CHAPTER- I

INTRODUCTION

C H A P T E R - I

INTRODUCTION

The subject of chemical kinetics deals with the quantitative study of the rate of chemical reaction and the various factors upon which it depends, such studies may throw light on the general principles of reactivity or may be useful in arriving at a probable reaction mechanism. Chemical kinetics might very well be called chemical dynamics.

Kinetics is concerned fundamentally with the details of the process, where by a system gets transformed from one stage to another and with the time required for such transition. Equilibrium can also be treated in principle, on the basis of kinetics, as that situation in which the rates of the forward and reverse reactions are equal.

Reaction rate cannot be understood on the basis of thermodynamics alone. Therefore, chemical kinetics may be considered a more fundamental science than thermodynamics. Unfortunately, the complexities are such that the theory of chemical kinetics is difficult to apply with accuracy. Therefore, it is said that, 'a kinetic problem like a crime; calls for a proof beyond reasonable doubt and not a mathematical proof. As a result we find that the thermodynamics will tell with precision the extent of reaction; but only kinetics will tell perhaps crudely the rate of the reaction.

The science of chemical kinetics may be of interest itself; as for example; in determining how changes in environment change the rate of a given reaction; as in chemical engineering applications. However, of greatest interest to most chemists is the fact, that the kinetics provides the most general method of determining the mechanism of reaction. The reaction mechanism may be regarded as detailed and pictorial representation of the reaction scheme, and this information can be obtained from spectroscopic methods; such as NMR, ESR techniques; stereochemical methods; the isolation and characterization of intermediates; the use of isotopes etc. The relation between reaction scheme and reaction mechanism has expressed by R.S. Nyhohm[1] saying "Kinetics to mechanism equals facts to fiction".

To suggest the mechanism of given chemical process with the help of kinetic study; we should get additional information such as the products of reaction; stereochemical evidences; use of isotopes; detection of short-lived intermediates and refinement of kinetic methods. The determination of reaction rates by conventional methods reduces to a study of concentrations as a function of time. In general analytical procedures may be divided into two broad categories; chemical and physical. It is found that physical methods of analysis are usually much more convenient than chemical methods. Common among physical methods are pressure measurements in gaseous reactions, dilatometry, or measurement of volume changes, optical methods such as polarimetry, refractometry, colorimetry and spectrophotometry, electrical methods such as conductometry, potentiometry,

polarography and mass spectrometry. Thereotically any property which changes sufficiently could be used to follow the course of a reaction As an example of spectrophotometric kinetic study, the results of Andrews[2] on the alcoholysis of cinnamylchloride are of interest.

$$C_6H_5 - CH = CH - CH_2 - Cl + C_2H_5OH \longrightarrow$$

$$C_6H_5 - \underset{\underset{OC_2H_5}{|}}{CH} - CH = CHCl + HCl$$
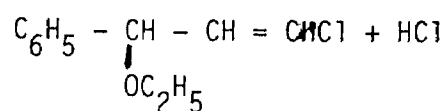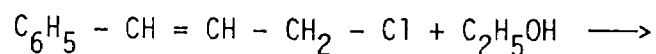
The cinnamyl chloride, having a double bond conjugated with the benzene ring, absorbs strongly, at 2600 A°; where as the product (1 - Chloro - 3 - phenyl - 1 - propene) being unconjugated does not absorb until 2100 A°. Accordingly a measurement of the optical density at 2600 A° as a function of time permits the rate of the reaction to be measured.

Any kinetic investigation generally comprised of two parts : first to establish the relationship between the rate of the reaction and various factors such as concentration of reactants; temperature and hydrostatic pressure, To these may be added some other factors such as primary and secondary salt effects; dielectric constant of the medium and catalysis. Identification of products of a reaction and detection of free radicals, intermediates etc., are also done. Second part of the investigation is to arrive at a suitable mechanism which can account for the results obtained on velocity measurements.

