KINETICS AND MECHANISM OF Hg[II] PROMOTED, ACID CATALYZED AND LIGAND INDUCED DISSOCIATION OF PENTACYANO *P*-NITROSOPHENOL AND PENTACYANO *P*-NITROSO-N,N'-DIMETHYLANILINE FERRATE[II].

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Kinetics and Mechanism of Hg[II] Promoted, Acid Catalyzed and Ligand Induced Dissociation of Pentacyano p-nitrosophenol and Pentacyano p-nitroso-N,N'-dimethylaniline ferrate[II].

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To my parents

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LIST OF ABBREVIATIONS USED

PNA = P-nitroso-N-N'-dimethylaniline

PNP = P-nitrosophenol

Py = pyridine

bipy = 2,2'-bipyridyl

phen = 1,10-phenanthroline

Nitroso-R-salt, NRS = sodium 2-hydroxy-1-nitrosonaphtalene-3, 6-disulphonat

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Abstract

KINETICS AND MECHANISM OF Hg(II) PROMOTED ACID CATALYZED AND LIGAND INDUCED DISSOCIATION OF PENTACYANO P-NITROSOPHENOL AND PENTACYANO P-NITROSO-N,N'-DIMETHYLANILINE FERRATE(II)

BY

MESFIN JANKA

Research Advisor: Dr. Saroja Raman

The kinetics of dissociation of pentacyano para-nitrosophenol and 4-nitroso N,N'-dimethyl aniline ferrate(II) complexes was studied under three different conditions: i) substitution of PNP and PNA with excess pyridine, ii) acid catalysed substitution of PNP and PNA and iii) Hg(II) promoted aquation of the nitroso complexes.

The rates of dissociation of $Fe[CN]_5PNA^{3-}$ and $Fe[CN]_5PNP^{3-}$ increased with the concentration of pyridine and reached limiting values at pyridine concentrations > 0.5 M. The pseudo first order rate constants varied as

$$k_{ob} = \frac{k_1 k_2 [py]}{k_{-1}[L] + k_2 [py]}$$

where k_1 is the dissociation rate constant of the complexes, and k_{-1} and k_2 are the association rate constants of $Fe[CN]_5^{3-}$ with L and py, respectively.

The enthalpy and entropy of activation are $\Delta H^{\#}$ = 95 ± 4 kJ mol^{-1}, $\Delta S^{\#}$ = 22 ± 7 J mol^{-1} K^{-1} for $Fe[CN]_5PNA^{3-}$ and $\Delta H^{\#}$ = 92 ± 3 kJ mol^{-1}, $\Delta S^{\#}$ = 14 ± 4 J mol^{-1} K^{-1} for $Fe[CN]_5PNP^{3-}$. The rate

pattern and entropy of activation are diagnostic of a limiting D-mechanism for dissociation.

The dissociation of $Fe[CN]_5PNA^{3-}$ and $Fe[CN]_5PNP^{3-}$ was catalysed by acids. $Fe[CN]_5PNA^{3-}$ was protonated at the ligand with $pK_{a1} = 4.1 \pm 0.05$. Second stage protonation occurred at the CN^- with estimated pK_{a2} of 1 ± 0.5. The enthalpy and entropy of activation for the dissociation of the monoprotonated complex was $\Delta H^{\#} = 113 \pm 2$ kJ mol^{-1} and $\Delta S^{\#} = 65 \pm 5$ J mol^{-1} K^{-1}, respectively. The dissociation of the diprotonated form $[Fe[CN]_5PNAH_2]^-$ was very much faster with $\Delta H^{\#} = 86 \pm 2$ kJ mol^{-1} and $\Delta S^{\#} = 22 \pm 4$ J mol^{-1} K^{-1}.

$Fe[CN]_5PNP^{3-}$ underwent protonation only at CN^- group with $pK_a = 1.6 \pm 0.3$. The rate of dissociation reached a limiting value. $\Delta H^{\#}$ and $\Delta S^{\#}$ were 91 ± 3 kJ mol^{-1} and 10 ± 5 J mol^{-1} K^{-1}, respectively.

The proton catalysed dissociation is thus through the formation of the protonated complexes in both cases. Positive $\Delta S^{\#}$ values are indicative of a dissociative mechanism.

$Fe[CN]_5PNA^{3-}$ and $Fe[CN]_5PNP^{3-}$ were completely aquated to give Fe^{2+} aquo ions, by the Hg(II) promoted abstraction of the CN^-. The rates reached limiting values at ($[HgCl_2]/[Complex]$) > 10. Intermediate formation of strong adducts between $Fe[CN]_5PNA/PNP^{3-}$ and Hg(II) of the composition of 1:2 was confirmed from spectral characteristics. The adducts dissociated to give Fe^{2+}(aquo) through abstraction of CN^- by Hg(II),

$$Fe[CN]_5PNA/PNP^{3-} + 2Hg(II) \overset{K}{\rightleftharpoons} Hg_2Fe[CN]_5PNA/PNP \xrightarrow{k_1} Fe^{2+} + 2HgCN_2 + PNP/PNA + CN^-.$$

The $\Delta H^{\#}$ and $\Delta S^{\#}$ for the $Fe[CN]_5PNA^{3-}$ and $Fe[CN]_5PNP^{3-}$ are

104 ± 3 kJ mol^{-1} 71 ± 6 J mol^{-1} K^{-1} and 86 ± 1 kJ mol^{-1} 16 ± 3 J mol^{-1} K^{-1}, respectively.

Hg(II) promoted abstraction of CN^- in acidic medium, indicated much weaker equilibrium for adduct formation in the case of $Fe[CN]_5PNP^{3-}$. The rates were linear with $[HgCl_2]$ and $K_{ob} = k_1k_e$. With $Fe[CN]_5PNA^{3-}$ the competition of Hg(II) was higher and the rates reached limiting value, even in 0.1 M acid.

Chapter 1

INTRODUCTION

Substitution reactions of metal complexes are reactions where ligand-metal bonds are broken and new ones are formed in their stead without change in their oxidation state. A general form of substitution reaction can be written as

$$ML_5L' + L'' \longrightarrow ML_5L'' + L'$$

These may be termed S_N (nucleophilic substitution) and S_E (electrophilic substitution) reactions, analogous to the terminology proposed by Huges and Ingold for describing organic reactions [1]. A nucleophilic reagent is one which donates electrons to an atomic nucleus in a reaction. An electrophilic reagent is one which acquires electrons from a nucleophilic reagent.

Generally, nucleophilic substitution reactions are classified into four specific types: Solvent exchange reaction, complex formation reaction, ligand exchange reaction, and acid-base catalyzed reaction.

To the above can be added a special type of ligand substitution reaction promoted by a metal ion. Most of the promoter ions are soft acids (class b) like Hg(II), Pd(II), and Ag(I) which are able to abstract soft ligands (class b) like CN^-, SCN^-, S^{2-} *etc*. The abstracted ligand can be replaced by incoming ligand, including water. The reaction can be written

as

$$M'L_5L' + L'' \xrightarrow{M''} M'L_5L'' + M''L'$$

These have found extensive analytical application in recent years for the trace determination of the promoter ions.

The mechanism of substitution reaction of metal complexes has been extensively studied in the last three decades, mostly with kinetics as the diagnostic tool. Some firm patterns have emerged as a result of these. Dissociation of the ligand to form an intermediate of one less coordination prior to attachment of incoming ligand, and association of the incoming ligand long before the dissociating ligand has broken away, are the two leading mechanisms that have been postulated. The former is called a D or Dissociative mechanism and the latter an A or Associative mechanism [2]. Intermediate cases of Dissociation, Id, and Associative, Ia, mechanisms have been postulated in some cases.

Among the most thoroughly studied systems are those involving $Co(NH_3)_5X^{2+}$. The kinetic data for the aquation of the complex with X (≡ Br^-, NO_3^-, NSC^-, NO_2^-) favour essentially limiting dissociative mechanism [3]. The halopentamines of Cr(III) undergo aquation with rate decreases along the sequence $I^- > Br^- > Cl^- >> NCS^-$. The rates are about ten times those of the analogous $Co(NH_3)_5X^{2+}$ and it is inferred that limiting associative mechanism holds for Cr(III) complexes [4].

One of the criteria for the D or A mechanism is the difference in ligand field stabilization energy of the parent complex and that of the intermediate. If the ligands have large ligand field stabilization energies and are also capable of π bonding with the metal ion, there is a favourable chance

for the formation of pentacoordinated intermediate species and a limiting D mechanism can occur. In this context, the low spin ion complexes of the type $Fe[CN]_5L$, where L is an aromatic nitrogen donor or sulphur donor ligand, are important, because they satisfy the above criteria.

$Fe[CN]_5L$ expresses interesting spectral and kinetic properties. While the CN^- is kinetically inert, L can be generally substituted by other ligands, and have been the subject of several studies. $Fe[CN]_5L$ types of complexes are further important because they offer a specific site for ligand substitution. Several biologically important compounds have been used to substitute L.

When L is an aromatic nitroso ligand, further interesting features are added on. For example, there are additional intense bands in the visible spectrum which makes possible easy characterization and quantification of the complex. There have been very few examples of the use of these complexes, both in mechanistic or analytical applications. Many of them have been with reference to the catalytic replacement of CN^- from hexacyanoferrate by aromatic nitroso ligands.

In view of the scarcity of attention that has been given to $Fe[CN]_5$Aromatic nitroso complexes, this study was planned to investigate the kinetics and mechanism of dissociation of $Fe[CN]_5PNP^{3-}$ and $Fe[CN]_5PNA^{3-}$ complexes under three conditions:

1. Exchange of PNA and PNP by Pyridine
2. Acid catalyzed dissociation
3. Hg(II) promoted aquation of the complexes, through abstraction of the CN^- ligands under neutral and acidic conditions.

The specific objectives of this investigation are:

1. To prepare PNP and PNA complexes and characterize their uv-vis spectra.
2. To study the nature and kinetics of pyridine induced dissociation of these complexes.
3. To determine the rate of aquation of these complexes in neutral and acidic media in the presence of Hg(II).
4. To study the effect of acid on the rates of dissociation of the complexes.
5. To determine the enthalpy and entropy of activation for these reactions from the measurement of rates at different temperatures.
6. To interpret the mechanisms of the above processes from kinetic data and activation parameters.
7. To explain the differences in the rates and the activation parameters on the basis of the nature of the substituents.

Chapter 2

REVIEW OF LITERATURE

The review of literature is composed of two parts. The first part pertains to the general theoretical background required for the study of substitution reaction and the second part deals with the kinetics and mechanism of ligand substitution reactions of $Fe[CN]_5X$ complexes.

2.1. Mechanisms of Nucleophilic Substitution[5-12]

The basic classification of nucleophilic substitution is into dissociative and associative (a terminology proposed by Langford and Gray [2]) or unimolecular and bimolecular processes based on the molecularity of the rate determining step. These are S_N1 and S_N2 mechanisms derived from organic chemistry [1]. Substitution of inorganic complexes is less straight forward and often intermediate in nature and hence the broad terminology of D and A has been preferred.

The ligand substitution reactions of metal complexes in general can be written as

$$ML_5L' + L'' \longrightarrow ML_5L'' + L'$$

In dissociative mechanism the rate determining step is unimolecular and involves the loss of L′ to give a coordinated intermediate with one ligand less, which takes on a molecule of the ligand L′′ in a fast step to give the final product ML_5L'',

$$ML_5L' + \overset{\text{slow}}{\rightleftharpoons} + ML_5 \xrightarrow[\text{fast}]{+ L''} ML_5L'' \quad .$$

In associative mechanism the rate determining step is bimolecular and involves the formation of an intermediate $ML_5L'L''$ with one extra ligand, which dissociates in a fast step, to give ML_5L''.

$$ML_5L' + L'' \overset{\text{slow}}{\rightleftharpoons} ML_5LL'' \xrightarrow{\text{fast}} ML_5L'' + L'$$

Many inorganic chemists use a slightly more detailed classification and subdivide the range of possible mechanisms into the following four mechanisms.

2.1.1. D Mechanism (Limiting dissociative mechanism)

In this limiting dissociative mechanism a transient intermediate of reduced coordination number is generated. It persists long enough to be able to discriminate between potential nucleophiles in its vicinity. In particular it can choose between reacting with the added nucleophile or recombining with the group which has just been lost. The latter alternative gives, of course, no net reaction.

$$ML_6^{n+} \rightleftharpoons ML_5^{n+} + L \xrightarrow{L'} ML_5L'^{n+}$$

A characteristic, saturation kinetics curve is obtained for the limiting D-mechanism on the plot of the observed rate constant against concentration. A linear plot is obtained for reciprocal of the observed rate constant against the reciprocal of concentration. The limiting rate will be the same for all incoming nucleophiles, but the curvature at lower incoming nucleophile concentrations reflects the competition between

incoming and outgoing groups.

