

CHAPTER I

CHAPTER-I

INTRODUCTION

Chemical Kinetics deals with the quantitative study of rate of chemical reaction and the various factors on which it depends. Such study may also throw light on general principles of reactivity or may be useful in arriving at a probable reaction mechanism. Chemical kinetics may also be called as chemical dynamics.

All details of the process in which a system gets transformed from one stage to another are obtained by the study of kinetics, viz. time required for such transition, the situation of equilibrium where the rate of forward and reverse reactions are equal.

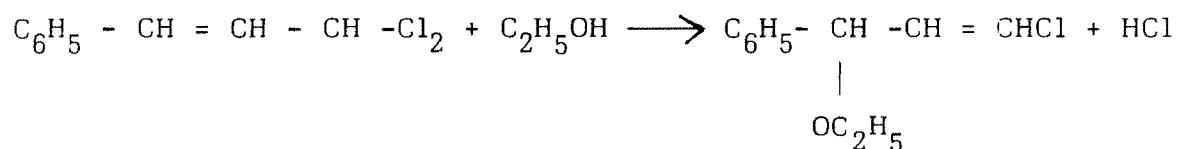
In order to understand the rate of reaction which is impossible only by thermodynamics. Therefore chemical kinetics may be considered as more fundamental science than thermodynamics. Unfortunately, the complexities are such that the theory of chemical kinetics is difficult to apply with accuracy. It is said that, 'a kinetic problem is like a crime; calls for a proof beyond reasonable doubt and not a mathematical proof. So thermodynamics will give, with precision, the extent of reaction, but only kinetics will give the rate of reaction.

Chemical kinetics, which is the branch of science may be of great interest itself as for example; one may be called upon to determine how the rate of reaction changes when environmental conditions undergo change. As an chemical engineering applications;

however, of great interest to most of the chemist because kinetics provides most general and reliable method to determine the mechanism of reaction. The reaction mechanism may be regarded as detailed representation of the reaction scheme in going from reactant to product. All the necessary informations are obtained from spectroscopic methods; such as NMR, ESR techniques, stereochemical methods, the isolation and characterisation of intermediate and the use of isotopes etc. R.S.Nyholm¹ has expressed the relation between reaction scheme and reaction mechanism by saying "Kinetics to mechanism equals facts to fiction."

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 a reaction. Generally, physical methods of analysis are much more convenient 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 kinetic

study, the results of Andrews² on the alcoholysis of cinnamyl chloride



The cinnamyl chloride, having a double bond conjugated with the benzene ring, absorbs strongly at 2600 Å°, where as the product (1-chloro-3-ethoxy-3 Phenyl-1-Propene) being unconjugated does not absorb until 2100 Å°. Accordingly, a measurement of the optical density at 2600 Å° 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 constant of the medium and catalysis. Identification of the product of reaction and detection of free radicals, intermediates 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 and hence, kinetic study carried in liquid phase reactions is in the greatest volume. Oxidation reactions are the most important in organic reactions especially in solution.

Oxidising agents such as nitric acid, chromic acid, potassium bromate, permanganates, potassium persulfate,⁵ potassium periodate, lead tetra acetate, ceric sulphate, thallium, $\text{Ti}(\text{CH}_3\text{COO})_3$, Cr(VI) oxide, peroxydisulphate, Mn(II) pyrophosphate,, Mn(III) acetate, Mn(III) sulphate, vanadium, Hexacyanoferrate, Chloramine-T, Bromanine-T, etc., have been applied 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 ^{ie} in a manner, 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 oxidants³ 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 dichromate,⁴ etc.

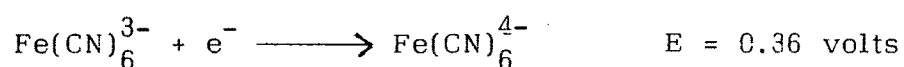
The Fe(III) is important 1-electron oxidant. Recently Fe(III) is widely used in comparison with other oxidants. Hence it is proposed here to take brief review of the work done on oxidation of organic compounds by Fe(III).

