CHAPTER - I

INTRODUCTION

C H A P T E R - I

INTRODUCTION

GENERAL :

Molecule consists of atoms arranged in definite positions relative to each other. The small displacement of any of the atoms produces restoring forces which tend to pull them back to their equilibrium position. If relatively large displacements are made in molecules, the molecules may not recover their initial structures; instead, the atoms may take up new stable configurations in new molecules and a chemical reaction may take place. To produce a large displacements and hence chemical reactions, energy is required in excess at a particular temperature, and at any particular temperature, collisions between molecules will produce a range of molecular energies and some molecules may acquire enough energy to react.

It is not possible to study the mechanism of an organic reaction directly i.e. while the reactants are converted into products via some intermediates. Thus, some indirect evidences have been given to determine the mechanism of reaction.

But there is no such thing as absolute proof of the correctness of a reaction mechanism.[1] To establish the mechanism of a particular reaction, it must fulfil the

following conditions.

a)   The proposed mechanism should be as simple as possible, while still accounting for the experimental facts.

b)   The proposed mechanism should, if possible, suggest tests of its correctness.

c)   Individual tests in the proposed mechanism should be either unimolecular or bimolecular.

d)   • The proposed mechanism should not violet the principle of microscopic reversibility.

e)   Individual reactions should be chemically reasonable.

f)   Individual reactions should be energetically reasonable.

After the establishment of the reaction product, the most important part of a reaction is the rate at which it takes place. All chemical reactions take place at some definite rate which is dependent on conditions such as temperature, pressure, concentration of species and presence of catalyst or inhibitors. Some reactions such as neutralization of strong acid with a strong base, are so rapid that they appear to reach equilibrium instantaneously while other reactions, equally or even more favourable thermodynamically are so slow that no reaction can be detected even over a long period of time. An example of such reaction is the reaction
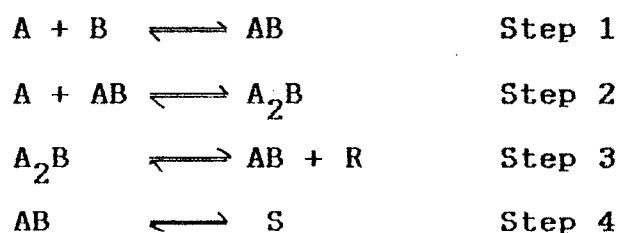
between oxygen and hydrogen at room temperature. The chemical kinetics is of considerable importance to analytical/industrial chemists, because through the knowledge of the kinetics of a system one can increase or decrease the rate of reaction by varying the conditions employed.

The order of reaction can be determined by studying the change in the concentration as a function of time for several runs under varying conditions. The rate constants can be obtained by graphical or numerical method. As it is the concentration which is usually measured, the integrated form of the rate expression is more convenient to study.

The most of chemical reactions are complex, taking place in a series of steps. These steps are the "mechanism" of the reaction. For example, the reaction

$$2A + B \rightleftharpoons R + S \qquad \dots (1.1)$$

might take place as follows :

$$A + B \rightleftharpoons AB \qquad \text{Step 1}$$

$$A + AB \rightleftharpoons A_2B \qquad \text{Step 2}$$

$$A_2B \rightleftharpoons AB + R \qquad \text{Step 3}$$

$$AB \rightleftharpoons S \qquad \text{Step 4}$$

One of these steps must be slower than others, and this step often determines the rate of an overall reaction.

During the study of mechanism of any given chemical process kinetically, we should get additional

information such as the products of reaction, stereochemical evidences, refinement of kinetic method, detection of short lived intermediate, use of isotopes etc. To determine the reaction rate by conventional methods reduces to a study of concentrations as a function of time. Analytical procedures, which can be either physical or chemical, can be used to follow the course of reaction. Generally, physical methods of analysis are much more conveninent than chemical methods. Among physical methods, most common methods are pressure measurement in gaseous reactions, dilatometry or measurement of volume changes, optical methods like polarimetry, refractometry, colorimetry and spectrophotometry; electrical methods such as conductometry, potentiometry, polarography and mass spectrometry. Theoretically any property which changes sufficiently used to follow the course of the reaction. As an example of spectroscopic study, the results of Andrews[2] on the alcoholysis of cinnamyl chloride

$$C_6H_5-CH=CH-CH-Cl_2+C_2H_5OH \longrightarrow C_6H_5-\underset{\underset{OC_2H_5}{|}}{CH}-CH=CHCl+HCl$$
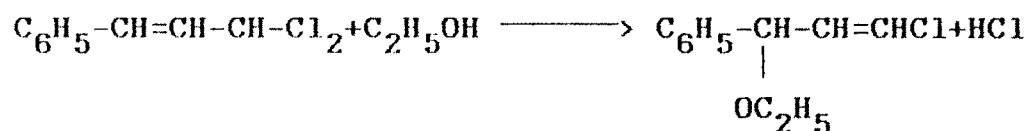
The cinnamyl chloride, having a double bond conjugated with the benzene ring, absorbs strongly at 2600 A^o whereas the product (1-chloro-3-ethoxy-3 phenyl-1-propene) being unconjugated does not absorb until 2100 A^o. Accordingly a measurement of the optical density at 2600 A^o as a

function of time permits the rate of the reaction to be measured.