2.1.2 Id Mechanism (dissociative interchange mechanism)

Here, transition state formation involves considerable extension of the metal-to-leaving-group bond, but very little interaction between the metal ion and the incoming group in the transition state. Nonetheless this mechanism does involve outer-sphere association between the starting complex and the incoming nucleophile. Because of this the incoming group is suitably placed to enter the primary coordination sphere of the metal ion as soon as the out-going group has left.

$$ML_6^{n+} + L' \rightleftharpoons ML_6^{n+},L' \longrightarrow [L_5M\text{-}L,L']^{\#} \xrightarrow{\text{rate determining step}} ML_5L'^{n+} + L$$

The outer-sphere associated species ML_6^{n+}-L′ is simply an ion-pair if the complex and the incoming group have opposite charges. However, it is not necessary for the incoming group to be charged for this mechanism to operate. In particular, when solvolysis or solvent exchange reactions take place the incoming L′ in the associated species ML_6^{n+},L′ will be present in the secondary solvation shell of the complex ML_6^{n+} and so suitably situated for interchange.

2.1.3 Ia Mechanism (associative interchange mechanism)

Here, just as in Id mechanism, there is interchange of ligands between the primary and secondary coordination regions. However, this time there is significant interaction between the incoming group and the metal ion in the transition state.

In this case in general the rate of the reaction is very sensitive to the nature of the entering group.

2.1.4 A Mechanism (Limiting associative mechanism)

At this extreme, the main feature is the formation of an intermediate rather than a transition state of increased coordination number.

$$ML_6^{n+} + L' \xrightarrow{slow} ML_6L'^{n+} \rightarrow ML_5L' + L$$

2.2. Types of Nucleophilic Substitutions at Complexes

The substitution reactions at complexes have been subdivided into several categories for convenience.

2.2.1. Solvent exchange reaction

It is the exchange of solvent molecules between the primary solvation shell of a cation and 'bulk' solvent.

$$MS_6^{n+} + {}^*S \rightarrow MS_5{}^*S^{n+} + S$$

The reaction of solvent exchange is very simple. The reagent and the product are identical, as are the ligand and the solvent. Thus Gibbs free energy change for the reaction is zero.

Rates of solvent exchange at metal ions vary enormously with the nature of the cation. The range of observed first order rate constants for aqueous solutions at 25 °C, is from almost 10^{10} s^{-1} for Cu^{2+} or for Cr^{2+} right down to less than 10^{-7} s^{-1} for Rh^{3+}. The exchange rate for a given cation is strongly solvent dependent. Two experimental methods suited to the determination of rates of solvent exchange are isotopic labelling for slow exchange, and NMR for fast exchange.

2.2.2. Complex formation reaction

It is the formation of a metal complex from a solvated metal ion and a ligand,

$$MS_6^{n+} + L \longrightarrow MS_5L^{n+} + S.$$

The basic mechanism for the formation of complexes from aquo-cations is that developed by Eign, and Wilkins, as it is known as Eign-Wilkins mechanism for complex mechanism.

2.2.3. Ligand exchange reaction

This type of substitution reaction represents the replacement of one ligand by another,

$$ML_6^{n+} + L' \longrightarrow ML_5L'^{n+} + L.$$

If the entering ligand , L', is the solvent itself, it is called solvolysis (or aquation in aqueous media). The reverse process, if the leaving group is the solvent, it is known as the anation reaction.

2.2.4. Acid-base catalyzed reaction

This type of substitution reaction represents the replacement of one ligand by another effected by the presence of an acid or a base. There are two cases of acid-base catalysis, if the substitution reaction is catalyzed specifically by H^+ or OH^- then it is a specific catalysis and if the substitution reaction is effected by acids or bases other than H^+ or OH^+ it is called general catalysis.

2.2.5. Metal ion promoted ligand exchange reactions

Metal ion promopted type of substitution reactions are a special class of ligand substitution reactions, wherein a ligand from a kinetically inert complex is dislodged due to the catalytic action of another metal ion, making a room for another ligand to enter. These are based on the affinity of class 'b' metal ions (soft acids) like Hg(II), Ag(I), Au(I & III), Pd(II), Pt(II & Iv) to large polarizable ligands (soft bases) like Cl^-, Br^-, I^-, CNS^-, CN^-, S^{2-}. The latter, when coordinated to class 'a' metal ions like Co(III), Cr(III), Rh(II), Ru(II), Fe(II), *etc.*, can be catalytically substituted by water or other ligands in the presence of class 'b' metal ions.

A typical ligand substitution reaction promoted by a metal ion or any of its species can be written as

$$M_1X_nL_1 \; + \; M_2 \xrightarrow{L_2} M_1X_nL_2 \; + \; M_2L_1$$

where M_2 is the metal ion promoting or assisting the replacement of a ligand L_1 coordinated to another metal (M_1) as $M_1X_nL_1$. L_2 may be water in an aqueous solution or any other ligand present in solution. The main criterion for such a reaction is that there should be a high degree of compatibility between L_1, the ligand being substituted, and the metal ion M_2 promoting its substitution. In other words, L_1 and M_2 should both belong to the same class. Almost all the reactions studied in this group are such that both L_1 and M_2 belong to the class 'b' or 'soft' category of base and acid. The class 'b' character of both L_1 and M_2 affords flexible electronic yoverlapping because they are easily polarizable and

comparatively large in size, so that strong interaction between them is ensured. For convenient kinetic studies, the complex $M_1X_nL_1$ should be inert, such that products of substitutions are well defined.

2.3. Kinetics in the prediction of mechanisms of reactions

In recent years increasing attention has been devoted to detailed kinetic studies of ligand replacement reactions, with the objective of learning details of the mechanism by which such reactions take place. Although a lot remains to be done, considerable advance has been made in this area. The range of systems accessible to such study depends on the experimental techniques available. At present the techniques can be classified into three broad categories; reaction rates for which they are generally used are identified by their half lives:

1. Static methods ($t_{1/2}$ > 1 min.)
2. Flow or rapid mixing techniques (1 min. > $t_{1/2}$ > 10^{-3} s)
3. Relaxation methods ($t_{1/2}$ < 10^{-3} s)

The static methods are the classical ones in which reactants are mixed simply by pouring them both into vessel and the progress of the reaction is then followed by observation of the time variation of some physical or chemical observables (*e.g.*, light absorption at a fixed wavelength, (spectrophotometry) volume of the liquid phase (dilatometry), the angle of optical rotation, gas evolution, conductance of solution, pH *etc.*). Flow and rapid mixing techniques differ mainly in achieving rapid mixing (10^{-3} s) of the reactants, but use many of the same observational techniques as in static

measurements. Relaxation methods are relatively new and have enormously increased the field accessible to study. The latter methods are capable of following very fast reactions and in many cases, rate constants up to the limit ($\approx 10^{10}$ s^{-1}) set by diffusion processes, have been measured by ultrasonic methods.

The direct result of a kinetic study can at best be a rate law, that is an equation showing how the velocity, v, of a reaction at a given temperature and in a given medium, varies as a function of the concentration of the reactants. The rate of reaction is expressed as the rate of formation of any product or the rate of disappearance of any reactant. For example, for the hypothetical reaction

$$aA + bB \longrightarrow cC + dD$$

the rate is expressed as

$$\text{Rate} = (-1/a)(d[A])/(dt) = (-1/b)(d[B])/(dt) = (1/c)(d[C])/(dt) = (1/d)\ (d[D])/(dt)\ .$$

The ultimate purpose of a rate study is usually to interpret the rate law correctly so as to determine the actual mechanism of the reaction. By mechanism, we mean a specification of what species actually combine to produce the activated complex, and what steps occur before and after the formation of the activated complex.

2.3.1. Thermodynamic Activation Parameters

2.3.1.1. Enthalpy and Entropy of Activation

In addition to the rate law, the thermodynamic activation parameters like free energy ($\Delta G^{\#}$) , enthalpy ($\Delta H^{\#}$), and entropy ($\Delta S^{\#}$) of activation often provide valuable and diagnostic clues in ascertaining the mechanism of a reaction.

The enthalpy and entropy of activation are determined by studying the temperature dependence of the rate constant and using the absolute reaction rate theory or the transition state theory equation,

$$k = \frac{RT}{Nh} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

or

$$k = \frac{RT}{Nh} e^{\frac{-\Delta H^{\ddagger}}{RT}} \cdot e^{\frac{\Delta S^{\ddagger}}{R}}$$

$$\left.\frac{\partial \ln k}{\partial T}\right|_p = \frac{-\Delta H^{\ddagger}}{RT} .$$

$\Delta H^{\#}$ indicates the bonding strength in the transition state complex and $\Delta S^{\#}$ is the entropy of activation, and the general distinction is that associative mechanisms have negative activation entropies, dissociative positive. Both these parameters have been useful in drawing valid inferences about the activated complexes. They are specially suitable in deciding the mechanism when a series of similar reactions are considered.

2.3.1.2. Volume of Activation

The volume of activation has been gaining importance recently in predicting the nature of the activated complex and hence the mechanism of substitution of inorganic complexes.

The volume of activation is determined from the effect of pressure on the rate of reaction at constant temperature,

$$\left.\frac{\partial \ln k}{\partial p}\right|_T = \frac{-\Delta H^{\ddagger}}{RT} .$$

In general, a positive activation volume suggests a dissociative process, a negative activation volume an associative process.

2.4. Crystal Field Stabilization Energy (CFSE)

Adamson *et al.* reported the use of crystal field considerations in the assignment of reaction mechanisms [13]. In their approach, the change in the CFSE and interelectronic repulsion energy in the formation of the transition state have been considered as giving a fair estimate of the activation energy for the substitution reaction. The activation energies for the aquation reactions of a number of Co(III) and Cr(III) complexes have thus been calculated for reactions occurring through each of the four different possible intermediate structures, viz: square pyramid (C_{4v}), trigonal bipyramidal (D_{3h}), pentagonal bipyramidal (D_{5h}), and trapezoidal octahedron (C_{2v}). These are compared with the experimental values for the assignment of reaction mechanisms and also for inferring about the structures of the intermediates. It has been concluded from this that the aquation of several complexes of Cr(III)

occur through a pentagonal bipyramidal intermediate, while similar complexes of Co(III) possibly react through a square pyramidal intermediate.

2.5. Pentacyano Ferrate(II) Complexes

2.5.1 Preparation of $Fe[CN]_5L^{(3-n)-}$ Complexes

The first synthetic method was given by Hoffman. Then it was modified by Asperger *et al.* [17], which was actually based on working with complicated mixture obtained by reduction of $Fe[CN]_5NO^{2-}$(aq.) by hydroxamine in strongly basic solution. The modified Hoffman procedure which was given by Asperger again suffered from strong disadvantages because of its complexty and also because pure products of analytical grade suitable for accurate work could not be obtained.

The methods of Hoffman and Asperger were abandoned after a simple method of preparation was discovered by Toma and Malin [16, 14]. The preparation method which was obtained by Toma and Malin is based on the generation of $Fe[CN]_5H_2O^{3-}$ by aquation of solid $Na_3Fe[CN]_5NH_3$, followed by reacting with the required ligand to form a complex. In addition to its simplicity, fastness, where the release of NH_3 from $Fe[CN]_5NH_3^{3-}$ was found to be $1.75x10^{-2}$ s^{-1} [21], the complexes can be isolated as solids of analytical grade, from its solution using a precipitant. A standard procedure for preparation of sodium pentacyano amine ferrate (II) from nitroprusside was given by D. J. Kenney *et al.* [18, 35]. The easy preparation of $Fe[CN]_5L^{(3-n)-}$ initiated a diversified study on the kinetic and mechanism of $Fe[CN]_5L^{(3-n)-}$

2.5.2. Spectral Properties of Some $Fe[CN]_5X^{(3-n)-}$ Complexes

The maximum absorption band of the aquo pentacyano ferrate (II) in the visible region occurs at λ = 440 nm with ϵ = 650 $dm^3\ mol^{-1}\ cm^{-1}$. It was assigned to the d-d transition [14].

Toma and Malin [14] studied the properties of pentacyano ferrate(II) complexes of py, pyrazine, and related aromatic N hetrocycles. Each complex showed a strong absorption band in the visible region which they assigned to a metal-to-ligand electron transfer transition ($d\pi$-$p\pi$ back donation).

Toma *et al.* [27] assigned the visible absorption band of pentacyano ferrate(II) complexes of imidazole, glycinate, and l-histidine to the d-d transition from the $^1A_1$ ground state to the $^1E(1)$ excited states based on a comparison with the absorption spectra of many other pentacyano ferrates. The visible absorption spectrum of the glycinato-complex was found to be similar to those of the corresponding complexes of ammonia and methylamine, so the coordination of glycinato was assigned to be through the amine group.