1.1 OXIDATION PROCESS AND OXIDISING AGENTS :

Kinetic study carried in liquid phase reactions is the greatest in volume, because these reactions are of keen interest to the organic and inorganic chemists. In the realm of organic reactions in solution, oxidation reactions are perhaps the most important. Oxidising agents such as nitric acid, chromic acid, permangenates, cerric sulphate, potassium persulphate, potassium periodate, potassium bromate, lead tetraacetate, thallium, Ti $(CH_3C6O)_3$, Cr(VI) oxide, peroxydisulphate, Mn(II) pyrophosphate, Mn(III) acetate Mn(III) sulphate, vanadium Hexacyanoferrate, Chloramine-T, Broma-mine-T etc., have been widely applied to study the oxidation of organic compounds.

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

Oxidation process is essentially a transfer of electrons from reductant to oxidant and by considering number of electrons trans-ferred 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. tetravalent vanadium, trivalent manganese, trivalent iron Fe(III) etc.

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

The important and ideal 1-electron oxidant is Fe(III). The use of Fe(III) as oxidant is comparatively more recent. Hence it is proposed here to take brief review of the work done on oxidation of organic compounds by Fe(III).

1.2 HEXACYANOFERRATE(III) AS AN OXIDANT :

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

Many of the reagents mentioned above have been discussed and reviewed in literature. However, no extensive summary is available on potassium ferricyanide as an oxidising agent in Organic Chemistry.

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

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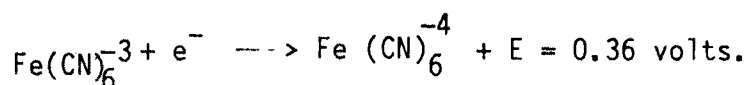
It is an example of oxidising agent in which one electron transfer is involved. Therefore, it acts as an one electron abstractor.

1.3.1 Oxidation of Olefins :

Moyell, Jospals[6] 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 glycols. The rate constants of an olefin $-$ Os^{8+} intermediate decomposition products are studied by visible spectroscopy.

1.3.2 Oxidation of Aromatic Hydrocarbons :

The kinetics and mechanism of hydrocarbon oxidation have been extensively studied by Noyes and Moses[7]. They have reported the oxidation of toluene, xylene and their derivatives to the corresponding benzoic acids.

Bhattacharjee and Mahanti[8] investigated the oxidation of xylenes by acid hexacyanoferrate(III) yielding aldehyde as a major product. The reaction was shown to be first order with respect to substrate, oxidant and acid, the radical intermediate was detected by ESR spectroscopy.

Oxidation of p-nitrotoluene and 2,4-dinitro toluene by hexacyanoferrate(III) have been reported by Radhakrishnamurti and co-workers[9]. The reaction was found to be first order in oxidant, substrate and alkali each.

The kinetics and oxidation of nitro toluenes[10] by acidic hexacyanoferrate was shown to yield the aldehyde as major oxidation product. The rate determining step is abstraction of hydrogen atom forming benzylic radical intermediate. Kasim and coworkers[11] have reported the oxidation of β -hydroxy, thiobenzoyl, p-methoxy styrene

in neutral and weak alkaline medium. Kinetics and mechanism of oxida-
tive cleavage of styrene[12] by acidic hexacyanoferrate ion was exten-
sively studied. The order with respect to oxidant, substrate and acid was
found to be one *in* each. The rate determining step involved cationic
intermediate, with subsequent cleavage of C-C bond yielding Ph-CHO
and HCHO respectively.

The osmium tetroxide catalysed and uncatalysed oxidation of
benzoin and its derivatives[13] in alkaline medium was investigated
spectro-photometrically. The rate was found to be decreased with
decrease in dielectric constant of medium. The total order was found
to be second, first order w.r.t. $[OH^-]$ and [Benzoin] but zero order
with $[Fe(CN)_6]^{3-}$.

Mahapatra and Khandual[14] reported the oxidation of chalcones
using OsO_4 catalyst in alkaline hexacyanoferrate(III), and the rate
was found to be first order in [Chalcone], [Os(VIII)] and [OH] each
but it was found to be independent of $[Fe(CN)_6^{-3}]$. The kinetics of
oxidation of Fluorene[15] has also been reported.

1.3.3 Oxidation of Alcohols :

The kinetics of oxidation of alcohols by alkaline hexacyano-
ferrate(III) has been widely studied.