Any kinetic investigation generally comprised of two steps. The first one is to establish the relationship between the rate of the reaction and various factors such as concentration of reactants, temperature and hydrostatic pressure, primary and secondary salt effects, dielectric constants of the medium and catalysis. Identification of the product of reaction and detection of free radicals, intermediate etc. are also done. The second step of investigation is to arrive at a suitable mechanism which can account for the results obtained on velocity measurements.

OXIDATION PROCESS AND OXIDISING AGENTS :

Liquid phase reactions are of keen interest to organic as well as inorganic chemists. Oxidation reactions are the most important in organic reactions especially, in solution. Oxidising agents such as nitric acid, chromic acid, potassium bromate, permangenate, potassium persulfate, potassium periodate, lead tetra acetate, cerric sulphate, thallium, Ti $(CH_3COO)_3$, Cr(VI) oxide, peroxydisulphate, Mn (II) pyrophosphate, Mn(III) acetate, Mn(III) sulphate, vanadium, hexacyano ferrate, chloramine-T, bromoamine T etc. have been employed to study the oxidation of organic compounds.

As oxidation reactions of organic compounds have vital importance in synthetic biological fields, variety of organic compounds like olefins, phenols, aldehydes, esters, alcohols, carboxylic acids, amines, carbohydrates, amino acids, ketones and many others have been studied with different oxidants. Oxidants can be classified according to the particular chemical transformation in a manner i.e. most familiar to the synthetic organic chemistry.

Actually oxidation is simply a transfer of electrons from reductant to oxidant and by considering number of electrons transferred to the oxidant during oxidative process, we can easily classify these processes as well as oxidants[3] as :

(i)   Oxidants which can accept one electron, e.g. trivalent iron Fe(III), tetravalent vanadium, trivalent manganese etc.;

(ii)   Oxidants which can accept two electrons, e.g. oxidation of 3-ethyl pentane with sodium dibromate[4].

The Fe(III) is an important 1-electron transfer oxidant. Recently Fe(III) is widely used in comparison with other oxidants. Hence it is proposed here to take brief review of the work done on oxidation of organic compounds by Fe(III).

LITERATURE SURVEY :

HEXACYANOFERRATE(III) AS AN OXIDANT :

Although $K_3Fe(CN)_6$ is an ideal 1-electron transfer oxidant, its use in oxidation was somewhat neglected as an oxidising agent. Selenium oxide, aluminium alkoxide, lead tetra acetate, osmium tetra oxide, tert-butyl chromate, chromium trioxide, pyridine complex, organic per acids, periodic acid, peroxytrifluro acetic acid and potassium ferricyanide etc. have been studied.

Most of the reagents mentioned above have been discussed and revealed in the available literature. However, no comprehensive summary is available on potassium ferricyanide as an oxidising agent in organic chemistry.

It falls in the class of oxidising agents comprising cerric sulphate, ammonniacal silver nitrate and Fehling's solution in all of which the oxidising species is a complex electron abstracting ion.

$$Fe(CN)_6^{3-} + e^- \longrightarrow Fe(CN)_6^{4-} \quad E = 0.36 \text{ volts}$$
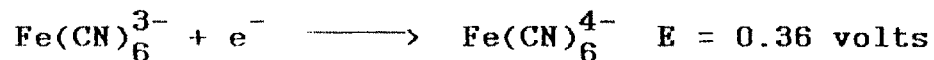
It is an example of oxidising agent in which one electron transfer is involved. Therefore, it acts as an one electron abstractor.

OXIDATION OF OLEFINS :

Moyell Jospals[5] studied for the first time the oxidation of olefins initiated by $Fe(CN)_6^{3-}$ using osmium tetroxide as a catalyst. The oxidation product was found to be glycol. The rate constants for the formation of an olefin-Os(VIII) inter-mediate complex and its decomposition to the products are studied by visible spectroscopy.

OXIDATION OF HYDROCARBONS :

Oxidation of p-nitrotoluene, 2,4-dinitrotoluene and methoxytoluene by hexacyanoferrate (III) has been reported by Radha Krishnamurti and co-workers[6]. The reaction was found to be first order in oxidant, substrate and alkali.

The kinetics and mechanism of oxidation of hydrocarbons have been extensively studied by Noyes and Moses[7].

The oxidation of xylene by acid hexacyano-ferrate(III) giving aldehyde as a major product was observed[8]. The reaction was found to be first order w.r.t. substrate, oxidant and acid. E.S.R. spectroscopy was used to detect the radical.

The oxidation of benzoin and its derivatives[9] catalysed and uncatalysed, in alkaline medium was investigated spectrophotometrically. The rate was found to be decreased with decrease in dielectric constant of the medium.

The total order was found to be second; first order w.r.t. [$\overline{O}H$] and [Benzoin] but zero order with $Fe(CN)_6^{3-}$.

The oxidation of chalcones by using osmium tetroxide as a catalyst in alkaline medium has been investigated[10] and the rate was found to be first order in [chalcone], [Os(VIII)] and [$\overline{O}H$] each; but it was found to be independent of [$Fe(CN)_6^{3-}$]. The kinetics of oxidation of fluorene[11] has also been reported.