McAuley and Macartney [34] studied the visible spectra of pentacyano ferrate(II) complexes of cysteine, glutathione, pencillamine and z-mercaptoethylamine at pH 5. The absorbance maximum of the complexes were found to be nearly identical to one another and were similar in position and absorption coefficients to other pentacyanoferrate(II) complexes with neutral sulphur and saturated nitrogen donor ligands. The coordination of the ligands to metal centre was attributed to occur through the sulphur of the thiol group instead of through

the nitrogen of the amine group.

McAuley and Macartney [33] assigned the coordination of thiourea and allylthiourea to metal centre to occur through the sulphur atom by studying the reaction of pentacyanoferrate(II) species with thioureas, where there was a rapid complex formation with shift in λ_{max} from 440 nm to 408 nm.

2.5.3. Kinetics of Dissociation of Pentacyanoferrate(II) Complexes

Toma and Malin [14] studied the kinetics and mechanism of ligand exchange of py, pyrazine and related aromatic N hetrocycles. Similar value of $\Delta H^{\#}$ (24 kcal mol^{-1}) and $\Delta S^{\#}$ ($\simeq$ 7 - 15 cal mol^{-1} K^{-1}) were reported. The authors proposed a limiting D mechanism for the substitution of the ligands.

Malin *et al.* [29] studied the kinetics of exchange of coordinated dimethyl sulphoxide for N-methyl pyrazinium. A rate saturation which is typical of a limiting D mechanism was observed.

Asperger *et al.* [15] studied the rate of replacement of nitrosobenzene by cyanide ion in the complex $[Fe[CN]_5(phNO)]^{3-}$ and found that the rate increases non-linearly with the cyanide ion concentration, reaching an asymptotic value at $[CN^-]$ = $20x10^{-3}$ M in $1.5x10^{-4}$ M complex solution. A limiting D-mechanism was proposed with a limiting rate constant k = $6x10^{-5}$ s^{-1} at 80 °C.

Asperger *et al.* [26] studied the kinetics of replacement of sulphite by cyanide ion in $Na_3[Fe[CN]_5SO_3]$ in aqueous solution. At 43 °C, the limiting rate was found to be(9.50 ±

$0.21)\times10^{-4}$ s^{-1}. The kinetic data were considered as evidence for a limiting D-mechanism.

Asperger *et al.* [20] reported the kinetics of replacement of the ligand in the pentacyano[ligand] ferrate(II) ions for the leaving ligands nitrosobenzene and sulphite, and for the entering ligands nitrosobenzene, 3-cyanopyridine, thiocyanate, nitrite, cyanide, and sulphite. Limiting reaction rates, at sufficiently large concentrations of entering ligand have been observed with all the leaving ligands.

Aymonino *et al.* [21] reported the kinetics of the release of ethylene diamine and monoprotonated ethylene diamine coordinated to the $[Fe[CN]_5]^{3-}$ moiety by following the appearance of $[Fe[CN]_5py]^{3-}$ or $[Fe[CN]_6]^{3-}$. Their results confirm previous predictions of a dissociative mechanism.

Burgess *et al.* [30] studied the kinetics of $[Fe[CN]_5[3,5-Me_2py]]^{3-}$, $[Fe[CN]_5[3-CNpy]]^{3-}$ and $[Fe[CN]_5[3-Clpy]]^{3-}$ with CN^- as incoming ligand, in water, 40 % ethylene glycol and 40 % t-butyl alcohol. They found that the rates of substitution at these $[Fe[CN]_5L]^{3-}$ anions are remarkably insensitive to the composition of the mixed aqueous solvent. They confirmed that the operation of the limiting D-mechanism in mixed aqueous solution form the characteristic curve for the dependence of K_{obs}, on cyanide concentration and a linear dependence of $1/K_{obs}$ on reciprocal cyanide concentration. They have also studied the kinetics of the above complexes with a range of incoming groups, SCN^-, thiourea, CN^-, N-methyl pyrazine and N-methyl pyrazinium ion and similar kinetic pattern as in the above case was observed.

Blesa *et al.* [25] studied aquation of 12 saturated amines

from pentacyanoamine ferrate(II) in 1 M pyridine solution. They found the same order of limiting rate constants, $K_{-1} \approx 10^{-3}$ s^{-1}. $\Delta H^{\#}$ and $\Delta S^{\#}$ vary within 24 ± 1 kcal mol^{-1} and 11 ± 5 cal mol^{-1} K^{-1}.

Aymonino *et al*. [23] reported the results of a study on the kinetics of release of ligand L from $[Fe[CN]_5L]^{n-}$ complexes in aqueous solutions at various pH and temperatures in presence of 1 M py solution. Where the ligands L are unidentate, unprotonated, or monoprotonated terminal diamines of general formula $NH_2[CH_2]_nNH_2$[n = 3 - 6). They found that the limiting rate of the monoprotonated diamine to be higher than the limiting rate for the release of the unprotonated diamine. Macartney and McAuley [33] reported the kinetics of the dissociation of thiourea, allyl thiourea, and N,N'-dimethyl thiourea using py as incoming ligand. The rate of dissociation of thiourea complexes was found to be about 10 times as fast as that for the dimethyl sulfoxide species, where in all the complexes the ligand is sulphur bonded to the metal. They attributed the difference in the rates in these sulphur bonded ligands, thiourea and dimethyl sulphoxide, in terms of the difference in strength of $d\pi$-$d\pi$ back bonding. The presence of an electronegative oxygen atom bonded to the donor sulphur in dimethyl sulphoxide increases the positive charge and so allow for a greater degree of electron delocalization from the metal. But in thioureas, the sulphur donors, being a thioketone, is less likely to interact strongly in dimethyl sulphoxide case and so some what weaker bond is expected and hence higher rate of dissociation. They also studied correlation of $\Delta H^{\#}$ and $\Delta S^{\#}$ in an isokinetic plot for a number of closely related

pentacyano ferrate(II) complexes with nitrogen- and sulphur-donor ligands. They found that the result is consistent with the limiting D-mechanism.

Macartney and McAuley [34] studied the dissociation kinetics of biologically important ligands, cysteine, pencillamine, glutathione, and 2-mercapto ethylamine. The complete dissociation of the ligand from the metal centre accomplished by the addition of excess of a strongly coordinated ligand, pyrazine. The rates of dissociation were measured in the pH range of 2.5 - 1, where both protonated and deprotonated forms of coordinated ligands may exist.

Bal Reddy and Van Eldik [36] studied a series of aquation reactions of octahedral complexes that are known to follow a limiting D-mechanism, of the type $[Fe[CN]_5NH_2R]^{3-}$ (R ≡ H, CH_3, C_2H_5, i-C_3H_7, and CH_2ph) for which it was possible to vary the size of the leaving group using py as entering group. They studied the dependence of the volume of activation for the proposed limiting D-mechanism on the size of the leaving group for the above pentacyano(amine) ferrate(II) complexes. The volume of activations are +16.4 ± 0.6 (R ≡ H), +24 ± 1.0 (R ≡ CH_3), +16.3 ± 1.5 (R ≡ C_2H_5), +18.5 ± 0.6 (R ≡ i-C_3H_7), and +17.4 ± 1.4 (R ≡ CH_2ph) $cm^3\ mol^{-1}$ at 25 °C. The volumes of activation have an average of +18 $cm^3\ mol^{-1}$ and do not exhibit a meaningful correlation with the size of NH_2R (*i.e.*, with their partial molar volumes). They compared their results with other octahedral substitution reactions in which a limiting dissociative mechanism was proposed, they found that similar conclusion is reached. They generalized that $\Delta H^{\#}$ for a limiting D-substitution step of octahedral complexes exhibit a

minor dependence on the size of the leaving group. This means that the extent of bond breakage in the transition state may vary with the nature of the leaving group to cause an almost constant volume increase. Furthermore, the position of the transition state along the reaction coordinate may vary with size of the leaving group and result in an 'early' or 'late' transition state on a volume basis.

2.5.4. Kinetics of Formation of Pentacyanoferrate(II) Complexes

Low-spin iron species $Fe[CN]_2L^{(3-n)-}$, particularly $Fe[CN]_5H_2O^{3-}$, represent models for active sites in biological systems. Most amino acids and peptides possess a number of functional groups which can participate in metal-binding processes. The success of a particular functional group competing against others in the vicinity becomes important for the understanding of metal-protein reactions, and also of biological systems in which the properties of proteins are modified by specific interactions with metal ions [31]. The interest in reactions of amino acids with the pentacyanoferrate(II) ion is mainly associated with the fact that this ion typically coordinates only one additional ligand and can be used as a probe for the binding properties of the several functional groups. The ease of water substitution [16] in $[Fe[CN]_5H_2O]^{3-}$ to form stable complexes with biologically important bases has been useful in preparing several model complexes of biological importance. Reactions with imidazole have been investigated in this regard by Shepherd [32].

Toma *et al*. [27] studied the kinetic properties of formation of pentacyano ferrate(II) complexes of three amino acids, imidazole, glycine, and L-histidine in aqueous solution. They found that the reactions are typically of first order with respect to the concentration of the ligands, with k_f = 28.0, 240, and 320 $dm^3\ cm^{-1}\ s^{-1}$ at 25 °C, respectively. They described the mechanism as limiting D or ion-pair dissociative (DIP) depending on the charges associated with the attacking ligands.

The results of a kinetic study of the formation of pentacyanoferrate(II) complexes with biologically important ligands, cysteine, penicillamine, glutathione, and 2-mercaptoethylamine was reported by Macartney and McAuley [34]. Formation rate measurements were made in range pH 1 - 10 and the observed acid dependencies are attributed to reaction of various forms of Iron(II) complexes, $[HFe[CN]_5H_2O]^{2-}$, $[Fe[CN]_5H_2O]^{3-}$ and $[Fe[CN]_5OH]^{4-}$. For the neutral ligands the rate constants for formation (k_f) of the complexes with cysteine, penicillamine, glutathione, and 2-mercaptoethyl amine are 330, 350, 370, and 200 $dm^3\ mol^{-1}\ s^{-1}$, respectively at 25 °C. Variation in the rate constants with the charge of the entering ligand was observed. They attributed this dependence on ligand and the insensitivity of the rate to the variations in the ligand type (N- vs S-bonded, *etc*.) to supporting evidence for the proposed ion-pair dissociative mechanism (Id). Toma and Malin [16] reported the kinetics of complexation of aqueous pentacyanoferrate(II), generated on dissolution of sodium pentacyanoamine ferrate(II), with the aromatic nitrogen hetrocycles 4-methyl pyridine, pyridine, isonicotineamide,

pyrazine, and N-methyl pyrazinium ion. In the presence of excess ligand, varied over a large number of concentrations, each reaction was found to obey the rate law

$$\frac{d[Fe[CN]_5L^{n-}]}{dt} = k_f[Fe[CN]_5H_2O^{3-}]\ [L]$$

with k_f varying from 3.6×10^2 to 5.5×10^2 M^{-1} s^{-1} at 25 °C. Measured values of the enthalpy of activation varied from 15 to 17 kcal mol^{-1}.

Malin *et al.* [29] studied the kinetics and mechanism of a complex from dimethyl sulphoxide and aqueous pentacyanoferrate(II). The rate law of the form (a) was obtained with $k_f = (2.4 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1} at 25 °C. Measured values of enthalpy and entropy of activations were 15.4 ± 0.5 kcal mol^{-1} and 4 ± 2 cal deg^{-1} mol^{-1}, respectively. They reported a limiting-D mechanism for the reaction.

Asperger *et al.* [20] studied complex formation between aqueous pentacyano ferrate(II) and various ligands, nitroso benzene, 3-cyano pyridine, thiocyanate, nitrite, cyanide, and sulphite. They found that when the entering ligand Y bears no electrical charge, the k_f values are very similar and in the range 200 - 300 L mol^{-1} s^{-1} at 25 °C. for singly negatively charged anions k_f = 40 - 60, and for doubly charged SO_3^{2-} ion k_f = 3.3 L mol^{-1} s^{-1}. Since the Id mechanism can explain equally well the experimental data, they conclude that their kinetic results do not allow them to distinguish between the D and Id mechanisms.