Singh and Pande[16] were the first to report that oxidation of
methanol, ethanol and 2-butanol catalysed by OsO_4 in alkaline hexa-
cyanoferrate(III) proceeds via the formation of activated complex
between alcohol and osmium tetroxide.

Rhodium(III) catalysed oxidation of Methanol[17], 2-propanol and 2-butanol[18] was studied by Singh and his coworkers and found that disproportionation of complex between catalyst and oxidant. On the contrary Ru(III) catalysed oxidation of Methyl, Ethyl, Isopropyl and n-butylalcohol[19], Cyclopentanol[20] and Benzyl alcohol[21] and Cyclic alcohols[22], by alkaline hexacyanoferrate(III) were extensively studied. Generally order with respect to oxidant was found to be one.

Ru(III) catalysed oxidation of amino alcohols[23] was studied spectrophotometrically and showed rapid initial reaction. The second order rate dependance found to be first order in both [Amino alc.] and [OH⁻]. Radhakrishnamurti and Sahu[24] studied the oxidation of aliphatic alcohols and diols catalysed by Ru(III). The oxidation of substituted alcohols such as 2-methyl propane-1-01, 3-methyl butane-1-ol, 4 methylpentane-2-ol, butane-2-ol[25] have been carried out recently.

Oxidation of n-Hexanol[26], Glycerol[27] and methyl and Ethyl-digol[28] were reported in alkaline hexacyanoferrate(III) in presence of OsO_4 catalyst.

Dwivedi and coworkers[29] investigated the oxidation by analogus catalyst of Ethane 1:2 diol and propane 1:3 diol in alkaline medium at constant ionic strength. The order with respect to Ruthenate ion was first and w.r.t. hexacyanoferrate(III) it was zero. The rate was found to increase with substrate concentration.

Oxidation of butane 1:4 diol and pentane 1:5 diol[30] catalysed by Ru(III) in alkaline hexacyanoferrate(III) was reported. The uncatalysed oxidation of propane 1:2 diol and butane 2:3 diol[31] by hexacyanoferrate(III) in alkaline medium was found to be first order w.r.t. both [OH⁻] and [substrate] in lower concentration region, but tend to zero order at higher concentration.

The kinetics and oxidation of 2-diethyl-amino-ethane thiol HCl[32] was investigated. The stoichiometry was found to be 1:1. The substrate was oxidised to disulphide. The order was found to be one both in hexacyanoferrate(III) and thiol HCl.

Krishnamurty and coworkers[33] studied the oxidation of hydroxyl ion by applied voltage potential of 0.45.

1.3.4 Oxidation of Phenols :

Radhakrishnamurti and coworkers[34] studied the oxidation of phenol and substituted phenols in 20%, ethanol at constant ionic strength by hexacyanoferrate(III). The product of oxidation was dienone which undergoes rearrangement by two electron transfer from substrate.

The oxidative coupling of phenols by hexacyanoferrate(III) and oxidation of Resorcinol[35,36], Guaiacol[37] and Pyrogallol[38] in alkaline medium were reported. The rate determining step involved radical intermediate, detected by ESR-spectroscopy. The first order rate constants with substrate, oxidant and alkali were reported.

The oxidation product p-benzoquinone was obtained from quinol[39]. The slow step of reaction involves benzo-semiquinone radical.

Kinetics and mechanism of oxidation of catechol[40], Pinacol and Pinacol hydrate[41] were studied in alkaline hexacyanoferrate(III), the product was found to be -o-quinone. The kinetic rate law was given as

$$k_{abs} = k^1 \; [\; Catechol \;] \; [\; OH^- \;]^2$$

with excess substrate. Semiquinone radical intermediate was reported in the rate determining step.

Singh and coworkers[42] investigated the OsO_4 catalysed oxidation of sorbitol and manitol by hexacyanoferrate(III) in alkaline medium and reported that the first order kinetics at lower OH^- concentration tends to zero order at higher OH^- concentration.

The Ru(III) catalysed oxidation of Dulcitol and xylitol[43] has been extensively studied.

Oxidation by acidic hexacyanoferrate(III) of the phenol has been reported by Makromol[44] and Lukashevich and Sergeyeva[45]. The reaction is extensively used in the rubber synthesis. The oxidation of 4,-tert-butyl-thio-phenol and 2-methyl-4-tert-butyl-thiophenol[46] was shown to involve 1:1 molar ratio of oxidant to substrate.