The Kasim and co-workers[12] have reported oxidation of β-hydroxy, thiobenzoyl, p-methoxy styrene in neutral and alkaline medium. Kinetics and mechanism of oxidative cleavage of styrene[13] by acidic hexacyannoferrate ion was extensively studied. The reaction was shown to be first order w.r.t. oxidant, substrate and acid. The rate determining step involved cationic intermediate with subsequent cleavage of C-C bond yielding Ph-CHO and HCHO respectively.

OXIDATION OF ALCOHOLS :

The kinetics of oxidation of alcohols by alkaline hexacyanoferrate (III) has been widely studied.

Krishna et al[14] were the first to examine the kinetic features of OsO_4 catalysed oxidation of methanol and ethanol by ferricyanide ion in aqueous alkaline medium. The rate of reaction is given by an expression:

$$Rate = k \text{ [substrate]} [\overline{OH}]$$

Rhodium(III) catalysed oxidation of methanol, 2-propanol and 2-butanol was studied by Singh[15,16] and his co-workers and found the disproportion of complex between catalyst and oxidant. On the contrary, Ru(III) catalysed oxidation of methyl, ethyl, isopropyl and n-butyl alcohols[17], unsaturated alcohols[18], cyclic alco- hols[19,20], glycols[21], aminoalcohols[22], Rh(III) catalysed oxidation of methanol[23], Os(VIII) catalysed oxidation of low molecular weight alcohols[24], 2-methoxy ethanol[25], 2-propanol[26], Ru(III) catalysed oxidation of propanol-1, and butanol-1[27] by hexacyannoferrate (III) has been investigated in alkaline medium. Generally order w.r.t. oxidant was found to be one.

Singh et al.[28] have reported that the OsO_4 catalysed oxidation of 2-propanol and 1-propanol by hexa-cyannoferrate(III) in alkaline medium proceeds via the formation of an activated complex between the alcohol molecule and OsO_4 which rapidly decomposes to an intermediate product and Os(VI) species. The Os(VI) thus produced is rapidly oxidised to Os(VII) with hexacyanoferrate(III) ion which does not appear in rate law.

The OsO_4 catalysed hexacyanoferrate(III) oxidation of sorbitol, mannitol,[29] n-hexanol,[30] methyl and ethyl digol[31] ($MeO-CH_2-CH_2-O-CH_2-CH_2-OH$) was found to be zero order in hexacyanoferrate(III) while OsO_4 catalysed oxidation of

glycerol,[32] Ru(III) oxidation of butanol-2 and iso butanol[33] was found to proceed via formation of substrate catalyst complex.

The OsO_4 catalysed oxidation of ethane 1:2, propane 1:2, butane 2:3 diols[34] and uncatalysed oxidation of propane 1:2, butane 2:3,[35] 2-methyl pentane 2:4, pentane 1:5[36] diols by hexacyanoferrate(III) in alkaline medium was found to be first order each in [$\overline{O}H$] and [substrate] at their lower concentration which tends to zero order at higher concentration of both [$\overline{O}H$] and [substrate]. However, order with respect of [oxidant] in catalysed and uncatalysed oxidation is zero and one respectively.

The Os(VIII) catalysed oxidation of methanol, ethanol, 2-butanol,[37] methyl cyclohexanol,[38] Ru(III) catalysed oxidation of butane 1:4, pentane 1:5 diols,[39] Pd(II) catalysed oxidation of allyl alcohol[40] and uncatalysed oxidation of pinacol,[41] 2-methyl propanol-1, 3-methyl butanol-1, 4 methyl pentanol-2, butanol-2,[42] and benzyl alcohol[43] by hexacyannoferrate(III) ion has been reported.

The oxidation of methanol, ethanol, propanol-1 and butanol-1[43A] by alkaline hexacyanoferrate(III) using iridium (III) chloride as a homogenous catalyst reveals first order kinetics at low concentrations, thereafter the rate of reaction became independent w.r.t. hexacyanoferrate(III) and hydroxide ion each at their higher concentration. The

reaction followed direct proportionality w.r.t. $[IrCl_3]$ and increase in the ionic strength of the medium effected the reaction rate in positive manner.

The Ru(III) catalysed oxidation of cyclopentanol[44] by alkaline hexacyannoferrate(III) has been shown zero order kinetics with respect to oxidant. Reaction velocity decreases with the increase in $[\overset{\bullet}{\overline{O}}H]$ and a first order kinetics at lower [cyclopentanol] tends towards lesser order at higher concentration.

The Ru(III) catalysed oxidation of aliphatic alcohols and diols with alkaline hexacyanoferrate has been reported by Radhakrishnamurti and Shahu[45] who observed zero order dependence of reaction rate on [Ru(III)] and [substrate] in limited range of concentration :

$$5.0 \times 10^{-3} - 1.0 \times 10^{-2} \text{ M.}$$

The oxidation of di- and tri-glycols,[46] propanol-2 and butanol-2,[47] methanol and ethanol,[48] dulcitol and xylitol[49] by alkaline hexacyanoferrate(III) ion has been studied in presence of Ruthenium(III) chloride, Rhodium(III) chloride, sodium ruthenate and Ruthenium(VIII) tetroxide catalysts respectively. The reactions are found to be zero order in [hexacyanoferrate(III)] but almost first order each in substrate and catalyst.