Asperger *et al.* [28] studied the kinetics of replacement of water in $[Fe[CN]_5H_2O]^{3-}$ with pyridine, 3-cyano pyridine,

nicotinamide, 4-amino pyridine, and cyanide in ethylene glycol solvent containing ≥ 0.055 mol^{-1} dm^3 water at 25 °C. They found that with excess of entering ligand Y, k_f is practically independent of water concentration variation. Values of $\Delta H^{\#}$ and $\Delta S^{\#}$ for the replacement of water by Y in the aqua-complex are almost identical for water and ethylene glycol solvents, supporting the assertion that Y replaces water in both solvent. From these they conclude that the formation of complex undergoes the Id mechanism and the D-mechanism is very unlikely.

Macartney and McAuley [33] studied the kinetics of the complex formation between the aquapenta cyanoferrate(II) and thiourea, allyl thiourea and N'N'-dimethyl thiourea in the pH range 2.8 - 9.0 in which the three reacting species, $HFe[CN]_5H_2O^{2-}$, $Fe[CN]_5H_2O^{3-}$ and $Fe[CN]_5OH^{4-}$ believed to exist. The substitution rate constants, measured in the pH range 2.8 - 9.0, showed a hydrogen ion dependence. The aquo species is found to be more reactive toward thiourea (k_f(25 °C) = 202 M^{-1} s^{-1}) than the hydroxy species (k_f(25 °C) = 100 M^{-1} s^{-1}) where the protonated aquo species (k_f(25 °C) = 2 M^{-1} s^{-1}) is much less reactive. An isokinetic plot of the activation parameters suggests the operation of the Id mechanism.

As can be seen from the above discussions, in the case of the complex formation reactions of $Fe[CN]_5H_2O^{3-}$ the mechanistic assignment seems controversial, Id or DIP mechanism was favoured by some groups and a limiting D mechanism by others. This is because the kinetic and equilibrium data obtained at ambient pressure could be equally well explained in terms of either Id, DIP, or limiting D mechanism. This apparent

mechanistic discrepancy was resolved by Van Eldik *et al.* [37]. They studied the pressure dependence of a series of complex formation reactions of $Fe[CN]_5H_2O^{3-}$ with neutral and negatively charged entering ligands in order to avoid significant ion-pairing effects and to distinguish between the limiting D or Id nature of the mechanism. The reported volumes of activation are all between +14 and +18 $cm^3\ mol^{-1}$ and they conclude that the limiting D-mechanism is favoured.

2.6. Kinetics and Mechanism of Hg(II) Promoted Ligand Exchange in Metal Complexes

Espenson *et al.* [39] studied the aquation of chloro complexes of Cr(III) ion catalyzed by Hg(II). The Hg(II) accelerates the release of Cl^- ion from the primary coordination sphere of $Cr(H_2O)_5Cl^{2+}$ ion. For each Hg(II) species which enhances this aquation, the observed rate followed the equation

$$\frac{-dln[Cr(H_2O)_5Cl^{2+}]}{dt} = (k_0 + k_{-1}[H^+]^{-1})[Hg(II)]$$

with chemical equation

$$Cr(H_2O)_5Cl^{2+} + HgCl_n^{2-n} = Cr^{3+} + HgCl_{n+1}^{1-n}$$

Espenson *et al.* [40, 41] studied the kinetics of reaction of mono cyano chromium(III) ion with Hg(II). Aquation in the presence of Hg[II] was described by the relation

$$d[cr^{3+}] / dt = k_{Hg}\ [CrCNHg^{4+}]$$

with $k_{Hg} = 6.69 \pm 0.9 \times 10^{-3}\ s^{-1}$.

Thus an intermediate adduct between $CrCN^{2+}$ and Hg(II) was formed with K = 10^5.

The kinetics and mechanism of reaction of $Cr(NH_3)_5Cl^{2+}$ with Hg(II) was reported by Espenson and Hubbard [42]. The mechanism was reported as

$$Cr(NH_3)_5Cl^{2+} + Hg^{2+} + H_2O \rightarrow Cr(NH_3)_5H_2O^{3+} + HgCl^{+}$$

$$Cr(NH_3)_5Cl^{2+} + HgCl^{+} + H_2O \rightarrow Cr(NH_3)_5H_2O^{3+} + HgCl_2.$$

The authors directed their attention towards the hydrogen ion dependence and comparison of the rates of spontaneous and catalyzed aquation. The temperature dependence of rate constants for catalyzed path were described in terms of the activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$, $\Delta H^{\#}$ = 14.9 ± 0.2 kcal mol^{-1} and $\Delta S^{\#}$ = -13.4 ± 0.7 cal mol^{-1} deg^{-1}.

Haim *et al.* [43] studied the equilibrium and kinetic aspects of the Hg(II) assisted aquation of $CrCNS^{2+}$ and proposed that the interaction between $CrCNS^{2+}$ and Hg^{2+} produces rapidly the binuclear complex, $CrNCSHg^{4+}$. The equilibrium quotient for the reaction

$$CrNCS^{2+} + Hg^{2+} \overset{K}{\rightleftharpoons} CrNCSHg^{4+}$$

is 1.66×10^4 M^{-1} at 25 °C and ionic strength 1.0 M. The associated thermodynamic parameters are $\Delta H^{\#}$ = 8.0 kcal mol^{-1} and $\Delta S^{\#}$ = -7.3 cal mol^{-1} deg^{-1}. The aquation of $CrNCSHg^{4+}$ proceeds by a dissociative mechanism according to them.

The kinetics of Hg(II) catalyzed aquation of trans and cis-dichlorotetraaquo Cr(II) ions was studied by Birk over a wide range of Hg^{+} and H^{+} concentration at 15 - 35 °C (I = 1.0 M) [44].

The aquation of the trans complex followed the rate

equation

$$\frac{d[trans\text{-}Cr(H_2O)_4Cl_2]}{dt} = (k_0 + k_{-1}[H^+]^{-1})[Hg^{2+}]$$

with k_0 = 30.7 M^{-1} s^{-1}, k_{-1} = 0.941 s^{-1} at 25 °C. The associated thermodynamic parameters are $\Delta H^{\ddagger}$ = 13.5 ± 0.4 kcal mol^{-1}, $\Delta S^{\ddagger}$ = -6.3 ± 0.4 cal mol^{-1} deg^{-1}, $\Delta H_{-1}^{\ddagger}$ = 19.0 ± 0.6 kcal mol^{-1}, $\Delta S_{-1}^{\ddagger}$ = 5.1 ± 2.1 cal mol^{-1} deg^{-1} .

The aquation of haloamine Co(III) complexes catalyzed by Hg^{2+} ions was studied by Sargeson and he proposed a five coordinated intermediate for the reaction [45, 46]

$$Co(NH_3)_5X^{2+} + Hg^{2+} \rightarrow Co(NH_3)_5^{3+} + HgX^{-}$$

$$Co(NH_3)_5^{3+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} .$$

Sutin and Oshanovic [47] reported the rate of mercury(II) catalyzed aquation and isomerization of the sulphur-bonded monothiocyanate complex of Cr(III).

Mercury(II) catalyzed isomerization and aquation was represented as

$$CrSCN^{2+} + Hg^{2+} \xrightarrow{k_{-1}^{2}} Cr^{3+} + HgSCN^{+1}$$

$$\xrightarrow{k_{-1}^{i}} CrNCSHg^{4+}$$

Very little work has been reported on the kinetics of metal ion assisted ligand exchange reactions in anionic complexes. Hexacyanoferrate(II) is perhaps the only species for which ligand exchange kinetics has been reported. All reports pertains to the catalytic effect of Hg(II) and Ag(I).

Asperger *et al.* [49] reported the kinetics of the reaction of potassium hexacyanoferrate(II) and $HgCl_2$ in the presence of

nitrosobenzene. The reaction was studied spectrophotometrically by measuring the absorbance of the violet complex ion, $Fe[CN]_5C_6H_5NO^{3-}$ at 528 nm. The activation energy was given as 19.8 kcal mol^{-1} mol^{-1}.

Asperger *et al.* [48] reported the kinetics and mechanism the reaction between hexacyanoferrate(II) and Hg(II) in the presence of nitrosobenzene at pH 4.1. The results suggested that ferrocyanide and Hg(II) form an ion-pair and the rate determining step was probably the attack of the Hg(II) ion, already in the solvation shell, on the cyano group to give $HgCN^+$ and $Fe[CN]_5H_2O^{3+}$ ions. In the presence of nitrosobenzene a water molecule was replaced by nitrosobenzene in a relatively fast reaction. The reaction scheme was as follows:

$$Fe[CN]_6^{4-} + Hg(II) \overset{K}{\rightleftharpoons} Fe[CN]_6^{4-}\text{-}Hg(II)$$

$$\downarrow H_2O$$

$$Fe[CN]_5H_2O^{3-} + HgCN^+$$

$$Fe[CN]_5H_2O^{3-} + C_6H_5NO \rightarrow Fe[CN]_5C_6H_5NO^{3-}$$

$$HgCN^+ + H^+ \rightarrow Hg^{2+} + HCN.$$

Saroja Raman [50, 51] reported detailed kinetic study of hexacyanoferrte(II) with $HgCl_2$ in the presence of 2,2′-bipyridyl. The products formed are tetracyano-bipy-Fe(II) and tris-bipy-Fe(II) depending on whether $Fe[CN]_6^{4-}$ or $HgCl_2$ is present in at least three to four fold excess. Where $([Fe[CN]_6^{4-}]/[HgCl_2]) \geq 4$, the rate was independent of the concentration of $Fe[CN]_6^{4-}$ and corresponds to the rate equation

$$\frac{d[p_1]}{dt} = k_{Hg}[Cl_2]$$

where p_1 represents the product $k_2[CN]_4$bipy-Fe(II) formed as a result of partial abstraction of CN^-.

When $HgCl_2$ was used in excess, $([HgCl_2]/[Fe[CN]_6^{4-}]) >> 3$ the rate of the reaction was independent of $HgCl_2$ concentration and varied linearly with the concentration of $Fe[CN]_6^{4-}$. The rate equation reported is

$$\frac{dp_2}{dt} = k_{Fe}[Fe[CN]_6^{4-}]$$

where p_2 is the tris-bipy-Fe[II] formed by complete abstraction of CN^-.

The mechanism of the reaction in presence of excess $K_4Fe[CN]_6$ and $HgCl_2$ was reported as follows:

<u>Excess $Fe[CN]_6^{4-}$</u>

$$Fe[CN]_6^{4-} + Hg(II) \rightleftharpoons Fe[CN]_6^{4-}\text{-}Hg(II)$$

$$\downarrow k_{Hg}$$

$$Fe[CN]_5^{3-} + HgCN^-$$

$$\text{fast} \downarrow \text{Bipyridine}$$

$$[CN]_4[Bipy]Fe(II) + Hg[CN]_2$$

<u>Excess $HgCl_2$</u>

$$Fe[CN]_6^{4-} + 2Hg(II) \rightleftharpoons Fe[CN]_6^{4-}\text{-}2Hg(II)$$

$$\downarrow k_{Fe}$$

$$Fe[CN]_4^{2-} + 2HgCN^-$$

$$\text{fast} \downarrow \text{Bipyridine}$$

$$[Bipy]_3Fe(II) + 2Hg[CN]_2 + 2CN^-$$

The kinetics and mechanism of Hg(II) catalyzed abstraction of CN^- to give $Fe[CN]_5PNA^{3-}$ and $Fe[CN]_5C_6H_5NO^{3-}$ was investigated by Vankateshwarlu [52].

2.7. Application of metal ion promoted reactions in the determination of metal Hg(II) metal ion.

Metal ion promoted ligand substitution reactions have engaged a lot of attention in recent years for the trace analysis of metal ions capable of catalyzing these reactions.

Kraljic *et al.* [53, 54] reported the catalytic decomposition of $K_4Fe[CN]_6$ by Hg(II), Ag(I), and Pd(II) in the presence of bipyridine and nitrosobenzene for the detection.

Feryl *et al.* [55] used the catalytic abstraction of CN^- from $Fe[CN]_6^{4-}$ by Hg(II) in the presence of phenanthroline and bipyridine for the detection of Hg(II) in pharmaceutical preparations.

Sub-micro determination of Hg(II) down to 10^{-3} M concentration level was reported by Saroja Raman using the reaction of $K_4Fe[CN]_6$ and Hg(II) in the presence of bipyramidine and phenanthroline [56]. The Hg(II) catalyzed replacement of cyanide in hexacyanoferrate(II) by p-nitroso-diphenyl amine in aqueous solution was reported by Phull and Nigam [57] for the microdetermination of Hg(II) and the detection limit was found to be $2x10^{-8}$ M, with relative standard deviation of 1.4 %.

Gadia and Mehra [58] determined in submicro quantities Ag(II), Au(III), and Hg(II) by their catalytic action on the ligand exchange reaction $Fe[CN]_5NH_3^{3-}$ by ferrocine.