HEXACYANOFERRATE (III) AS AN OXIDANT :

Although $K_3 Fe(CN)_6$ is an ideal 1-electron oxidant, because its use in oxidation was somewhat neglected as an oxidising agent. Selenium oxide, aluminium alkoxide, lead tetra-acetate, osmium tetroxide, tert-butyl chromate, chromium trioxide, pyridine complex, organic per acids, periodic acid, peroxytrifluoro 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 ceric sulphate, ammoniacal silver nitrate and Febling's solution in all of which the oxidising species is a complex electron abstracting ion.



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 Jospals⁵ 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.

OXIDATION OF HYDROCARBONS :

Oxidation of p-nitrotoluene, 2,4-dinitrotoluene and methoxytoluene by hexacyanoferrate(III) has been reported by Radhakrishnamurti and co-workers⁶. The reaction was found to be first order in oxidant, substrate and alkali.

The kinetics and mechanism of hydrocarbon oxidation have been extensively studied by Noyes and Moses.⁷

The oxidation of xylenes by acid hexacyanoferrate(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 derivatives⁹ 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. [OH] and [Benzoin] but zero order with $\text{Fe}(\text{CN})_6^{3-}$.

The oxidation of chalcones by using osmium tetroxide as a catalyst in alkaline medium has been investigated¹⁰ and the rate was found to be first order in [chalcone], [OS(VIII)] and [OH] each; but it was found to be independent of $[\text{Fe}(\text{CN})_6^{3-}]$. The kinetics of oxidation of fluorene¹¹ has also been reported.

The kasim and co-workers¹² have reported the oxidation of β -hydroxy, thiobenzoyl, P-methoxy styrene in neutral and alkaline

medium. Kinetics and mechanism of oxidative cleavage of styrene¹³ by acetic hexacyanoferrate 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.

Singh and Pande¹⁴ were the first to report that oxidation of methanol, ethanol and 2-butanol catalysed by OsO_4 in alkaline hexacyanoferrate(III) proceeds via the formation of activated complex between alcohol and OsO_4 . The kinetic oxidation of methanol and ethanol by hexacyanoferrate(III) in alkaline medium in the presence of osmium tetroxide as catalyst was also studied by Krishna, B.et.al.¹⁵ It has been observed that the reaction rate is unimolecular both w.r.t.alcohol as well as hydroxyl ion and dependent of the ferricyanide ion concentration.

Rhodium (III) catalysed oxidation of methanol¹⁶ 2-propanol and 2-butanol¹⁷ was studied by Singh and his co-workers and found that disproportion of complex between catalyst and oxidant. On the contrary, Ru(III) catalysed oxidation of Methyl, Ethyl, Isopropyl and n-butyl alcohols¹⁸ cyclopentanol¹⁹ and benzyl alcohol²¹ and cyclic alcohols²² by alkaline hexacyanoferrate(III) were extensively studied. Generally order w.r.t.oxidant was found to be one.

Ruthenium (III) chloride catalysed oxidation of propanol-1, butanol-1, propanol-2 and butanol-2 by hexacyanoferrate(III) in sodium carbonate medium is reported²⁰. Rate of the reaction is directly proportional to [alcohol] and [OH] in low concentration regions. The rate is found to be zero order in hexacyanoferrate (III).

Ru(III) catalysed oxidation of amino alcohols²¹ was studied spectrophotometrically and showed rapid initial reaction. The second order rate dependence found to be first order in both [Amino alcohols] and [OH]. Radhakrishnamurti and Shahu²² 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-1-01, 4-Methyl pentane-2-01, butane-2-01²³ have been carried out recently.

The kinetic oxidation study of Pd(II) catalysed oxidation of allyl alcohol,²⁴ osmium catalysed oxidation of methanol, ethanol and 2-butanol,²⁵ ruthenium(III) catalysed oxidation of methyl digol and ethyl digol,²⁶ benzyl alcohol,²⁷ dulcitol²⁸ by alkaline hexacyanoferrate(III) have been reported.