Recently Singh and co-workers[50] have reported the Ru(III) chloride catalysed oxidation of propanol-1, butanol-1, propanol-1 and butanol-2 by hexacyanoferrate(III) in sodium carbonate medium. The rate of reaction is independent of initial concentration of hexacyanoferrate(III) but directly proportional to [alcohol] and [$\bar{O}H$] in low concentration regions. The higher concentration of either of these is found to decrease the reaction rate. A suitable mechanism involving abstraction of hydride ion by Ru(III) in rate determining step is proposed to explain the experimental facts.

OXIDATION OF PHENOLS :

The oxidation of phenol by acidic hexacyanoferrate (III) has been reported by Makromol[51] and later on reviewed by Lukashevich et.al.[52] The reaction is extensively used in the rubber synthesis.

The kinetics and mechanism of oxidation of phenol and substituted phenols in 20% ethanol at constant ionic strength by hexacyanoferrate(III) have been studied by Radhakrishnamurti and co-workers.[53] The major product of the oxidation is dione. The mechanism involving a two-electron transfer from the substrate is suggested.

The oxidation of phloroglucinol[54] and naphthols[55] with alkaline hexacyanoferrate(III) has been investigated by

Bhatacharjee and Mahanti. The reaction was found to be first order with respect to oxidant, substrate and alkali. The formation of coupled products is explained via radical intermediates which are detected by ESR spectroscopy.

Kinetics and mechanism of oxidation of catachol[56] by hexacyanoferrate in alkaline medium at $30^{\circ}C$ yielded o-quinone via formation of the semiquinone radical intermediate in rate determining step. The reaction followed the rate law :

$$k_{obs} = k_{[catachol][\bar{O}H]^2}$$

with excess of susbtrate.

The oxidation of resorcinol[57,58], guaicol[59] and pyragallol[60] in alkaline medium and the oxidative coupling of phenols by hexacyanoferrate(III) were reported. The rate determining step involved radical intermediate, detected by E.S.R. spectroscopy. The order was found to be first w.r.t. substrate, oxidant and alkali. The oxidation product p-benzoquinone was obtained from quinol.[61] The slow step of reaction involves benzosemiquinone radical.

OXIDATION OF GLYCOLS :

Oxidation of D-glucose and D-fructose[62] by alkaline hexacyanoferrate has been reported. It was found that the rate was directly proportional to sugar and ammonia concentration and independent of oxidant concentration. The rate

was found to be decreased with decrease in salt concentration.

Kinetics and mechanism of oxidation of D-glucose and galactose by hexacyanoferrate(III) was investigated by Shrivastava and co-workers[63]. The order w.r.t. oxidant was found to be zero and that w.r.t. [sugar] and [$\overline{O}H$] was first.

Oxidation of disaccharides[64,65] by hexacyanoferrate in alkaline medium has been studied extensively. The kinetics of the reaction was found to be zero order w.r.t. oxidant and first order w.r.t. reducing sugar.

OXIDATION OF ALDEHYDES AND KETONES :

The Os(VIII) catalysed oxidation of acetone and ethyl methyl ketone[66] has been reported to be first order in [substrate] but zero order in [$Fe(CN)_6^{3-}$]. A marginal decrease in reaction rate with increase in [ketone] is attributed to the dielectric effect of medium, whereas zero order w.r.t. oxidant is explained by assuming oxidation of reduced osmium to its original octavalent state by hexacyanoferrate(III) in the fast step. The order of reactivity, ethyl methyl ketone > acetone is attributed to the enol content and its thermodynamic stability.

Oxidation of formaldehyde by hexacyannoferrate(III) has been reported.[67] It was shown that the reaction is rapid initially, then follows first order w.r.t. hexacyanoferrate,

formaldehyde and hydroxide ion.

Radhakrishnamurti and co-workers[68] reported the role of dimethyl sulfoxide in the oxidation of substituted acetophenones by hexacyanoferrate(III) in alkaline medium. It was observed that the rate of reaction is retarded upto 0.1447 mole fraction of DMSO and accelerated when mole fraction of DMSO > 0.1447. The decrease in the rate is attributed to the competible solvent effect on ion-ion reaction whereas acceleration of rate is explained by assuming stabilization of transition state by larger solvation shell of Me_2SO.

UV spectrometric kinetic study of oxidation of 2,3, 4-trihydroxy benzophenone[69] by hexacyanoferrate(III) in alkaline medium has been reported by McDonald and coworkers. The reaction is first order each in [oxidant] and [substrate]. The rate of reaction is increased by increase in pH but inhibited by increase in $[Fe(CN)_6^{4-}]$. The reaction shows positive salt effect and specific cation effect. A radical aromatic substitution mechanism is proposed to explain the formation of 2:6 dihydroxy-xanthone quantitatively.

Kinetics of oxidation of cyclopentanone, cyclo-hexanone, cycloheptanone and cyclooctanone[70] by alkaline hexacyanoferrate in ethanol-water and pyridine-water solvent systems has been reported. The reaction was found to be first order w.r.t. substrate, oxidant and alkali. Cyclohexanone

reacts faster than the other ketones, which is attributed to higher enol content of cyclohexanone. The solvent effect indicates the ion-ion reaction.