Venkateshwarlu and Saroja Raman [59] studied the reaction of $K_4Fe[CN]_6$ with Hg(II) in the presence of nitroso-R-salt and

exploited this reaction for rapid determination of Hg^{2+} from 1 - 20 μ ml^{-1}.

Katz and Lis [60] reported the reaction of $Fe[CN]_5NH_3^{3-}$ and Hg(II) in the presence of bipyridine and phenanthroline for micro determination of Hg(II).

Saroja Raman and Reddy [67, 71] studied the reaction of $K_4Fe[CN]_6$ with Ag(I) and Hg(II) in the presence of nitrosobenzene and they found that it was suitable for the spectrophotometric determination of Ag(I) and Hg(II) in microquantities.

Ag(I) promoted abstraction of CN^- from $K_4Fe(CN)_6$ in the presence of excess nitroso-R-salt has been studied for the spectrophotometric determination of Ag(I) in the concentration ranges 0.05 - 0.5 μg ml^{-1} at pH 4.0 and 60 °C and 0.5 - 11.0 μg ml^{-1} at pH 6.6 - 7.0 and 85 °C by Saroja Raman and Reddy [68]. They have also reported [69] that Ag(I) can be determined in the concentration range 0.1 - 27 μg ml^{-1} using the reaction of hexacyano ferrate(II) and 2,2'-bipyridyl in the presence of Ag(I).

Chapter 3

EXPERIMENTAL

3.1 Chemicals and Preparation of Solutions

Potassium hexacyano ferrate(II) (Reidel-de Haën), mercuric chloride (KEBO), sodium perchlorate (BDH, Analar), 35 % (w/w) hydrochloric acid (BDH, Analar), 70 % (w/w) nitric acid (Reidel-de Haën), 70 % (w/w) perchloric acid (Merck), pyridine (INTERCHEM, Inc.), anhydrous sodium carbonate (BDH, Analar), 2,2'-bipyridine (BDH), 1,10-phenanthroline (Sigma), sodium hydroxide pellets (BDH) and hydroxyammonium chloride (HOPKIN and Analar). Potassium pentacyano amine ferrate(II), p-nitrosophenol, and p-nitroso-N,N'-dimethyl aniline, were supplied by Fisher chemical company and Chemologue. All chemicals were used without further purification.

Double distilled water (in glass) was used through out the experiment. The acids were diluted to the desired volume standardized against anhydrous sodium carbonate to a methyl orange end point [61]. Dilute solutions of $K_4Fe[CN]_6$ and $HgCl_2$ were prepared daily to prevent photoxidation of the former and adsorption on glass of the latter [62]. All the solutions were prepared fresh and never kept for more than 8 hours.

3.2 Instruments and Experimental Conditions

Beckmann Du-65 UV-Visible spectrophotometer was used for the measurement of absorbance. Thermostat (Indian Equipment Corporation) was used to heat the solutions to the required temperature.

A Beckmann CHEM MATE pH meter was used for the measurement of pH. It was standardized against aqueous universal buffer solutions.

The solutions were preequilibriated to the desired temperature before mixing and transferred within 15 - 20 s of mixing, to the cell of Beckmann DU-65 UV_VIS Spectrophotometer. Fresh solutions were replaced from the thermostat after each reading. Temperatures varying from 1 °C to 40 °C were used.

3.3 Preparation of Complexes

The complexes, pentacyano p-nitrosophenol ferrate(II) and pentacyano p-nitroso-N,N'-dimethylaniline ferrate(II) were prepared by reacting aqueous pentacyano ferrate(II), generated by dissolution of sodium pentacyano amine ferrate(II) with p-nitrosophenol and p-nitroso-N,N'-dimethyl aniline, respectively.

3.4 Kinetic Studies

3.4.1 General Methodology Used

The kinetics of the reactions of $Fe[CN]_5PNA^{3-}$ and $Fe[CN]_5PNP^{3-}$ with py, $Fe[CN]_5PNA^{3-}$ and $Fe[CN]_5PNP^{3-}$ with $HgCl_2$ in neutral media, $Fe[CN]_5PNA^{3-}$ and $Fe[CN]_5PNP^{3-}$ with $HgCl_2$ in acidic media, and acid catalysis of $Fe[CN]_5PNA^{3-}$ and $Fe[CN]_5PNP^{3-}$ were

studied in detail. In all the cases, the absorption characteristics of the complexes, $Fe[CN]_5PNA^{3-}$ and $Fe[CN]_5PNP^{3-}$ in the visible region was quite different from those of the reaction products that have been confirmed, and also quite different from that of the products formed in the above different reactions. Hence the kinetics of the reactions was easily followed by noting the absorbance at λ_{max} of the complexes at regular time intervals without interference from the reactants.

The range of concentrations of $Fe[CN]_5PNA^{3-}$, $Fe[CN]_5PNP^{3-}$, $HgCl_2$, py, and the acids were chosen by trial and error to optimize various factors like rate, range and sensitivity of measurable absorbance *etc.* In general, the reactions were all carried out under pseudo first order conditions. In all the cases, the reactions were monitored at least for 2 - 3 half lives, if not more.

3.4.2 Rate Equations

The rate equations were determined by studying the effect of the concentrations of each of the reactants (keeping the concentration of other constants) on the rate. Since the rates were mostly measured under pseudo first order conditions, first order rate equation was applicable. Under these conditions, the rate of formation could be written as

$$\frac{dp}{dt} = \frac{-dc}{dt} = kc$$

or

$$\frac{dX}{dt} = k[C_0-X]$$

where the integral form of the latter equation is $\ln(C_0/(C_0-X)) = kt$. Since C_0 and C_0-X are proportional to $A_\infty-A_0$ and $A_\infty-A_t$, respectively, the slope of $\ln((A_\infty-A_0)/(A_\infty-A_t))$ versus t gives the pseudo first order rate constant.

3.4.3 Thermodynamic Activation Parameters

Thermodynamic parameters were calculated from the absolute reaction rate theory

$$k = \frac{RT}{Nh} e^{\frac{-\Delta H^*}{RT}} . e^{\frac{\Delta S^*}{R}}$$

where k is rate constant $\Delta H^\#$ is enthalpy of activation and $\Delta S^\#$ is entropy of activation, R is the universal gas constant, h Planck's constant, N Avogadro's number, and T absolute temperature. Enthalpy of activation was calculated from a plot of ln(k/T) versus 1/T. Entropy of activation was calculated by using the value of $\Delta H^\#$ in the above equation.

3.5 Characterization of Adducts

3.5.1 Characterization of $Fe[CN]_5PNA^{3-}$ and Hg(II) adduct

When solutions of $Fe[CN]_5PNA^{3-}$ (4 ml, 2×10^{-4} M) and $HgCl_2$ (8 ml, 10^{-2} M) were mixed at 4 °C, a dark green precipitate was formed which is probably the adduct of $Fe[CN]_5PNA^{3-}$ and Hg(II). The precipitate was filtered out and washed with cold water and diethylether. Then the priecipitate was decomposed with

concentrated HNO_3 and analyzed for Hg(II) and Fe(II) as follows.

For Hg(II) determination in the extract, solution of $K_4Fe[CN]_6$ (2 ml, 10^{-2}), 2 mL extract and 5 mL PNA ligand were mixed and the pH of the solutions were adjusted to 6 - 7 . The solutions were kept for more than 5 hs till the reaction was complete and the absorbance was measured at 650 nm. Correspondingly blanks without extracts were treated identically, to compensate for thermal decomposition and their absorbance subtracted to give net absorbance due to reaction with Hg(II) alone in the extract.

For Fe(II) determination in the extract, solutions of bipy (2 ml, 10^{-2} M in small amount of alcohol) and three mL extract were mixed and the pH of the solutions were adjusted to 6 - 7. Solid hydroxyammonium chloride was added to ensure that the Iron(II) is in +2 state. The solutions were kept for more than 5 hs till the reaction was complete and the absorbance was measured at 552 nm. Correspondingly blanks without extract were treated identically. The same procedure was repeated using phen (2 ml, 10^{-2} M in a little alcohol) and the absorbance was measured at 510 nm.

3.5.2 Characterization of $Fe[CN]_5PNP^{3-}$ and Hg(II) adduct

When solutions of $Fe[CN]_5PNP^{3-}$ (4 ml, $2x10^{-2}$ M) were mixed at 4 °C, a dark blue precipitate was formed which is probably the adduct of $Fe[CN]_5PNP^{3-}$ and Hg(II). The precipitate was filtered out and washed with small amounts of cold water and diethyl ether. Then the precipitate was decomposed with concentrated HNO_3 and analyzed for Hg(II) and Fe(II) as

follows.

For Hg(II) determination in the extract, solutions of $K_4Fe[CN]_6$ (2 ml, 10^{-2} M), 2 mL extract and 5 mL PNP ligand were mixed and the pH of the solutions were adjusted to 6 - 7. The solutions were kept for more than 5 hs till the reaction was complete and the absorbance was measured at 575 nm. Corresponding blanks without extract were treated identically and their absorbance subtracted to give net absorbance due to reaction with Hg(II) alone in the extract.

For Fe(II) determination in the extract, solutions of bipy (2 ml, 10^{-2} M in a little alcohol) and 3 mL extract were mixed and the pH of the solutions were adjusted to 6 - 7. Then solid hydroxyammonium chloride was added. The solutions were kept for more than 5 hs till the reaction was complete and the absorbance was measured at 522 nm. Corresponding blanks without extract were treated identically. The same procedure was repeated using phen (2 mL, 10^{-2} M in a little alcohol) and the absorbance was measured at 510 nm.

Chapter 4

RESULTS and DISCUSSION

4.1 The complexes

4.1.1 Preparation and spectral characterization of the complexes

The complexes, pentacyano p-nitrosophenol ferrate[II], pentacyano p-nitroso-N,N-dimethylaniline ferrate[II] and pentacyano pyridine ferrate [II] were prepared by the method of Toma and Malin [16] by reacting aqueous pentacyano aquo ferrate[II], generated by dissolution of sodium pentacyano ammineferrate[II] with p-nitrosophenol, p-nitroso-N,N-dimethylaniline and pyridine, respectively.

Complexes	λ_{max} (nm)	Molar Absorptivity (M^{-1} cm)
pentacyano aquoferrate[II]	400	450±50
pentacyano p-nitrosophenol ferrate[II]	575	$1.75\pm0.05\times10^4$
pentacyano p-nitroso-N,N-dimethyl aniline ferrate[II]	650	$1.6\pm0.05\times10^4$
Pentacyano pyridine ferrate[II]	365	$3.2 \pm 0.5\times10^3$

4.1.2 Stability of the complexes

The complexes were scanned continuously at 30 minutes intervals and it was found that the complexes stabilized after 1 h and no appreciable change in absorbance was generally observed within 24 hs. The complexes were kept for 1 h in dark before any kinetic run and were freshly prepared every day.

The spectra of the free ligands and the corresponding

complexes are given in Figs. 1 and 2. As seen from this, there is negligible absorption of the free ligands in the visible spectra, as compared to the high absorbance of the complexes.