Oxidation of n-Hexanol,²⁹ Glycerol³⁰ were reported in alkaline hexacyanoferrate(III) in presence of OsO₄ catalyst. The oxidation of ethane 1:2 diol and propane 1:3 diol by analogous catalyst in alkaline medium at constant ionic strength were reported by Dwivedi and co-workers.³¹ The order w.r.t Ruthenate ion was first and w.r.t. hexacyanoferrate(III) it was zero. The rate was

found to be increased with increase in substrate concentration.

Oxidation of butane 1:4 diol and pentane 1:5 diol³² catalysed by Ru(III) in alkaline hexacyanoferrate(III) was reported. The uncatalysed oxidation of propane 1:2 diol and butane 2:3 diol³³ by hexacyanoferrate(III) in alkaline medium was found to be first order w.r.t. both $[\text{OH}^-]$ and $[\text{substrate}]$ in lower concentration region but tends to zero order at higher concentration.

Kinetics of Ru(III) catalysed oxidation of unsaturated alcohol,³⁴ cyclic alcohols,³⁵ amino alcohols³⁶ Rh(III) catalysed oxidation of methanol¹⁶ Os(VIII) catalysed oxidation of 2-ethoxy ethanol,³⁷ the low molecular weight alcohols³⁸ by alkaline hexacyanoferrate have been listed in the chemical literature.

OXIDATION OF PHENOLS :

Radhakrishnamurti and co-workers³⁹ studied the oxidation of phenol and substituted phenols in 20% ethanol at constant ionic strength by hexacyanoferrate(III). The major product of the oxidation is dienone, the mechanism involving a two-electron transfer from the substrate is suggested.

The oxidation of resorcinol,^{40,41} guaiacol⁴² and pyrogallol⁴³ 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 quinol⁴⁴. The slow step of reaction involves benzo-semiquinone radical.

Oxidation by acidic hexacyanoferrate(III) of the phenol has been reported by Makromol,⁴⁵ Lukashevich and sergeyeva.⁴⁶ The reaction is extensively used in the rubber synthesis. The oxidation of 4-tert-butyl-thio-phenol and 2-Methyl-4-tert-butyl-thio-phenol⁴⁷ was shown to involve 1:1 molar ratio of oxidant to substrate. The oxidation products are corresponding disulfides. The mechanism of the reaction involves the generation of the thioalkyl radical. The dielectric constant decreases the rate. Kinetics and Mechanism of oxidation of catechol.⁴⁸ Phenols, resorcinol⁴⁹ Pinacol and pinacol hydrate⁵⁰ in alkaline hexacyanoferrate involving radical intermediate have been described.

The Ru(III) catalysed oxidation of Dulcitol and Xylitol⁵¹ has been extensively studied.

The Singh and co-workers⁵² investigated the OsO₄ catalysed oxidation of sorbitol and manitol by hexacyanoferrate(III).

OXIDATION OF GLYCOLS :

Kinetics of oxidation of D-glucose and D-fructose⁵³ by alkaline hexacyanoferrate(III) have 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 decreases with decrease in salt concentration.

Shrivastava and co-workers⁵⁴ investigated the oxidation of D-glucose and galactose by hexacyanoferrate(III). The order found w.r.t.oxidant was zero and that w.r.t. (sugars) and $[\bar{\text{O}}\text{H}]$ was first.

The base catalysed oxidation of disaccharides^{55,56} 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 w.r.t. oxidant and first order w.r.t. reducing sugar. The alkaline hexacyanoferrate(III) oxidation of borate sugar complexes⁵⁷ was reported by Sambert Jones.

OXIDATION OF ALDEHYDES AND KETONES :

The kinetics of the reaction between formaldehyde and hexacyanoferrate(III) has been reported.⁵⁸ The data showed that the reaction is rapid initially, then follow first order rate w.r.t. hexacyanoferrate(III) formaldehyde and hydroxide ions.

The role of dimethyl sulfoxide in the oxidation of ketones by alkaline hexacyanoferrate(III) has been mentioned.⁵⁹ The rate of oxidation of substituted acetophenones (R=H, Me, Br) was regarded progressively by the addition of 0-144 mole fraction of dimethyl sulfoxide, but at mole fraction of dimethyl sulfoxide 0-144, the ketone oxidation was accelerated. The decrease in the rate was compatible with solvent effect with ion-ion reaction. While the acceleration of the rate was due to anion desolvation and transition state stabilization by large solvation shell of Me_2SO_4 .