1.3.5 <u>Oxidation of Glycols</u> :

Kinetics of oxidation of D-glucose and D-fructose[47] by alkaline hexacyanoferrate(III) have been reported. It was found that rate was independent of oxidant concentration but was directly propor tional to sugar and ammonia concentrations. The rate was found to decrease with increase in salt concentration.

Shrivastava and coworkers[48] have investigated the oxidation of D-glucose and galactose by hexacyanoferrate(III). The order found with respect to oxidant was zero and that with respect to [Sugars] and [OH⁻] was first.

The base catalysed oxidation of disaccharides[49,50] by hexacyanoferrate(III) has been studied extensively. The oxidation was found to follow the order Melibiose > Maltose > Cellibiose > Lactose. The kinetics of the reaction was found to be zero order with respect to oxidant and first-order w.r.t. reducing sugar. The alkaline hexacyanoferrate(III) oxidation of borate sugar complexes[51] was reported by Sambert Jones.

1.3.6 Oxidation of Aldehydes and Ketones :

Singh and coworkers[52] studied the first order kinetics each in [hexacyanoferrate(III)], [aldehyde] and [alkali] by alkaline hexacyanoferrate(III). The oxidation of formaldehyde and catalysed oxidation by Ru(III) and Os(VIII) of aromatic aldehydes[53,54] have shown that Hammett plot is linear with ρ + 2.0, which has suggested an ionic pathway involving rate-determining deprotonation. Here the order with respect to [catalyst], [OH⁻] to be one in each and zero order w.r.t. [oxidant].

Kinetics and oxidation of cyclopentanone, hexanone, heptanone and octanone[55] in ethanol-water and pyridine-water by hexacyanoferrate(III) were investigated at constant ionic strength. The reaction was found first order in [substrate], [oxidant] and [alkali] The plot of log k vs pH was linear. Radhakrishnamurti and Devishukla[56]

investigated the role of dimethyl sulfoxide in the oxidation of ketone and found that addition of DMSO upto 0.1447 mole fraction retards the reaction, but when mole ratio of DMSO was increased the ketone oxidation was accelerated. Irridum(III) catalysed oxidation of propane-2-one[57] was undertaken and the rate of formation of activated complex between substrate and Ir(III) was reported.

1.3.7 Oxidation of Thiols :

Oxidation of thiourea and thioacetamide by alkaline hexacyano ferrate(III) was reported by Agarwal and Mushran[58], the rate was found to be first order in urea, hexacyanoferrate(III) and OH^- concen tration. In the second compound the rate was found to be zero order in hexacyanoferrate(III) and first order each in thioacetamide and OH^-. The effect of salt and dielectric constant on the rate of reaction was studied.

Kasim Ahmad[59] has reported the outer sphere mechanism of oxidation of dithiozone with acidic hexacyanoferrate(III) at pH<2.5.

Oxidation of Indole derivatives by alkaline hexacyanoferrate (III) has been reported by Harley and Manson[60].

The kinetics and oxidation of piperidine[61] and quaternary salt of pyridine[62] showed that the rate determining step of substrate with oxidant involved the formation of complex intermediate with transfer of one electron.

1.3.8 Oxidation of Carboxylic acids and Esters :

Some important kinetic studies of organic acids include the OsO_4 catalysed oxidation of glycollic[63],benzylphenyl glycollic[64], glyoxylic and pyruvic[65] acids by hexacyanoferrate(III), while those of uncatalysed oxidation by hexacyanoferrate(III) include thiosalicylic acid[66] in acidic medium, transcinnamic, crotonic[67] and thioglycollic[68] acids. Some of these were reported to be first order in organic substrate and zero, 0.5 and 1.5 order in oxidant.

The oxidation of β-phenyl pyruvic acid[69] both catalysed and uncatalysed by alkaline hexacyanoferrate(III) was studied spectrophotometrically.

Soni and Menghani[70] investigated the Os(VIII) catalysed oxidation of Maleate ion. Maleate and fumarate ions[71] and found that the reaction rate was proportional to [Maleate ion], [OH^-] and [Os(VIII)] but independent of [$Fe(CN)_6^{3-}$].