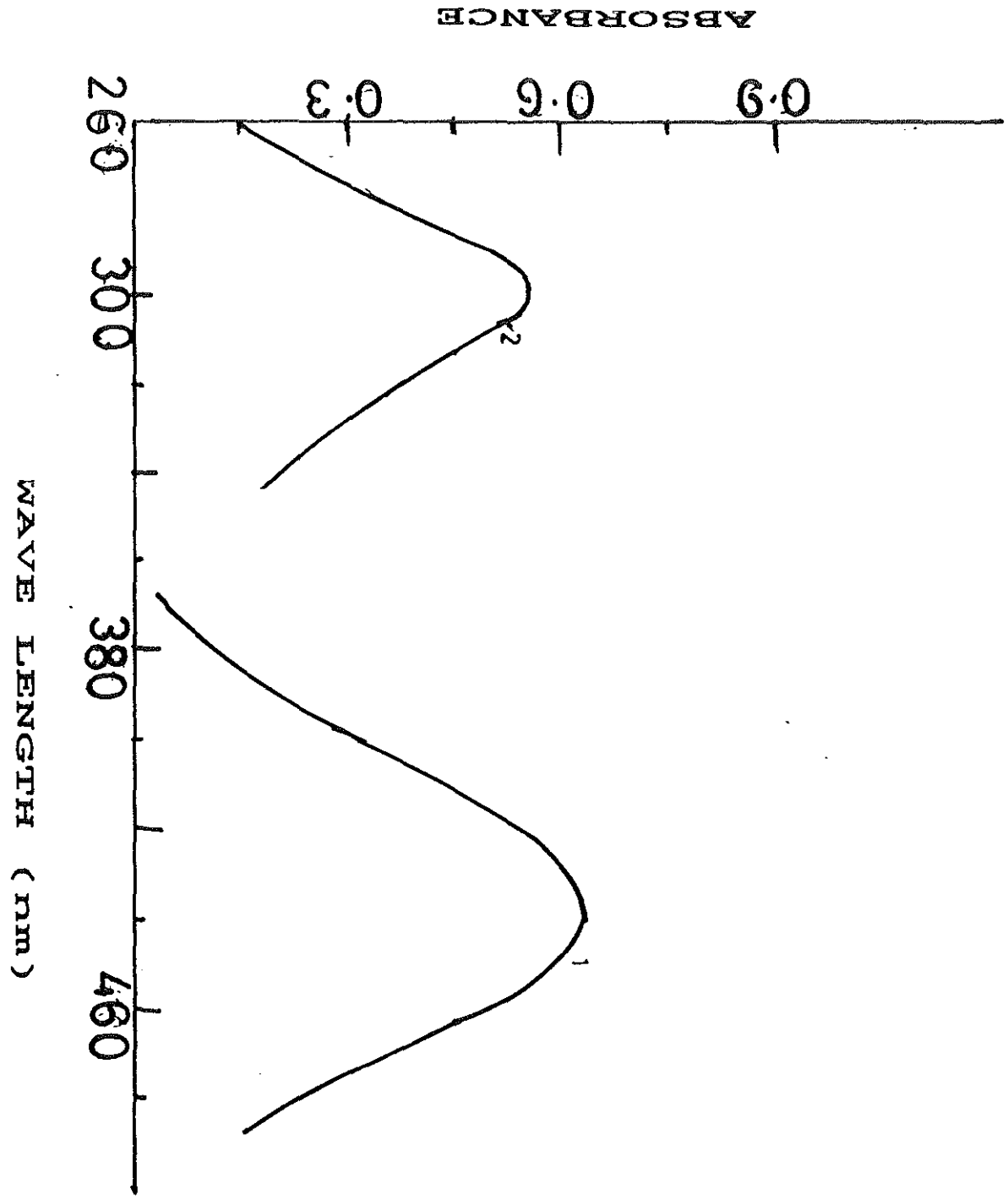


Fig.1. Spectra of:
1. 10^{-4} M PNA ligand
2. 10^{-4} M PNP ligand

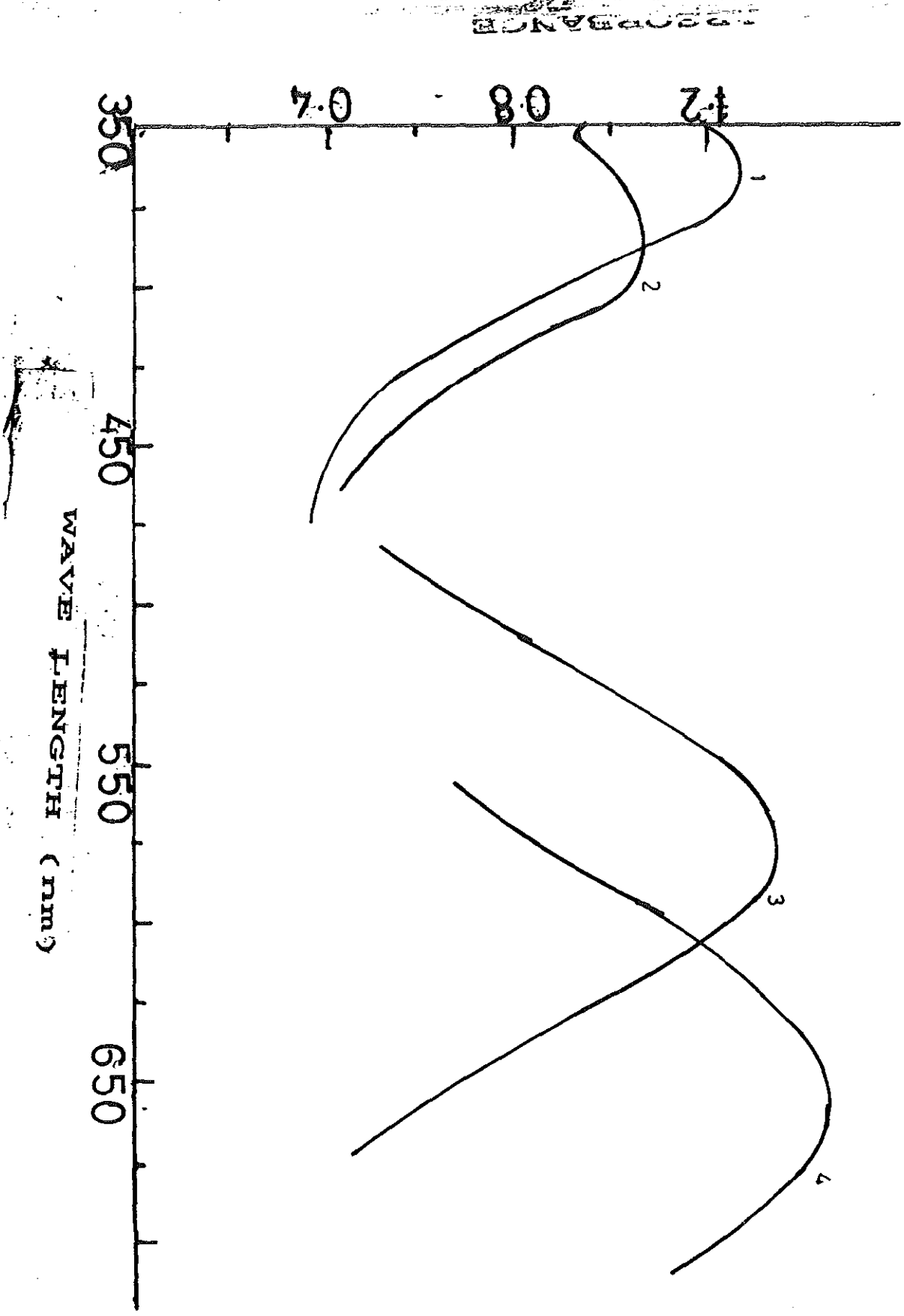


Fig.2. Spectra of:

1. $4x10^{-4}$ M $Fe[CN]_5Py^{3-}$
2. $1x10^{-3}$ M $Fe[CN]_5H_2O^{3-}$
3. $5x10^{-5}$ M $Fe[CN]_5PNP^{3-}$
4. $5x10^{-5}$ M $Fe[CN]_5PNA^{2-}$

4.2 Kinetics of dissociation of $Fe[CN]_5PNA^{3-}$ through ligand exchange with pyridine

RESULTS

The dissociation of $Fe[CN]_5PNA^{3-}$ could not be measured under normal conditions because the stability of the complexes is very high. Hence ligand exchange of PNA with pyridine was taken up.

4.2.1 Nature of the product and stoichiometry

Absorbance measurements with time of solutions containing $Fe(CN)_5PNA^{3-}$ and pyridine showed that there is an increase in absorbance at 365 nm where the pentacyano pyridine ferrate [11] complex exhibits a characteristic maximum and a concurrent decrease in absorbance at 650 nm which is λ_{max} of $Fe[CN]_5PNA^{3-}$. Therefore the reaction takes place according to the equation

$$Fe[CN]_5PNA^{3-} + Py \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe[CN]_5Py^{3-} + PNA \qquad (1)$$

4.2.2 Kinetics

The rate of the reaction was measured from the rate of the disappearance of $Fe[CN]_5PNA^{3-}$ complex. For this, the absorbance at 650 nm was monitored at suitable time intervals. All the runs were carried out under pseudo first order conditions with excess pyridine. First order rate conditions for different concentrations of the pyridine are given in Table 1.

As can be seen from the table, the rate constants increased initially with an increase in Py concentrations and

reached nearly constant values at [Py] > 0.3 M (Fig. 3.)

Since the rate data suggested a dissociative type of substitution, the pseudo first order rate constant (k_{ob}) was analyzed as follows:-

$$k_{ob} = \frac{k_1 k_2 \ [Py]}{k_{-1} \ [PNA] \ + \ k_2 \ [Py]} \qquad (2)$$

or

$$\frac{1}{k_{ob}} = \frac{k_{-1} \ [PNA]}{k_1 k_2 \ [Py]} + \frac{1}{k_1} \qquad (3)$$

where k_1 is the limiting rate. The data were plotted as k_{ob}^{-1} versus $[Py]^{-1}$, and k_1 was obtained from the reciprocal of the intercept. The calculated value of the limiting rate tallied very closely with the experimentally determined rate. The plot of $1/k_{ob}$ versus $[Py]^{-1}$ is given in Fig. 4. The calculated value of the limiting rate is given in Table 2.

4.2.3 Activation parameters

The rate constants at different temperatures are given in Table 3. The entropy and enthalpy of activation were calculated from absolute reaction rate theory from ln(k/T) versus 1/T, Fig. 5, are given in Table 4.

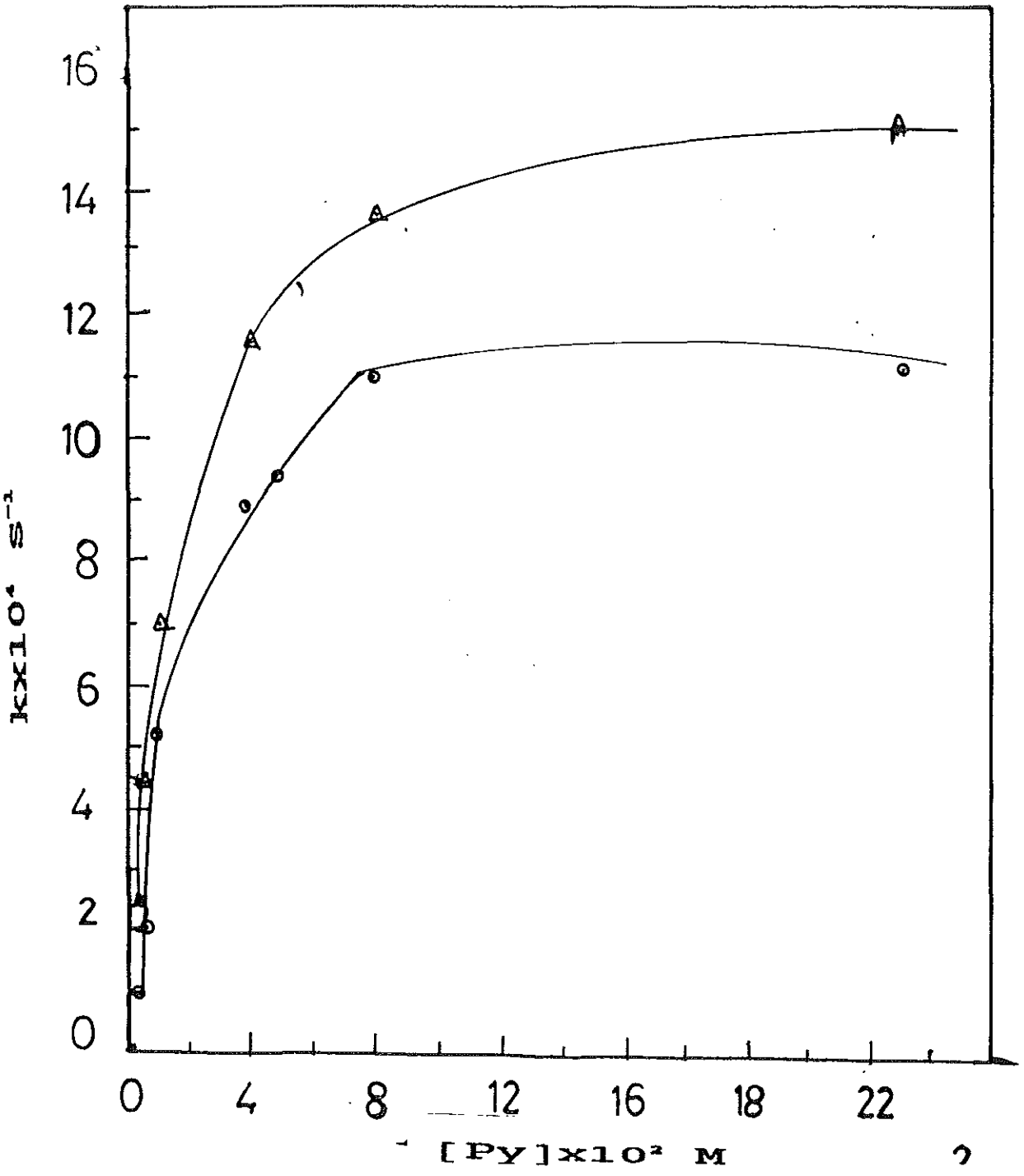


Fig.3. Rate Constants Vs. [Py.]