A thorough UV kinetic study of oxidation of 2,3,4-trihydroxy benzophenone⁶⁰ to form 2,6-dihydroxy anthone has been mentioned in the chemical literature. The results were explained on the basis of a radical aromatic substitution reaction.

Radhakrishnamurti et.al⁶¹ reported the oxidation kinetics of cyclic ketones such as cyclopentanone, cyclohexanone, cycloheptanone, and cyclooctanone in ethanol-water and pyridine-water solvent systems. Cyclohexanone reacts faster than the other ketones, which is attributed to higher enol content of cyclohexanone. The solvent effect indicates the ion-ion reaction.

Ru(III) catalysed oxidation of substituted aromatic aldehydes⁶² has been studied. A Hammett's plot is linear with $p = +1.41$. The rate determining step involves the decomposition of complex between Ru(III) and hydrated aldehyde similarly, Os(VIII) catalysed oxidation kinetics of substituted benzaldehydes⁶³ by alkaline hexacyanoferrate(III) gave a linear Hammett's plot with $p = +2.0$ indicating ion pathway involving rate determining deprotonation has been shown. Iridium(III) catalysed oxidation of propan-2-one⁶⁴ indicated the formation of the complex between the substrate and iridium (III). This complex gives another complex which slowly decomposes into products, through the intermediate species.

OXIDATION OF THIOLS :

Oxidation of thiourea and thioacetamide by alkaline hexacyanoferrate(III) was reported by Agarwal and Mushran⁶⁵ the

rate was found to be first order in urea, hexacyanoferrate(III) and OH concentration. In the second compound the rate was found to be zero order in hexacyanoferrate(III) and first order each in thioacetamide and $\bar{\text{O}}\text{H}$. The effect of salt and dielectric constant on the rate of reaction was studied.

The outer sphere mechanism of oxidation of dithiozone with acidic hexacyanoferrate(III) at $\text{PH} < 2.5$ was reported by Kasim Ahamad.⁶⁶ Harley and Manson⁶⁷ reported the oxidation of Indole derivatives by alkaline hexacyanoferrate(III).

The kinetics and oxidation of piperidine and quarternary salt of pyridine⁶⁵ showed that the rate determining step of substrate with oxidant involved the formation of complex intermediate with transfer of one electron.

OXIDATION OF CARBOXYLIC ACIDS AND ESTERS :

Some important kinetic studies of organic acids include the OsO_4 catalysed oxidation of glycollic,⁶⁸ benzylphenyl glycollic,⁶⁹ glyoxylic and pyruvic⁷⁰ acids by hexacyanoferrate(III). While those of uncatalysed oxidation by hexacyanoferrate(III) includes thiosalicylic acid⁷¹ in acidic medium transcinnamic, crotonic⁷² and thioglycollic⁷³ 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 B-Phenyl pyruvic acid⁷⁴ both catalysed and uncatalysed by alkaline hexacyanoferrate(III) was studied spectrophotometrically.

The oxidation of Maleate ion catalysed by Os(VIII) investigated by Soni and Menghani.⁷⁵ The reaction rate in case of Maleate and fumarate ions⁷⁶ was proportional to [Maleate ion], [OH] and [Os(VIII)] but independent of $[\text{Fe}(\text{CN})_6^{3-}]$.

Kinetics of 2 electron transfer in the rate determining step has been reported by Singh and co-workers⁷⁷ in alkaline hexacyanoferrate(III) oxidation of tartarate ion.

Kumar and Mathur⁷⁸ 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 acid⁷⁹ 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 kinetics and oxidation of diethylene triamine penta acetic acid⁸⁰ by alkaline-hexacyanoferrate(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 $\text{Fe}(\text{CN})_6^{3-}$ to substrate followed by decomposition is shown.

The Cu(II)-catalysed oxidation of tartaric,⁸¹ citric⁸² and hydroxy propionic acids⁸³ by hexacyanoferrate(III) have been

found to be generally first order in Cu(II) and substrate but addition of salt increases the reaction rate. The investigation⁸⁴ of Ru(II) catalysed oxidation of glycolate, lactate and mandolate ions and reported approximate zero order in hexacyanoferrate(III) and first order in $[\text{Ru(III)}]$. 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.