Kinetics of 2 electron transfer in the rate determining step has been reported by Singh and coworkers[72] in alkaline hexacyanoferrate(III) oxidation of tartarate ion.

Kumar and Makthur[73] worked on OsO_4 catalysed oxidation of cinnamate ion by iodometric method. They investigated that the rate of the reaction increases with increase in OH^- concentration upto 0.008 M, beyond which the rate decreases.

Oxidation of derivatives of propionic acid[74] catalysed by Os(VIII) in alkaline hexacyanoferrate(III) was shown to proceed

through activated complex. Kinetics of first order in catalyst at low OH^- concentration and zero at higher concentration were reported.

The uncatalysed oxidation of levulinic[75], thiomalic acids[76,77] in alkaline medium was investigated colorimetrically. Stoichiometry was shown to be 1:1 and the salt effect was also studied.

The kinetics and oxidation of diethylene triamine penta-acetic acid[78] by alkaline-hexacyano ferrate(III) has been extensively investigated spectrophotometrically at 410 nm and found the first order dependence each in oxidant, substrate and pH. Transfer of electron from $Fe(CN)_6^{3-}$ to substrate followed by decomposition is shown.

The Cu(II)-catalysed oxidation of tartaric[79], citric[80] and hydroxy propionic acids[81] by hexacyanoferrate(III) have been found to be generally first order in Cu(II) and substrate but addition of salt increases the reaction rate. Singh and Tikoo[82] studied Ru(III) catalysed oxidation of glycolate, lactate and mandolate ions and reported approximate zero order in hexacyanoferrate(III) and first order in [Ru(III)]. The rate was found to decrease with increase in OH^- concentration. They showed that at low substrate concentration the first order rate became zero order at higher concentration.

1.3.9 Oxidation of Amino Acids :

Recently some generalizations have been drawn about mechanistic aspects by Upadhyay and coworkers[83] of Os(VIII) catalysed oxidation of glycine, leucine, phenyl alanine, DL-alanine and DL-

valine by hexacyanoferrate(III). The reaction was found to be first order in both amino acid and catalyst. Formation of ferrocyanide-amino acid complex as an intermediate has been reported and the product ferrocyanide ions were found to accelerate the rate of oxidation strongly.

Analogous oxidation of valine, alanine and phenyl alanine[84] was studied. The rates were independent of [ferricyanide] and the order was found unity in [amino acid] and [Os(VIII)].

The Os(VIII) catalysed oxidation of amino acids[85] by alkaline hexacyanoferrate(III) was investigated. The product of oxidation was aldehyde. The reaction was found to proceed with formation of a transient amino acid complex with $[OsO_4(OH)_2]$. The kinetics and oxidation of leucine, glutamic, glutamine and aspartic acids[86] have also been studied extensively.

Acharya and coworkers[87] have reported the oxidation of amino acids catalysed by OsO_4 and found that the primary rate determining step was dependent on active oxidising species.

The uncatalysed oxidation of glycine[88], valine[89] and methionine[90] by alkaline hexacyanoferrate(III) have been studied. Generally the rate was found to be first order in oxidant, substrate and alkali. The radical intermediate mechanism was proposed. The oxidation of N-methyl morpholine[91] by alkaline hexacyanoferrate(III) has also been investigated.

ı.4.0 Oxidation of Amines :

Aliphatic amines such at N-methyl and N-N-dimethyl, tertiary amines[92] were easily oxidized by alkaline hexacyanoferrate(III) at room temperature. Stoichiometry of oxidant to amine was found 2:1. The kinetic study indicates the rate law -

$$-d\frac{[Fe(CN)_6]^{-3}}{dt} = k_2[amine]\ [Fe(CN)_6^{-3}]$$

The mechanism accounting for an irreversible electron abstraction from the nitrogen lone pair is the rate determining step. The oxidation shows overall second order kinetics.

Dasgupta et.al[93] recently carried out oxidation of methyl and dimethyl amines in alkaline hexacyanoferrate(III). The reaction was found to be first order each in oxidant and amine but zero order in alkali in the range studied.