△ $Fe(CN)_5PNP^{3-}$
⊙ $Fe(CN)_5PNA^{3-}$

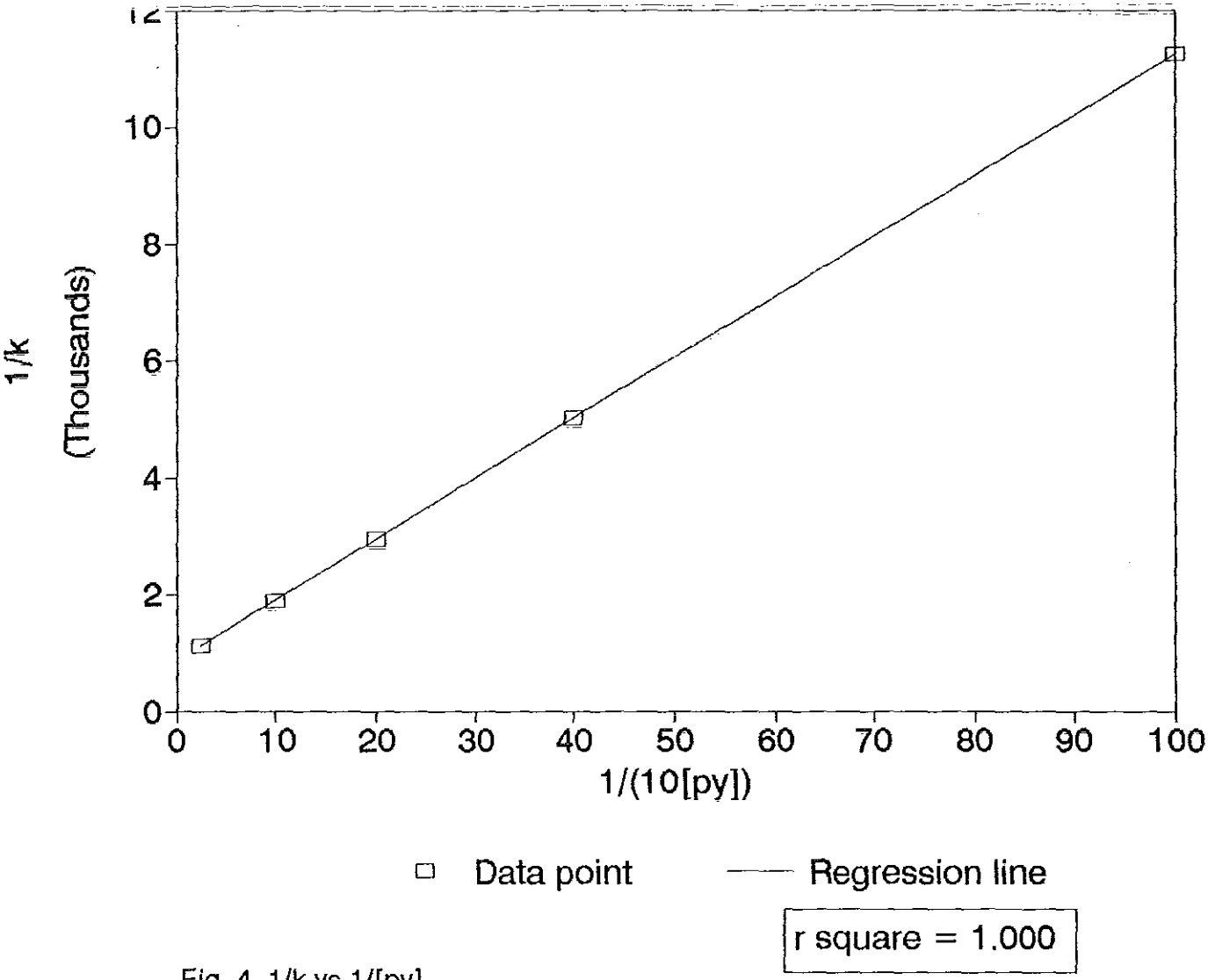


Fig. 4. 1/k vs 1/[py]

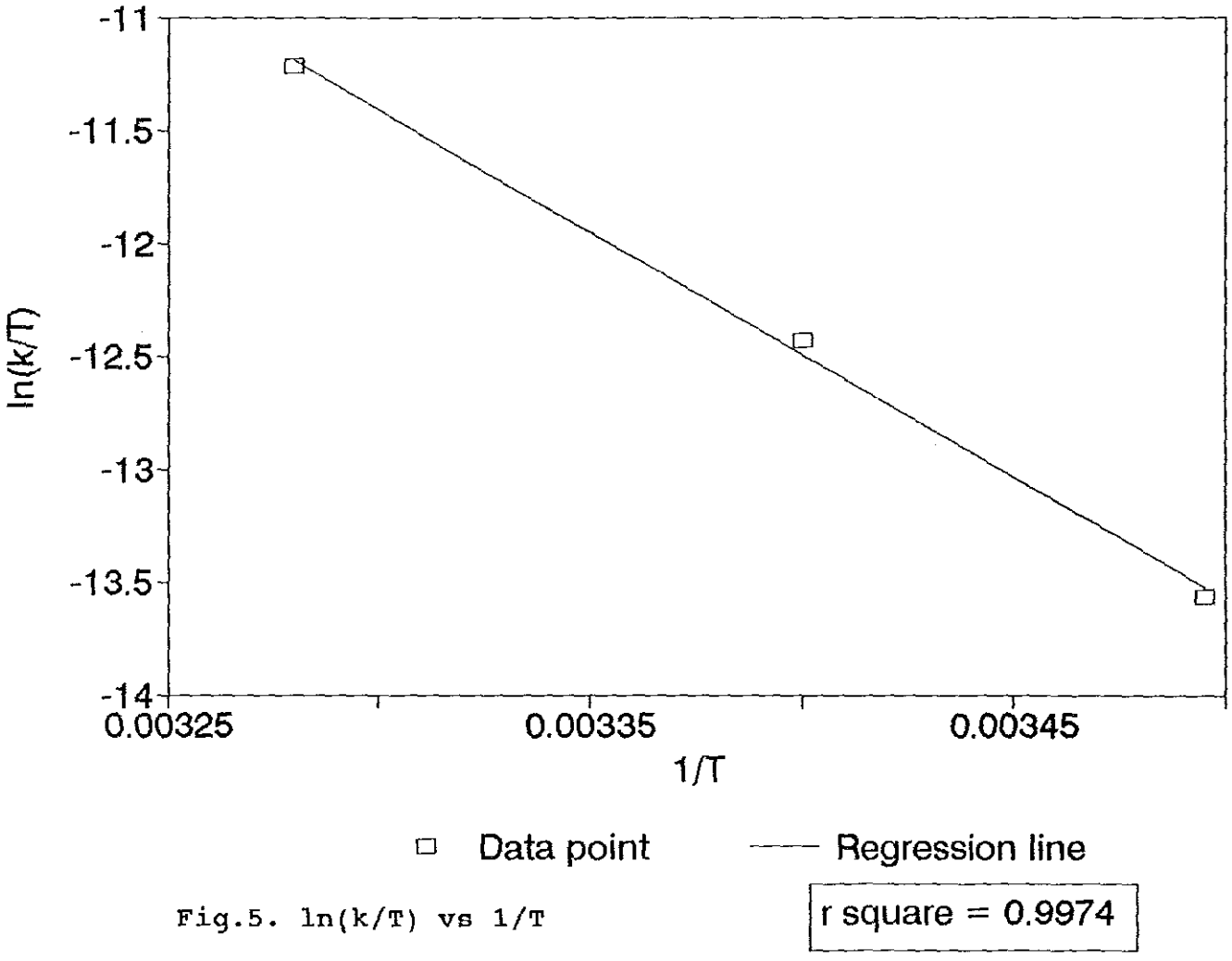


Fig.5. ln(k/T) vs 1/T

Table 1. Variation in the rate of dissociation of $Fe[CN]_5PNA^{3-}$ with Py concentration.

Concentration of [Py]x10, M	Rate Constant ($kx10^3$)*, s^{-1}
4.00	1.21 ± 0.05
2.50	1.21 ± 0.09
0.80	1.20 ± 0.08
0.50	0.93 ± 0.05
0.40	0.89 ± 0.05
0.10	0.53 ± 0.06
0.05	0.34 ± 0.06
0.025	0.20 ± 0.01
0.010	0.09 ± 0.008

* Average of minimum of three replicates;
$[Fe[CN]_5PNA^{3-}] = 2x10^{-5}$ M; T = 292.15 k.

Table 2. Limiting rates for the dissociation of $Fe[CN]_5PNA^{3-}$.

Temperature, K	Experimental $kx10^3$, s^{-1}	Calculated $kx10^3$, s^{-1}
292.15	1.21 ± 0.09	1.71 ± 1.1

Table 3. Rate of dissociation of $Fe[CN]_5PNA^{3-}$ at different temperatures.

Temperature, K	305.15	294.15	286.15
Rate Constant*, $kx10^3$, s^{-1}	4.03 ± 0.04	1.19 ± 0.08	0.37 ± 0.06

* Average of minimum of three replicates.

Table 4. Activation parameters for the dissociation $Fe[CN]_5PNA^{3-}$

$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
95 ± 4	22 ± 7

4.3 Kinetics of dissociation of $Fe[CN]_5PNP^{3-}$ through ligand exchange with pyridine

RESULTS

4.3.1 Nature of the products and stoichiometry of the reaction

Absorbance measurements of solutions containing $Fe[CN]_5PNP^{3-}$ and excess pyridine confirmed that $Fe[CN]_5PNP^{3-}$ disappeared and $Fe[CN]_5Py^{3-}$ was formed with time. The reaction stoichiometry is represented by

$$Fe[CN]_5PNP^{3-} + Py \rightleftharpoons Fe[CN]_5Py^{3-} + PNP \qquad (4)$$

4.3.2 Kinetics

The rate of disappearance of $Fe[CN]_5PNP^{3-}$ at 575 nm was monitored at suitable time intervals. Kinetic runs were carried out under pseudo first order conditions with excess pyridine. Pseudo first order rate constants for different concentrations of Py is given in Table 5.

Saturation kinetics with respect to the concentration of Py ligand were observed (Fig. 3). The pseudo first order rate constants fitted very well to the k_{ob} expression given by

$$k_{ob} = \frac{k_1 k_2 [Py]}{k_{-1}[PNP] + k_2 [Py]} \qquad (5)$$

where k_1 is the limiting rate. The plot of $1/k_{ob}$ versus $1/[Py]$ is given in Fig. 6. The calculated value of the limiting rate is given in Table 6.

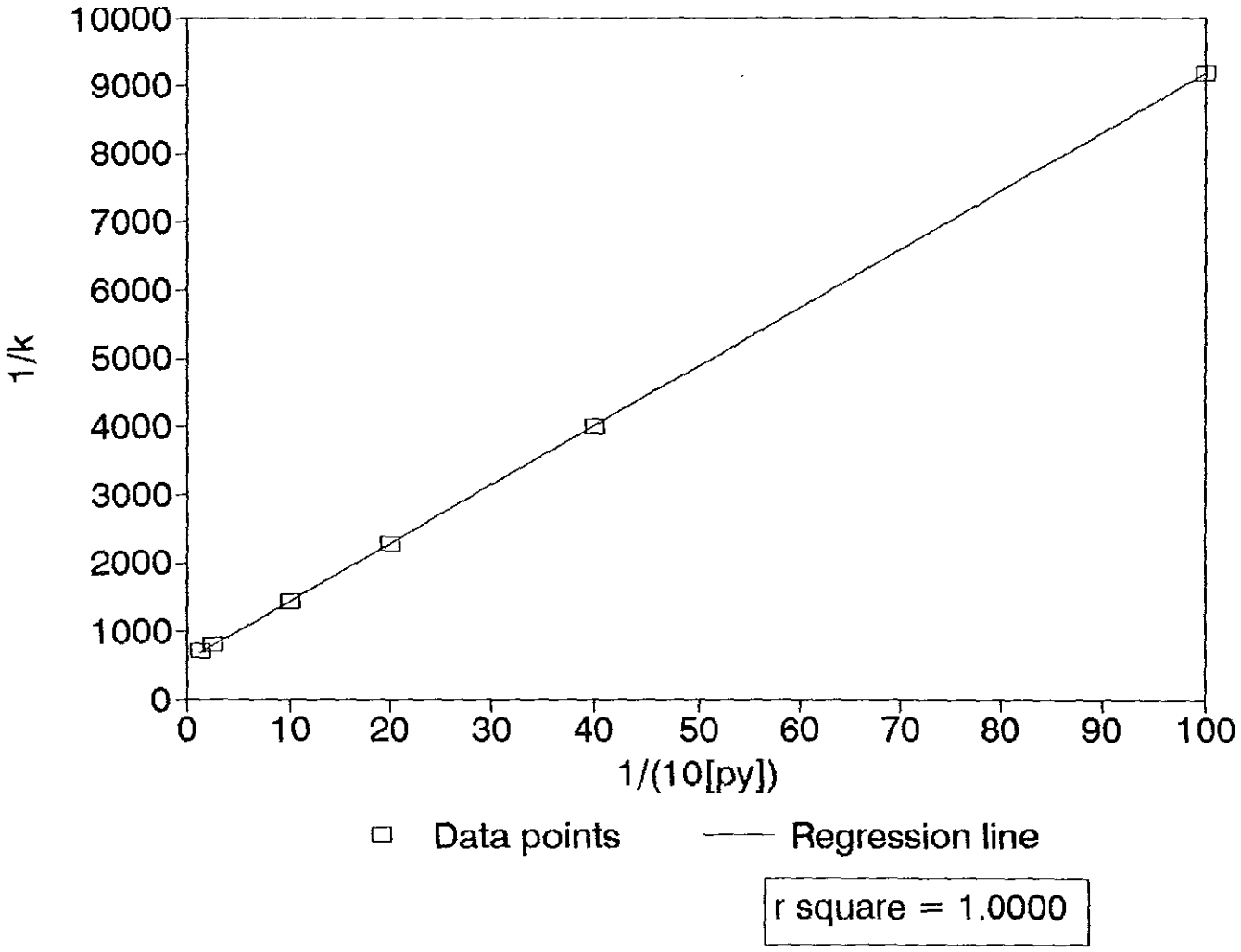


Fig. 6. 1/k vs 1/[py]