The uncatalysed oxidation of levulinic,⁸⁵ thiomalic acids^{86,87} in alkaline medium was investigated colorimetrically. Stoichiometry was shown to be 1:1 and the salt effect was also studied.

OXIDATION OF AMINO ACIDS :

The oxidation of α -amino acids such as Leucine, glycine⁸⁸ DL-alanine, alanine, DL-valine⁸⁹ by hexacyanoferrate(III). The reaction was found to be first order in both amino acids 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. The reaction between diethylene triamine penta-acetic acid and hexacyanoferrate(III) was investigated spectrophotometrically.⁹⁰

The oxidation of α -amino acids such as Leucine, glutamic acid, glutamine and aspartic acid in the presence of Os(VIII) by alkaline hexacyanoferrate(III) has been carried out in excess of ferrocyanide. At low amino acid concentration, the reaction is first order in amino acid and zero order in Fe(CN)_6^{3-} whereas at large amino acid concentration, the reaction is independent of amino acid concentration.

The oxidation of some amino acids^{91,92} by excess of ferrocyanide using Os(VIII) as a catalyst is investigated by upadhyay et.al. The same 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.

The kinetics of Os(VIII) catalysed oxidation of B-Phenyl-Pyruvic acid⁷⁴, propionic acid⁷⁹, α -hydroxy-propionic acid catalysed by Cu(II) involving Cu(II) complex.⁸² Ru(III) catalysed oxidation of α -hydroxy carboxylate⁸³ ions involving an intermediate complex between Ru(III) and substrate were studied.

The oxidation of thioglycolic⁷³ acid by acid hexacyanoferrate(III) gave dithiodiglycolic acid. Evidence for the formation of a radical intermediate in solution was not obtained by E.S.R. spectroscopy owing to the degeneracy of π -orbitals and the large value for substrate.

Osmium(III) catalysed ferricyanide oxidation of glycine, DL-alanine, DL-valine, Phenyl alanine isoleucine, lysine and glutamic acid⁹³ indicated that amino acids were degraded through intermediate keto acids. The interaction between the conjugate base of the amino acids and the oxidising species of Os(VIII) form a transient complex in the primary rate determining step.

Copper (II) catalysed oxidation of tartaric acid⁸⁰ Os(VIII) catalysed oxidation of crotonic acid⁹⁴, cinnamate ions⁷⁸ thiomatic acid,⁸⁷ levulinic acid⁸⁰ by hexacyanoferrate(III) have been

described in the literature.

The kinetic study of Ru(III) catalysed oxidation of lactic acid & acrylic acid,⁹⁵ L-ascorbic acid,⁹⁶ Ru(VI) catalysed oxidation of sodium salt of lactic, tartaric & glycolic acids,⁹⁷ Os(VIII) catalysed oxidation of bromopropionic acid⁹⁸ & benzyl phenyl glycolic acid⁹⁹ by hexacyanoferrate(III) have been made & the results were explained with a suitable mechanism.

The oxidation of trans-cinnamic & transcrotonic acids⁷² by hexacyanoferrate in perchloric acid showed that the primary reaction is direct attack of protonated hexacyanoferrate(III) at the double bond by electron transfer with the formation of cationic intermediates, which was supported by an inverse secondary kinetic isotopic effect $K_D/K_H = 1.2$ & 'P' value is -0.4. The cationic intermediates reacts with H_2O to give a hydroxylic compound, which is rapidly oxidised by hexacyanoferrate (III) in successive stages until the stable product is formed. Phenyl conjugation accelerates the rate of oxidation.

Mahanti et.al.have carried out extensive work in the field of oxidation kinetics by hexacyanoferrate (III) such as oxidation of amino acids like methionine,¹⁰⁰ valine⁷³ have explained their results on the basis of the radical mechanism. The oxidation of N-methyl morpholine¹⁰¹ by alkaline hexacyanoferrate(III) has also been investigated.