The Ru(II) catalysed oxidation of $EtNH_2$, $BuNH_2$ and $MeCH_2NH_2$[94] was investigated spectrophotometrically. The order was found to be one each in substrate, oxidant and catalyst.

Os(VIII) catalysed oxidation of methylamine by hexacyanoferrate(III) in alkaline medium has been reported by Upadhyay and coworkers[95] and found first order rate each in $MeNH_2$, OH^-, catalyst and oxidant concentration. Analogous scheme of oxidation results were observed for n-butylamine[96] catalysed by Cu(II) ions, positive salt effect was reported.

Kinetics and oxidation of substituted amines like trimethyl amine[97] and N-N-dimethyl phenethylamine[98] with alkaline hexacyano-

ferrate(III) have been studied and reported that tertiary amines having electron withdrawing effect of the substituents reduce the ease of oxidation. The rate was found to be first order in substrate and oxidant.

Shukla and coworkers[99,100] have undertaken the study of kintics and oxidation of diethanol and triethanol amines. The first order rate kinetics was observed in amine, oxidant and OH^- concentration. Increase in dielectric constant enhances the rate of reaction. The plot of log of rate constant vs 1/D was shown to be linear.

Uncatalysed and Ru(II) catalysed oxidation of benzyl amine[101,102] by alkaline hexacyanoferrate(III) were investigated and found that, order with respect to substrate and oxidant was one in each and zero in alkali concentration, but in catalysed oxidation the rate was zero with respect to oxidant and first order at lower concentration of substrate, Ru(II) and alkali. Free radical mechanism was proposed.

Dasgupta and coworkers[103] have studied the oxidation of anilines at constant ionic strength by hexacyanoferrate(III). The products of N-alkyl side chain were characterized as PhNR'CHO (R'=Me, H) was reported.

Kinetics and mechanism of oxidation of diphenyl amine[104] by hexacyanoferrate(III) has been studied, the orange coloured product formed was found to change into green in alkaline medium. This is used to establish the mechanism of the formation of diphenyl benzidine orange.

The rates of oxidation of unsubstituted and substituted diphenyl amines[105] were reported to be first order in [substrate] and [oxidant] but independent of alkali. The pH dependance rate controlling step of oxidation of p-amino phenol[106] with aqueous hexacyanoferrate(III) has been studied.

Oxidation of N,N-dialkyl hydroxyl amine with alkaline hexacyanoferrate(III) yielded N-alkyl ketoxime[107].

1.4.1 Oxidation of Hydrazines :

Kinetics and oxidation of hydrazines and unsymmetrical dimethyl hydrazine[108,] were studied potentiometrically by alkaline hexacyanoferrate(III). The complexity of results in hydrazine indicates that oxidation does not proceed a purely by one electron transfer but multiple inflexions invariably obtained in the curve supports the hypothesis of polyhydronitrogen formation.

Kolthoff and coworkers[109] have studied oxidation of hydrazine in absence of oxygen at pH 6-13. First order kinetics was found in hydrazine and hexacyanoferrate(III).

Oxidation of hydrazine[110] by hexacyanoferrate(III) in water-methanol mixture was investigated in the pH range of pH 9.90-11.45. The reaction was found to be first order with respect to hydrazine, oxidant but zero order with respect to OH^- concentration. Increase in methanol concentration retarded the rate , specific ion effect was observed by addition of salt.

Kinetics and oxidation of phenyl hydrazine and phenyl hydrazine sulfonic acid by hexacyanoferrate(III) were studied by Verwey and coworkers[111]. Similarly the substituted phenyl hydrazines such as 2,4,-dinitrophenyl hydrazine and p-tolyl-hydrazine[112] were also studied extensively. The reaction was found to be dependent on hydrogen ion concentration.

Oxidation of benzoyl hydrazine by hexacyanoferrate(III) in presence of 1:10-phenonthroline was investigated spectrophotometrically by Frank and Krishnarao[113]. The reaction was found to be first order in [oxidant]. A mixed ligand complex between Fe(III), substrate and 1:10 phenonthrolins was postulated to explain the graph of 1/ki vs 1/[sub.].