The OsO_4 catalysed oxidation of benzaldehyde[71] with alkaline hexacyanoferrate(III) was found to be first order each in the [OsO_4], [substrate] and [$\bar{O}H$] but zero order in [$Fe(CN)_6^{3-}$]. An ionic pathway involving a proton loss in the rate determining step is supported by linear Hammett's plot with a σ value of +2.0.

Ru catalysed oxidation of aromatic aldehydes[72] with alkaline hexacyanoferrate(III) was found to follow the Michaelis Menten type kinetics in which the rate determining step involves the decomposition of complex between Ru(III) and hydrated aldehyde.

The OsO_4 catalysed and uncatalysed oxidation of benzoin and its derivative[73] by hexacyanoferrate in alkaline medium was studied spectrophotometrically. The rate of reaction was found to increase with increase in dielectric constant of medium. The raction was found to be first order each in [$\bar{O}H$] and [substrate] but zero order with respect to [$Fe(CN)_6^{3-}$].

The kinetics and mechanism of Os(VIII) catalysed oxidation of acetaldehyde, propanaldehyde and butyraldehyde[74] by hexacyanoferrate(III) in sodium carbonate-bicarbonate buffer has been reported in which the anion of the hydrated

aldehyde is mentioned as reactive species.

Recently, Gupta and coworkers[75] studied the oxida-
tion of o, m and p-hydroxy acetophenones by alkaline hexa-
cyanoferrate(III). The reaction is first order each in
[acetophenone] and [hexacyanoferrate(III)]. The rate of
reaction increases proportionately with an increase in [$\overline{O}H$]
and shows positive salt effect. The rate determining step
involving enolate ion and hexacyanoferrate(III) ion
interaction gives radical which consumes further 3 moles of
$Fe(CN)_6^{3-}$ in subsequent steps to yield the final products.

OXIDATION OF HYDROXY ACIDS AND KETO ACIDS :

The OsO_4 catalysed oxidation of α-hydroxy acids
with alkaline hexacyanoferrate(III) has been studied by Singh
et al.[76,77] who observed that reaction proceeds extremely
slowly or stagnant in absence of catalyst.

Kinetic studies of organic acids include the OsO_4
catalysed oxidation of glycolic,[78] benzyl phenyl glycolic,[79]
glyoxylic and pyruvic[80] acids by hexacyanoferrate(III) while
those of uncatalysed oxidation by hexacyanoferrate(III)
include thiosalicylic acid[81] and crotonic[82]acid. Some of
these were reported to be first order in organic substrate
and zero -0.5 and 1.5 order in oxidant.

Kinetics of osmium tetroxide catalysed oxidation of
benzilic acid[83] by alkaline hexacyanoferrate(III) have been

studied in 30% (v/v) t-butanol-water mixture at a constant ionic strength. The reaction was found to be first order each in [substrate], [OsVIII] and [$\bar{O}H$] but independent of [hexacyano ferrate(III)]. The rate of reaction was decreased with the decrease in dielectric constant and increased with increase in ionic strength of the medium. The entropy of activation was found to be negative.

Oxidation of tartarate[84,85] ion both catalysed and uncatalysed with alkaline hexacyanoferrate has been investigated and mechanism involving formation of Cu(II)-tartarate complex and its subsequent oxidation to another Cu(III)-tartarate complex by hexacyanoferrate(III) is suggested for Cu(II) catalysed oxidation whereas 2 electron transfer in the rate determining step is reported in uncatalysed oxidation.

The oxidation of malate and fumarate ions by hexacyanoferrate(III) ion in alkaline pH using Os(VIII) as catalyst has been studied by Singh et.al.[86] It was observed that the rate of oxidation of malate ion is greater than that of fumarate ion.

The kinetics of Os(VIII) catalysed oxidation of propionic acid[87] by hexacyanoferrate(III) was studied in alkaline medium. The first order with respect to Os(VIII) at low concentration of [$\bar{O}H$] becomes zero order at higher concentration of [$\bar{O}H$]. It has been shown that the reaction proceeds with the formation of substrate-catalyst complex.

The OsO_4 catalysed oxidation of cinnamate ion[88] by hexacyanoferrate(III) ion has been reported iodometrically. The rate of reaction increases with increase in $\bar{O}H$ ion concentration upto 8.0×10^{-3} M beyond which the rate decreases. It was observed that the ferricyanide oxidation of crotonic acid[89] is also catalysed by Os(VIII).

Os(VIII) catalysed oxidation of bromo-propionic acid[90] with alkaline hexacyanoferrate(III) has been reported.

Bhattacharjee and Mahanti[91] investigated the oxidation of trans-cinnamic and crotonic acids by hexacyanoferrate (III) in perchloric acid medium. The rate of reaction was dependent on the first power of the concentrations of the substrate, oxidant and $HClO_4$. The reaction is favoured in a medium of low dielectric constant.

The uncatalysed oxidation of levulinic[92] and thiomalic acids[93,94] in alkaline medium was investigatged colorimetrically. Stoichiometry was shown to be 1:1 and the salt effect was also studied.