OXIDATION OF AMINES :

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

$$\frac{-d [\text{Fe}(\text{CN})_6]^{3-}}{dt} = K_2 [\text{amine}] [\text{Fe}(\text{CN})_6]^{3-}$$

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.

Kinetics and oxidation of substituted amines like trimethyl amine¹⁰³ and N-N-dimethyl phenethylamine¹⁰⁴ with alkaline hexacyanoferrate(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.

A very complex kinetic study of oxidation of n-butylamine¹⁰⁵ catalysed by Cu(II) and oxidation of aliphatic primary amines¹⁰⁶ catalysed by Os(VIII) have been described.

The reaction involving the conversion of hydroxylamine into N-substituted oximes by ferricyanide are not fully explored.¹⁰⁷ The oxidation of N:N dialkyl hydroxyl amines with alkaline ferricyanide gives excellent yields of the corresponding N-alkyl ketoxime. The oxidation of NH_2OH by ferricyanide was efficiently catalysed by Fe(III) complex with EDTA.

Dasgupta et.al¹⁰² 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 kinetics of oxidation of triethanolamine¹⁰⁴ trimethyl



amine¹⁰⁸ by hexacyanoferrate(III) in alkaline medium showed first order dependence in substrate, reagent and alkali concentration each. The reaction mechanism involving 'H' abstraction to form a radical with 9-9 line ESR spectrum has been proposed in the oxidation of trimethylamine.

Oxidation kinetics of tertiary amines¹⁰⁹ has been described to study the effect of the structure on the reactivity of alkyl amines towards hexacyanoferrate(III). The relative rate of the reaction k_H/k_D for Bu_2 , NMe and Bu_2NCD_3 was 1.04 confirmed that the rate determining step is an electron transfer from nitrogen to hexacyanoferrate(III). The kinetic result showed that the formation of the intermediate aminium radical cation rather than the substrate. The ease of oxidation increased from bridge head bicyclic amines triethylene diamine, monomethiodide, quiniclidine and triethylene diamine have been mentioned.

The kinetics of oxidation of secondary amines¹¹⁰ like diethanol amine by alkaline hexacyanoferrate(III) involved the formation of an intermediate amino anion. The reaction of substituted and unsubstituted diphenyl amines¹¹¹ in aqueous ethanol showed the first order kinetics each in [substrate] and [oxidant] and are independent of [alkali]. The Hammett's plot yielded $\rho = -1.0$. The mechanism involving the formation of diphenyl aminyl radicals which were characterised by ESR spectroscopy has been described. Recently, Muralikrishna¹¹² et.al carried out the oxidation of diphenyl amine by hexacyanoferrate(III) and the orange coloured

product formed was identified by diphenylbenzidine. The direct oxidation of tertiary amines with alkaline ferricyanide furnished the corresponding product, pyridine-dl-aspartenine gives dl-oxyaspartenine on 35 percent yield and β -isoaspartenine to oxo- β -iso-aspartenine in 25 percent yields.^{113,114}

The Ru(II) catalysed oxidation of $F\text{-NH}_2$, BuNH_2 , and MeCH_2NH_2 ¹¹⁵ was investigated spectrophotometrically. The order was found to be one each in substrate, oxidant and catalyst.

OXIDATION OF AMIDES :

The oxidation of thiourea and thio acetamide¹¹⁶ and diphenyl thiocarbazon¹¹⁷ with alkaline hexacyanoferrate(III) in aqueous solution were studied. The mechanism of the reaction proceeding by an outer sphere mechanism involving the reaction of the thiol and thiolate form, has been proposed.

OXIDATION OF HYDRAZINES :

Kinetics and oxidation of phenyl hydrazine and phenyl hydrazine sulfonic acid by hexacyanoferrate(III) were studied by verwey and co-workers¹¹⁸ similarly the substituted phenyl hydrazines such as 2,4 dinitrophenyl hydrazine and p-tolyl-hydrazine were also studied extensively. The reaction rate was found to be dependent on $[\text{H}^+]$ ion concentration.