Oxidation of nicotinoyl and iso-nicotinoyl hydrazines[114] was studied at pH 7.8. The rate was found to increase with pH and the rate was second order in [hexacyanoferrate(III)]. Evidence for complexation of iso-nicotinoyl hydrazine with both $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ were reported.

1.4.2 Oxidation of Hydrazides :

Kalb and Gross[115] have studied extensively the oxidation of aromatic acid hydrazides and found that most of the acid hydrazides gave the aldehyde as product as per the reactions.

$$2\ RCONHNH_2 + [O] \rightarrow RCH = N-NHCOR + N_2 + H_2O$$

$$RCONHNH_2 + [O] \rightarrow RCON = NHRCHO + N_2$$
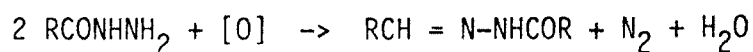
Two moles of oxidant are not completely used up by hydrazide in the oxidation.

The kinetics of oxidation of hydrazides has been studied recently and it is reported that di-imides or free radicals were intermediates. The oxidation of hydrazides by lead tetra-acetate[116] leads to the formation of corresponding acids and nitrogen.

The oxidation of phenyl hydrazides[117] by MnO_2 has been studied through a preliminary oxidation of the hydrazide to azo compounds.

The kinetics of oxidation of hydrazides by iodine in aqueous hydrochloric acid has been studied by Krishna Rao and Kodanda[118] and found that at high concentration of iodine, the reaction was first order with respect to both oxidant and substrate. Kinetics of oxidation of phenyl acetyl hydrazide[119] by Vanadium(V) in aqueous perchloric acid has been studied. The reaction was found to be first order each in [oxidant] and [substrate]. The oxidation of salicylic acid hydrazide and substituted salicylic acid hydrazide by active MnO_2 was studied by Haskar et. al[120].

Hogale and Jagdale investigated the kinetics of Ag^+ catalysed oxidation by peroxydisulphate ion, of picolinic, nicotinic and iso-nicotinic acid hydrazides[121], phenyl acetic acid hydrazide[122] and benzhydrazides[123]. They found that the reaction was first order in $S_2O_8^{-2}$ and zero order in hydrazide .

The kinetics of oxidation of nicotinoyl and isonicotinoyl hydrazides by iron(III)[124] in presence of 1:10 phenanthroline 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. Patil and Patil[125] reported the kinetics of oxidation of acetic, propionic, n-butyric, iso-butyric, n-valeric and iso-valeric acid hydrazides by peroxydisulphate ion. The order with respect to oxidant was found to be one, increase in $S_2O_8^{2-}$ concentration resulted in the decrease of specific rate in the oxidation reaction.

The oxidation of n-valeric and iso-valeric acid hydrazides[126] has been studied by Chloramine-T. It was found that the order with respect to [hydrazide] and [oxidant] is one in each and independent of sodium hydroxide concentration. The products of oxidation were identified as bishydrazides and nitrogen.

Ag-catalysed oxidation of n-caproic and n-heptanoic acid hydrazides[127] was studied and the rate was found to be first order in [$S_2O_8^{2-}$], zero order with respect to [substrate], and directly proportional to the concentration of silver nitrate.

The chemistry of hydrazides is very important and interesting branch of organic chemistry due to the fact that many hydrazides are found to have physiological activities. They have been extensively studied. Since the discovery of "iso-nicotinic acid hydrazide" as a strong anti-tuberculostatic agent[128]. Many derivatives of this compound have been synthesised and tested for anti-bacterial activity[129-130]. Diacyl hydrazine group in certain derivatives of hydrazides has been supposed to be biologically active[131]. Carboxylic acid 1,2 diaryl hydrazides have been reported to possess anti-inflamatory

properties[132]. Isoxazole carboxylic acid hydrazide[133] is active against leprosy and phenothiazine carboxylic acid hydrazide[134] has been reported to have anti-convulsive action. Dihydrazides have recently been introduced as anti-thelminties[135] maleic acid hydrazide is used to regulate and inhibit the growth of the plants[136]. Apart from the physiological activity of hydrazides, some of them are important starting materials and intermediates in the synthesis of certain amines, aldehydes and heterocyclic compounds.