OXIDATION OF AMINES :

Oxidation of different amines with hexacyanoferrate (III) has been studied by different authors[95-97] who observed that the rate of oxidation is first order each in [oxidant] and [amine]. Generally rate of reaction is increased by the

presence of $\overline{O}H$ but inhibited by the added hexacyannoferrate (II).

Lindsay and Mead[98] investigated the effect of structure on the reaction rate of oxidation of alkyl tertiary amines with alkaline hexacyanoferrate(III).

It has been reported that the oxidation of N:N dialkyl hydroxyl amine by hexacyanoferrate in alkaline medium gives N-alkyl ketoxime.[99]

The oxidation of diethanolamine[100] by alkaline hexacyanoferrate(III) has been reported to be first order each in [amine] and [$\overline{O}H$]. The first order with respect to [hexacyanoferrate(III)] at its lower concentration becomes zero order at higher concentration. The reaction shows positive salt effect and is found to be sensitive to common ion effect.

The kinetics of Os(VIII) catalysed oxidation of ethyl amine, isopropyl amine, n-butyl amine[101] and methyl amine[102] in alkaline medium has been investigated spectrophotometrically. The rate dependence on oxidant is found to be zero order in the former but first order in the latter case, while order with respect to [catalyst] is one in both the cases. The order in [amine] and [alkali] decreases from unity at their higher concentration.

Kinetics and mechanism of oxidation of triallyl-amine[103] by alkaline hexacyanoferrate(III) was investigated. The rate was found to be independent of the concentration of $Fe(CN)_6^{3-}$ while order in [triallylamine] and [$\bar{O}H$] was nearly unity and 0.33 respectively. The rate of reaction was not retarded by added $Fe(CN)_6^{4-}$ ion. The reaction has shown positive salt effect.

The uncatalysed[104,105] oxidation of triethanolamine by alkaline hexacyanoferrate(III) shows first order rate dependence on [hexacyanoferrate(III)]. The order in [triethanol amine] and [$\bar{O}H$] is one each.

Oxidation of substituted tertiary amines[106] by alkaline hexacyanoferrate shows first order rate dependence each on [oxidant] and [amine]. The rate of oxidation is reduced by the presence of electron withdrawing substituents.

Oxidation of aliphatic amines like N-methyl, N:N dimethyl and tertiary amines[107] by hexacyanoferrate in alkaline medium followed the rate law :

Rate $= k_2$[amine][hexacyanoferrate(III)]

An abstraction of an electron from the loan pair of electrons on nitrogen is suggested as irreversible rate determining step.

Ru(III) catalysed oxidation of ethylamine, n-butyl amine and iso propyl amine[108] by alkaline hexacyanoferrate(III) has been reported. The rate was found to be independent of [$\overline{O}H$] but first order each in the [amine], [Ru(III)] and [hexacyanoferrate(III)]. The order in oxidant decreases at its higher concentration.

Ru(III) catalysed oxidation of benzylamine[109] with hexacyanoferrate(III) and in aqueous methanol[110] has been investigated by different authors. The catalysed oxidation involves decomposition of the catalyst-substrate complex in rate determining step whereas oxidation in aqueous methanol proceeds via formation of radical intermediate.

Kinetics of oxidation of triethylene tetramine[111] by alkaline hexacyanoferrate has been reported. The rate was found to be first order each in [hexacyanoferrate(III)] and [amine]. The rate constant increases in pH range of 8.5 to 11.85 while effect of ionic strength is found to be negligible.

OXIDATION OF AMINO ACIDS :

Os(VIII) catalysed oxidation of glycine, L-leucine, L-phenylalanine, DL-α-alanine and DL-valine by hexacyanoferrate(III) in alkaline medium was studied spectrophoto-metrically.[112] The reaction was found to first order with respect to both [amino acid] and [catalyst]. The effect of

alkali is slightly positive at high concentration [>0.2 M] only. The raction rate is independent of [oxidant] but it shows specific hexacyanoferrate(II) ion catalysis.

Kinetics of uncatalysed oxidation of valine[113] and methionine[114] by ferricyanicde in alkaline medium has been reported. The reaction was found to be first order with respect to [oxidant], [substrate] and [alkali]. The experimental results are explained on the basis of radical mechanism.

The kinetics of reaction between diethylene triamine peta-acetic acid[115] and hexacyanoferrate(III) was studied spectrophotometrically.

The oxidation of some amino acids[116,117] with excess of ferricyanide using Os(VIII) as a catalyst is investigated by Upadhyay et al. The reaction showed a very complex kinetics. The main oxidising species is Os(VIII) and ferricyanide is mainly used in generating the Os(VIII) species from the Os(VI) formed. A suitable mechanism involving the formation of transient complex is proposed.

Lambert and Jones[118] showed that the uncatalysed reaction is extremely slow even at high ionic strength while Malik and Aslam[119] reported the formation of complex between amino acid and hexacyanoferrate(III).

HALLIDES :

Kinetics of oxidation of phenacyl bromides[119A] in aqueous acetonitrile by hexacyanoferrate(III) at $10^{o}C$ has been studied. The reaction was found to be first order in oxidant, phenacyl bromide and hydroxide. The enolate of phenacyl bromide and ferricyanide are the reactive species. Suitable mechanism was suggested.