Mechan et.al.¹¹⁹ studied the reaction between hexacyanoferrate(III) and 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. The pH dependence of the rate indicated that the rate determining step is an irreversible one; electron transfer between hexacyanoferrate(III) and the neutral hydrazine molecule. Some effects indicated that the rate determining step is not completely understood. -

Kinetics and oxidation of hydrazines and unsymmetrical dimethyl hydrazine¹²⁰ were studied potentiometrically by alkaline hexacyanoferrate(III). The observation is that reaction does not proceed purely by one electron transfer but by multiple inflexions invariably obtained.

Oxidation of aroyl hydrazine like isonicotinoyl and nicotinoyl by hexacyanoferrate(III) studied at PH 7-8 spectrophotometrically. The evidence for the complexation of isonicotinoyl hydrazine with both $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ has been given by Krishna Rao et.al.¹²¹

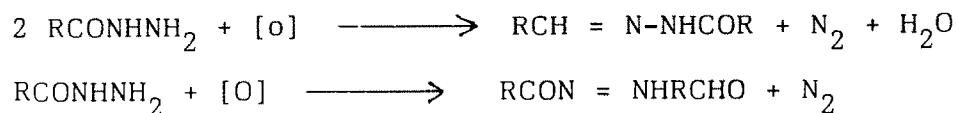
Oxidation of hydrazine¹¹⁸ by hexacyanoferrate(III) in water methanol mixture was investigated in the pH range of 9.90 - 11.45. The reaction is first order w.r.t. hydrazines, oxidant but zero order with respect to $\overline{\text{OH}}$ concentration. Increase in methanol concentration retarded the rate, specific ion effect was observed by addition of salt.

Oxidation of benzoyl hydrazine by hexacyanoferrate(III) in presence of 1:10 phenonthroline was investigated spectrophoto-

metrically by Frank and Krishnarao¹²¹. 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 $1/K$ vs $1/[\text{sub}]$.

OXIDATION OF HYDRAZIDES :

Kalb and Gross¹²² have studied extensively the oxidation of aromatic acid hydrazides and found that the most of the acid hydrazides gave the aldehyde as product as per the reaction.



Two moles of oxidant are not completely used by hydrazide in the oxidation.

The kinetics of oxidation of hydrazide has been recently studied and it is reported that di-imides or free radical were intermediates. The oxidation of hydrazide by lead tetra acetate¹²³ leads to the formation of corresponding acid and nitrogen. The oxidation of Phenyl hydrazides¹²⁴ by MnO_2 has been studied through a preliminary oxidation of the hydrazides to azo compounds.

Krishna Rao and Kodanda¹²⁵ investigated the kinetics of oxidation of hydrazides by iodine in aqueous hydrochloric acid and 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 hydrazide¹²⁶ 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.¹²⁷

The oxidation of iso-valeric acid, n-valeric, iso-butyric, propionic, acetic, n-butyric acid, hydrazides by peroxydisulphate ion is reported by Patil and Patil.¹²⁸ The order w.r.t. oxidant was found to be one, increase in $\text{S}_2\text{O}_8^{2-}$ concentration resulted in the decrease in specific rate in the oxidation reaction. The kinetics of oxidation of series of arylhydrazides. X-Ph-Co-NHNH_2 ($\text{X} = \text{H}, \text{P} - \text{Cl}, \text{P} - \text{CH}_3$ and $\text{P} - \text{NO}_2$) by alkaline hexacyanoferrate (III) have been investigated.¹²⁹ The order of the reaction was one.

The kinetics of Ag^+ -catalysed oxidation of picolinic, nicotinic and iso-nicotinic acid hydrazides¹³⁰ phenyl acetic hydrazide¹³¹ and benzhydrazides¹³² was carried out. It was found that the reaction was first order in $\text{S}_2\text{O}_8^{2-}$ and zero order in hydrazide. Ag^+ catalysed oxidation of n-caproic and n-heptanoic acid hydrazides¹³³ was studied. The order of the reaction was one in $[\text{S}_2\text{O}_8^{2-}]$. Zero w.r.t. [substrate] and directly proportional to the concentration of silver nitrate.