Hydrazides and their derivatives[137] are used in heat and corrosive stabilisation of cellulose. They are also used as anti-oxidants for polyolefines and polyurethanes, which are oxidised in presence of copper.

An incorporation of hydrazides[138] has improved the applicability in plastics and cable insulations. The small amount of hydrazide is useful in sensitising electrophotographic layers made up of polyvinyl carbazole[139]. Dihydrazides can be used in cigarette filters for the selective removal of aldehydes from tobacco smoke.

The hydrazides are the derivatives of carboxylic acids and hydrazine. The preferred nomenclature is to describe any hydrazide as carboxylic acid hydrazide. This nomenclature is also used in chemical abstract. The nitrogen atoms of the hydrazides are designated as 1 and 2 or and or N and N'. The first nitrogen for each pair denotes the nitrogen, where the acyl group is inserted[140]. The structure of isonicotinic acid hydrazide has been determined by X-ray crystallography[141].
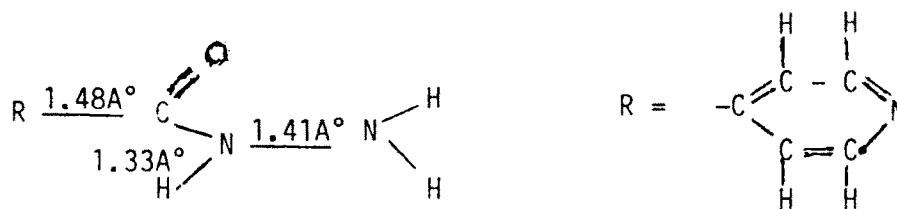
$$\alpha \ = \ 101°$$
$$\beta \ = \ 98°$$
$$\gamma \ = \ 109°$$

The N-N bond length is always between 1.39 and 1.42 A°, which is shorter than that in hydrazine, which is between 1.46 and 1.47 A°. This is due to the formal charge effect and the electron attracting acyl group, which reduces the repulsion between the lone pair of electrons on nitrogen atoms. The C-N bond length is 1.33 A°, this bond, therefore, must acquire roughly 50% double bond character. The two nitrogen atoms are in the same plane.

The hydrazide group is stabilized due to the resonance between amide form (I) to the tautomeric enol form (II) by the shift of a hydrogen atom from nitrogen to the oxygen.

(I)   (II)
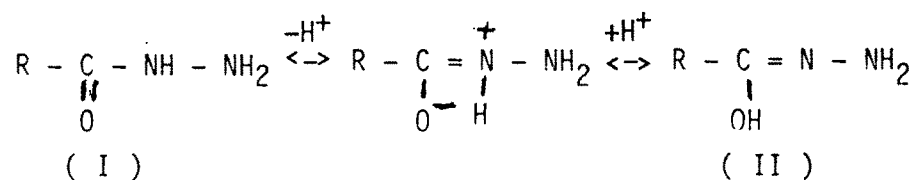
Due to resonance stabilization of hydrazide group, its basicity is decreased. In addition to this, the electron attracting phenyl group lowers the basicity of hydrazides and the compound assumes an acidic character.

The spectra recorded for hydrazides in solution are different as regards the position and number of absorption bands. U.V. absorption spectra of hydrazides have not been investigated extensively but they are expected to resemble those of amides.

1.4.3   Present Study and its Object   :

The above discussion and the literature survey indicate that the kinetics of oxidation of aromatic acid hydrazides by variety of oxidants have been studied extensively but that of aliphatic acid hydrazides seems to have received much little attention. It is clear that very little information regarding mechanism of oxidation of hydrazides by Hexacyanoferrate(III) ion is available. Hence study of the kinetics and oxidation of aliphatic acid hydrazides by alkaline hexacyanoferrate(III) has been undertaken. The hydrazides selected for kinetic study are n-butyric and iso-butyric acid hydrazides. They are structural isomers, so that the effect of branching on reaction rate and on the mechanism of the reaction can be established.

The two aliphatic acid hydrazides selected for the kinetic study are :

1) $CH_3 - CH_2 \, CH_2 \, CO -NH \, NH_2$

(n-butyric acid hydrazide)

2) $CH_3 - CH - CO - NH - NH_2$

CH_3

(iso-butyric acid hydrazide)

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