OXIDATION OF HYDRAZINE AND ITS DERIVATIVES :

The oxidation of phenyl hydrazine and its sulphonic acids[120] by hexacyanoferrate(III) was studied in aqueous perchloric acid. The reaction is first order in [hexacyanoferrate(III)] and apart from the small ion pairing contribution, also the first order in [hydrazine]. The dependence of reaction rate on $[H^{+}]$ shows a competition between the oxidation of the protonated and the unprotonated forms of phenylhydrazines.

Mechan et al.[121] reported the oxidation of hydrazine at pH 6-13. The reaction followed the first order kinetics both in substrate and reagent. The hydrazine is oxidised quantitatively to N-cyanide. An irreversible transfer of one electron between $Fe(CN)_6^{3-}$ and neutral hydrazine molecules is inferred as rate determining step from the pH dependence of the reaction rate.

Kinetics and oxidation of hydrazines and unsymme-trical dimethyl hydrazine[122] were studied potentiometrically by alkaline hexacyanoferrate(III).

The kinetics and mechanism of oxidation of hydrazine by hexacyanoferrate(III) in aqueous methanol[123] was investigated in the pH range 9.9 to 11.45. The reaction was found to be first order w.r.t. [hydrazine] and [hexacyano-ferrate(III)] but zero order with respect to [$\bar{O}H$]. Increase in methanol content of solvent reduces the reaction rate and also it shows specific ion effect.

Gupta et al.[124] reported the oxidation of phenyl hydrazine with hexacyanoferrate(III) ion. The kinetics of oxidation of 2:4 dinitrophenyl hydrazine, p-nitrophenyl hydrazine and p-tolyhydrazine with potassium hexacyanoferrate (III) has been investigated in perchlorate medium[125]. The order with respect to $Fe(CN)_6^{3-}$ is found to be one in oxida-tion of all substrates. The rate of reaction shows first order dependence on substrate in the case of [p-nitrophenyl hydrazine] and [p-tolylhydrazine] but for [dinitrophenyl hydrazine] the rate increases and tends to attain a limiting value with increase in [dinitrophenyl hydrazine] indicating formation of complex with hexacyanoferrate(III) ion.

Krisna Rao et al.[126] have reported the oxidation of aroyl hydrazine like nicotinoyl and isonicotinoyl hydrazines with hexacyanoferrate(III) in the pH range 7 to 8 using

phosphate buffer. The reaction shows a novel second order dependence of the rate on [hexacyanoferrate(III)]. The rate of reaction is increased with the increase in pH of medium but markedly retarded by added hexacyanoferrate(II) ions. The evidence for the complexation of substrate with both $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ has been given and mechanism involving formation of intermediate radical ion in rate determining step is proposed.

OXIDATION OF HYDRAZIDES :

The oxidation of hydrazides has been recently studied and formation of di-imides or a free radical as the reaction intermediates is observed in most of the cases. The oxidation of hydrazides by lead tetracetate[127] gives corresponding acids and nitrogen.

The hydrazides of salicylic acid and substituted salicylic acids on oxidation with MnO_2 in different solvents gave corresponding acids.[128] In addition to acids, the formation of benzamides was also observed in the presence of ammonia. This leads to conclusion that the reaction proceeds with the formation of free radical intermediate. The oxidation of phenyl hydrazides[129] by MnO_2 is a preliminary oxidation of the hydrazides to azo compounds which get solvolysed to acid.

Hogale and Jagdale studied the oxidation of

hydrazides of phenyl acetic[130], picolinic, nicotinic and isonicotinic[131] by $S_2O_8^{2-}$ using Ag(I) as catalyst. The reaction was found to be first order w.r.t. [oxidant] and zero order w.r.t. [hydrazide]. Oxidation of aroyl hydrazides with peroxydisulphate using Ag(I) as catalyst has also been carried out and results are explained in terms of simple as well as consecutive reactions.[132-134]

The oxidation of n-valeric, iso-valeric, n-butyric, iso-butyric, acetic and propionic acid hydrazides by peroxy-disulphate using Ag(I) catalyst has been studied by Patil and Patil.[135] The reaction is found to be first order in [oxidant] but zero order in [hydrazides]. The specific rate of reaction is directly proportional to concentration of $AgNO_3$. The reaction exhibits negative salt effect and specific inhibitary effect of added cation which is in the order $K^+ > Na^+ > Li^+ > Al^{3+} > Mg^{2+}$.

The oxidation of nicotinoyl and iso-nicotinoyl hydrazides by iron(III)[136] in the presence of 1:10 phenan-throline has been investigated. The oxidation reaction involved the formation of 1:1 complex with substrate. The retardation of the rate by the presence of H^+ ions was observed and formation of di-imide radical intermediate has been proposed.

Oxidation of hydrazides by iodine in aqueous hydrochloric acid was investigated by Krishna Rao and

Kodanda[137]. It was found that at high concentration of iodine, the reaction was first order w.r.t. both [oxidant] and [substrate].

Kinetics of oxidation of phenyl acetyl hydrazide[138] by vanadium(V) in aqueous perchloric acid has been studied. The reaction was found to be first order each in [oxidant] and [substrate].