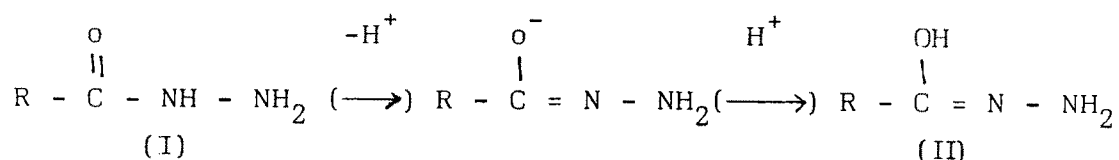
The investigation of kinetics of oxidation of nicotinoyl and iso-nicotinoyl hydrazides by Iron(III)¹³⁴ in the presence of 1:10 phenanthroline has been investigated. The oxidation reaction

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.

The hydrazides are the derivatives of carboxylic acids and hydrazine. The preferred nomenclature is to describe any hydrazide as carboxylic acid hydrazide.

The nitrogen atoms of hydrazide are designated as 1 and 2 or α and β or N and N's the first number of each pair denotes the nitrogen where the acyl group is inserted.¹³⁵ The structure of hydrazide is determined by modern techniques of structure determination and x-ray studies.¹³⁶ I.R. spectra of hydrazide showed an amide band at 1610-1620 cm^{-1} due to the carbonyl group. A weak band at 1610-1620 cm^{-1} is attributed to NH deformation¹³⁷ UV spectrum resembles to those of amides.¹³⁸

The hydrazide group can change from its resonance stabilized amide form(I) to the tautomeric enol form(II) by the shift of a hydrogen from nitrogen to oxygen.



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 oxidation of n-valeric and iso-valeric acid hydrazides¹³⁹ has been studied by chloramine-T. The order w.r.t. [hydrazide] and [oxidant] is one in each and independent of sodium hydroxide concentration. The products of oxidation were identified as bi-s-hydrazides and nitrogen.

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 "isonicotinic acid hydrazide" as a strong antituberculostatic agent.¹⁴⁹ Many derivatives of this compounds have been synthesised and tested for anti-bacterial activity.^{141,142} Diacyl hydrazine group in certain derivatives of hydrazides has been supposed to be biologically active.¹⁴³ Carboxylic acid 1.2 diary hydrazides have been reported to possess anti-inflammatory properties.¹⁴⁴ Isoxazole carboxylic acid hydrazide¹⁴⁵ is active against leprosy and phenothiazine carboxylic acid hydrazide¹⁴⁶ has been reported to have anti-convulsive action. Dihydrazides have been recently introduced as anti-thelmintics.¹⁴⁷ Maleic acid hydrazide is used to regulate and inhibit the growth of the plants.¹⁴⁸ Other than the physiological activity of hydrazides, some of them are important starting materials and intermediates in the synthesis of certain amines, aldehydes and heterocyclic compounds.

The hydrazides and their derivatives¹⁴⁹ 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.

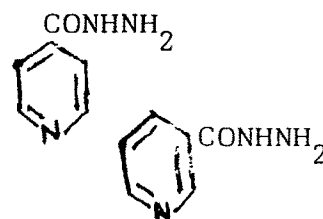
An incorporation of hydrazides¹⁵⁰ has improved the applicability in plastics and cable insulations. The small amount of hydrazide is useful in sensitising electrographic layers made up of polyvinyl carbazole¹⁵¹ - Dinydrazides can be used in cigarette filters for the selective removal of aldehydes from tobacco smoke.

PRESENT STUDY AND IT'S OBJECT :

The above discussion and literature survey indicate that the kinetics of oxidation of aliphatic as well as aromatic acid hydrazides by variety of oxidants has been studied. It is clear that little information regarding the mechanism of oxidation of hydrazides by hexacyanoferrate(III) ion is available. Therefore, the study of kinetics and oxidation of heterocyclic acid hydrazides by alkaline hexacyanoferrate(III) has been undertaken. The hydrazides selected for the kinetic study are

A) iso-Nicotinic acid hydrazide

B) Nicotinic acid hydrazide



We are much more interested in finding out the effect of position of hydrazide group w.r.t. cyclic nitrogen on the rate of oxidation of these hydrazides.

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