in H^+ ion. The rate of the reaction increases with increasing acetic acid content of the medium. A mechanism involving rate determining formation of a bromate ester which decomposes to products in a fast step has been proposed.

1.8 f OXIDATION BY CERIUM (IV)⁶²

The kinetics of oxidation of benzaldehyde to benzoic acid by Cerium(IV) was studied in 85 % aqueous acetic acid. The first reaction was the formation of 1:1 benzaldehyde ceric ion complex. This was followed by an acid catalysed decomposition of the complex as well as of a 2:1 benzaldehyde ceric ion complex which is present in relatively low concentration. Evidence was found for the formation of benzoyl radical as an intermediate and the reaction was found to give a kinetic isotope effect.

1.8 g OXIDATION BY CHROMIC ACID⁶³ :

The kinetics of oxidation of benzaldehyde by chromic acid has been studied in 91 % acetic acid medium. The reaction was found to have deuterium isotope effect of 4.3 and manganous ion was found to decrease markedly the rate of reaction.

The rate of oxidation of benzaldehyde by chromic acid in water at 80°C increases with the first power of $[C_6H_5CHO]$,⁷⁸ with the first power of concentration of acid chromate ion and with the more complicated function of the concentration of acid. The data is consistent with the mechanism for the oxidation-reduction process which involves the chromic acid ester of hydrated benzaldehyde as an intermediate.

1.9 SCOPE OF THE PRESENT WORK :

From the above literature survey, it is observed that large volume of work has been done on oxidation by Mn(III) acetate and very little work is done on Mn(III) sulphate. Further it is observed that very little work is done on the oxidation of aldehydes. Hence, it is proposed here to investigate the kinetics of oxidation of formaldehyde in sulphuric acid medium and benzaldehyde in sulphuric acid-acetic acid mixture by Mn(III) sulphate and the investigation proposed will include the study of the following factors.

- (1) Determination of order of the reaction with respect to the substrate and the oxidant and also the overall order of reaction. The reactions will be studied using different concentrations of the substrates as well as the oxidant. Isolation method and also Van't Hoff's differential method will be used to determine order of the reaction. Pseudo-first order rate constants will be obtained graphically.
- (2) Effect of Mn^{++} on the reaction will be studied by adding different amount of Mn(II) sulphate in the reaction mixture because Mn(II) sulphate is formed in the course of reaction. Effect of sulphuric acid and acetic acid will be studied by using different concentrations of the acids in the reaction mixture.



- (3) Determination of temperature coefficient of the reaction and evaluation of thermodynamic parameters. The reactions will be studied at different temperatures from 35°C to 60°C. The temperature coefficients of the reactions will be calculated. The energy of activation and frequency factor will be calculated by using Arrhenius equation.

$$k_1 = A e^{-E_a/RT}$$

The energy of activation will be calculated by graphical method using above equation as well as by direct substitution of k_1 and k_2 at temperatures T_1 and T_2 into the equation

$$E_a = \frac{2.303 \log (k_2/k_1) R T_1 T_2}{T_2 - T_1}$$

ΔH^* will be determined from the graph of $\log k_1/T$ against $1/T$.

$$\text{Slope} = - \frac{\Delta H^*}{2.303 R}$$

ΔS^* and ΔG^* for the reactions will be then calculated.

Existence of free radical during the course of reaction will be shown by acrylonitrile polymerisation test. The end products of the reaction will be detected and confirmed.

By using all these observations and results and with the help of the literature survey, the probable mechanism of

the reactions will be proposed and the results will be interpreted on the basis of the mechanism suggested. The results obtained for formaldehyde and benzaldehyde will be compared.