Kinetics and mechanism of oxidation of hydrazides by chloroamine-T has been investigated in 50% (v/v) aqueous methanol by Nimbalkar et al.[139] The rate followed first order kinetics in [chloroamine-T] and [hydrazide]. NaCl had no effect on reaction rate. Rate constant is increased with decrease in methanol %

Oxidation of carbohydrazide by chloramine-T and bromoamine-T in acid and buffered aqueous media has been studied by B.Thimme Gowda[140] and co-workers.

The kinetics of oxidation of series of aryl hydrazides[141] by hexacyanoferrate(III) has been investigated. The reactions were found to be first order each in [oxidant] and [substrate]. The effects of added hexacyanoferrate and other ions on the rate of oxidation have been investigated. The kinetics reveals a pronounced positive salt effect as well as specific ion effect. A suitable mechanism and a rate law consistant with the experimental results have been proposed.

Oxidation of n-valeric and iso-valeric acid hydrazides by hexacyanoferrate(III) in acidic medium has been reported by Patil and Hongekar.(112) →142 The reaction was found to be first order in [substrate] and in $[Fe(CN)_6^{3-}]$. The reaction has shown positive salt effect.

Kinetic and mechanism of nicotinic acid and iso-nicotinic acid[143] hydrazide by alkaline hexacyanoferrate(III) has been investigated recently. The reaction was found to be first order each in [hydrazide] and [hexacyanoferrate (III)].Positive salt effect was observed. Specific reaction rate is increased with decrease in dielectric constant.

IMPORTANCE OF HYDRAZIDES :

The chemistry of hydrazides is very important because of their pharmaceutical applications. They have been extensively studied since the discovery of "isonicotinic acid" as a strong antituberculostatic agent.[144] Many derivatives of this compound have been synthesised and tested for anti-bacterial activity.[145,146] Some of hydrazides have been reported to possess anti inflammatory[147] and diuretic activities.[148] Diacyl hydrazine group in certain derivatives of hydrazides has been supposed to be biologically active.[149] Isoxazole carboxylic acid hydrazide[150] has been reported to have antileprosy and phenothiazine carboxylic acid hydrazide[151] has been reported to have anticonvulsive action.

Maleic acid hydrazide is used to regulate and inhibit the growth of the plants.[152] Recently dihydrazides have been reported as anti-thelminties.[153] Very recently hydrazides[154] derived from N-(p-nitro benzoyl)-DL-asparagine and N-(p-acyl amino benzoyl) DL-aspargine have been reported effective against tuberculosis.

Hydrazides are used as antioxidants for polyolefines and polyurethanes which are otherwise oxidised in presence of copper and are also used in heat and corrosive stabilisation of cellulose.[155] An incorporation of hydrazides[156] has improved the applicability in plastics and cable insulations.

PRESENT WORK AND ITS AIM :

The above discussion and literature survey indicate that the kinetics of oxidation of aliphatic as well as aromatic acid hydrazides by various oxidants has been studied. It is clear that little information regarding the mechanism of oxidation of hydrazides by hexacyanoferrate(III) ion is available. Hence, the study of kinetics and mechanism of oxidation of aryl hydrazides by alkaline hexacyanoferrate (III) in water-dioxane mixture has been undertaken.

The following hydrazides are selected for the kinetic study :

i)   o-Chloro benzoic acid hydrazide – $CONHNH_2$

ii) p-Chloro benzoic acid hydrazide – $CONHNH_2$
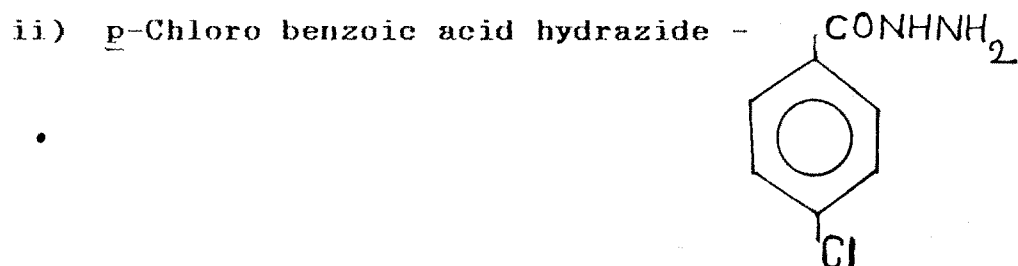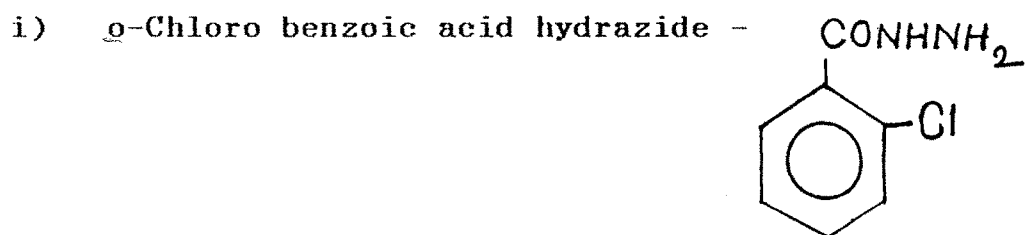
Two hydrazides selected for kinetic study are chlorine substituted, in one it is at ortho and in other it is at para position. We are mainly interested in studying the effect of position of chlorine atom on the rate of oxidation.

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