4.3.3 Activation parameters

The rate constants at different temperatures are given in Table 7. The enthalpy and entropy of activation for the reaction calculated from the absolute rate theory from ln(k/T) versus 1/T (Fig. 7) are given in Table 8.

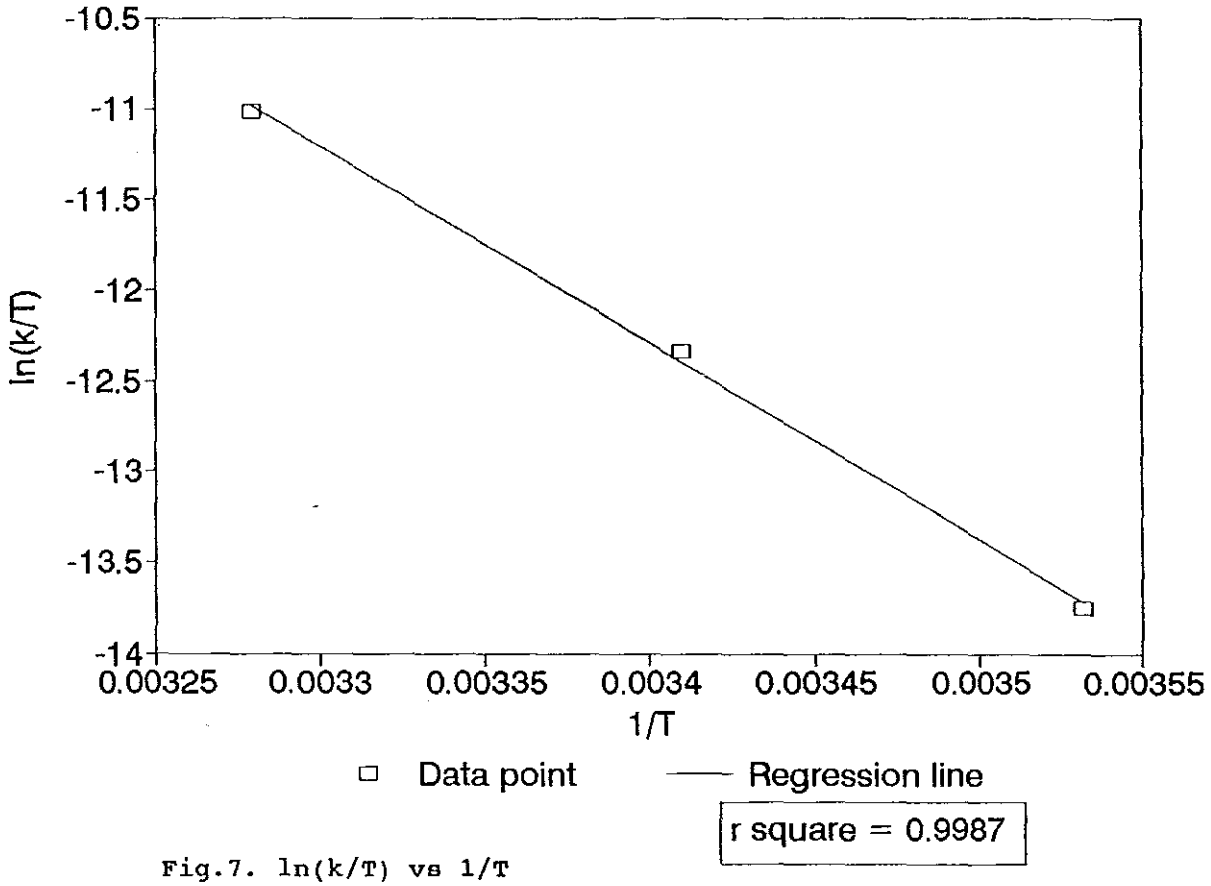


Fig.7. ln(k/T) vs 1/T

Table 5. Variation in the rate of dissociation of $Fe[CN]_5PNP^{3-}$ with Py concentration.

Concentration of Pyx10, M	Rate Constant ($kx10^3$)*, s^{-1}
4.00	1.68 ± 0.06
2.50	1.67 ± 0.09
0.80	1.46 ± 0.15
0.40	1.26 ± 0.20
0.10	0.70 ± 0.25
0.05	0.44 ± 0.25
0.025	0.25 ± 0.15
0.010	0.11 ± 0.08

* Average of minimum of three replicates;

$[Fe[CN]_5PNP^{3-}] = 5x10^{-5}$ M; T = 292.15 k.

Table 6. Limiting rate for the dissociation $Fe[CN]_5PNP^{3-}$.

Temperature, K	Experimental $kx10^3$, s^{-1}	Calculated $kx10^3$, s^{-1}
292.15	1.68 ± 0.06	1.67 ± 1.2

Table 7. Rate of dissociation of $Fe[CN]_5PNP^{3-}$ at different temperatures.

Rate Constant*, $kx10^3$, s^{-1}	5.07 ± 0.11	1.58 ± 0.09	0.31 ± 0.10
Temperature, K	305.15	293.15	283.15

* Average of minimum of three replicates.

Table 8. Activation parameters for the dissociation $Fe[CN]_5PNP^{3-}$

$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
92 ± 3	14 ± 4

DISCUSSION

As seen from the results, the same trend is observed for the reaction between py and $Fe[CN]_5PNA^{3-}$ and py and $Fe[CN]_5PNP^{3-}$. The kinetic study of the overall substitution reaction (6) under pseudo first order condition with excess py concentration shows that the order with respect to $Fe[CN]_5L^{3-}$ is one and the general rate law should be depicted as in (7)

$$Fe[CN]_5L^{3-} + py \rightleftharpoons Fe[CN]_5py^{3-} + L \qquad (6)$$

$$Rate = k_{ob}[Fe[CN]_5L^{3-}] \qquad (7)$$

where L = PNP or PNA. The observed saturation kinetics with respect to the concentration of py, the entering ligand, shows that the release of L becomes the rate-limiting step when the concentration of py is high. This means that ligand substitution involves the formation of an intermediate which combines with py to form the product in the fast step. The kinetics is thus indicative of a D-mechanism for the dissociation of $Fe[CN]_5PNP^{3-}$ and $Fe[CN]_5PNA^{3-}$. The following mechanism is suggested for the dissociation:

$$Fe[CN]_5L^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe[CN]_5^{3-} + L$$

$$Fe[CN]_5^{3-} + py \xrightarrow{k_2} Fe[CN]_5py^{3-} .$$

The rate law for the mechanism is

$$-\frac{d[Fe[CN]_5L^{3-}]}{dt} = \frac{d[Fe[CN]_5py^{3-}]}{dt} = k_2[Fe[CN]_5^{3-}].[py] \qquad (9)$$

$$\frac{d[Fe[CN]_5^{3-}]}{dt} = k_1[Fe[CN]_5L^{3-}] - k_{-1}[Fe[CN]_5][L] - k_2[Fe(CN)_5^{3-}[Py] ($$

Assuming steady state concentration for $[Fe[CN]_5^{3-}]$

$$[Fe[CN]_5^{3-}]_{ss} = \frac{k_1[Fe[CN]_5L^{3-}}{k_{-1}[L] + k_2[Py]} \qquad (11)$$

On substituting Eq. (11) in Eq. (9), we obtain

$$-\frac{d[Fe[CN]_5L^{3-}]}{dt} = \frac{k_1k_2[Fe[CN]_5L^{3-}][py]}{k_{-1}[L] + k_2[py]} \quad . \qquad (12)$$

From Eqs. (7) and (12), the pseudo first order rate constant, k_{ob}, is

$$k_{ob} = \frac{k_1k_2[py]}{k_{-1}[L] + k_2[py]} \quad . \qquad (13)$$

For high concentration of py, such that $k_2[py] >> k_{-1}[L]$,

$$-\frac{d[Fe[CN]_5L^{3-}]}{dt} = k_1[Fe[CN]_5L^{3-}] \qquad (14)$$

i.e., first order in $[Fe[CN]_5L^{3-}]$, zero order in [py] and $k_{ob} = k_1$. Expression (13) for k_{ob} is confirmed from the plot of $1/k_{ob}$ versus 1/[py]. There is excellent conformity between the observed and the calculated values of the limiting rates for both the complexes.

The mechanism of dissociation of octahedral complexes has engaged the attention of inorganic chemists for the past three decades. A vast data concerns the dissociation of Co(III) complexes which are kinetically inert. In general, a dissociative mechanism has been shown to apply for these complexes, though an Id mechanism is often kinetically indistinguishable from a limiting D-mechanism.

Pentacyanoferrate(II) ($Fe[CN]_5X^{3-}$) complexes are an interesting group of low spin Fe(II) complexes which came into prominence with the studies of Toma and Malin on the preparation and rates of dissociation of these complexes where

X is a series of nitrogen hetrocycles [14]. Some others also later reported such studies as discussed in the review of literature .There are just two sketchy references to the dissociation of pentacyano ferrate[II] nitroso complexes in the literature [22, 15]. This is the first time that a detailed study of the kinetics of the dissociation and mechanism of pentacyano aromatic nitroso complexes is reported. As mentioned elsewhere, these are important complexes with convenient absorption bands in the visible spectral region and with high molar absorptivities. These make them ideal candidates for spectrophotometric studies.

As seen from the results, the dissociation of these two complexes also follow the same pattern as observed initially by Toma and Malin [14] and suggests a limiting D-mechanism as indicated by the rate law. The rates of dissociation of $Fe[CN]_5PNP^{3-}$ and $Fe[CN]_5PNA^{3-}$ are of similar magnitude as reported for several other pentacyano ferrates. The rates of dissociation of sulphur bonding ligands like thioureas, cysteine, penicillamine, glutathione are, however, an order of magnitude higher [34, 27], indicating that the sulphur bonding ligands are less energetically held. The rate of dissociation of $Fe[CN]_5PNP^{3-}$ is slightly higher than that of $Fe[CN]_5PNA^{3-}$, indicating a stronger bond in the latter. This is corroborated by the higher enthalpy of activation also for the same. From the slopes of the plot of $1/k_{ob}$ versus $1/[py]$ it has been estimated that k_{-1}/k_2 is $> 10^3$ which suggests that the stability constants of these complexes are at least about three order of magnitude higher than the py complex.

In almost all the studies reported in the literature on

the kinetics of dissociation of $Fe[CN]_5L$ type of compounds, the limiting rates are dependent on the leaving group L, and independent of the replacing ligands which were py [25, 14], DMSO [27], pyrazine [34], methyl pyrazine [22]. Further, the entropy of activation in almost all these cases is positive [25,34] and this is a very strong point in favour of a limiting D-mechanism. Recently Bal Reddy, *et al.* [36] have shown that the dissociation of $Fe[CN]_5L$ complexes gives rise to positive volume of activation which is a strong indication of a D-mechanism for dissociation. It is interesting to note that the complexation of $Fe[CN]_5H_2O^{3-}$ by ligands, which show a first order dependence on the entering ligand and were therefore, earlier assigned an associative or Id mechanism [20, 26] have now been shown to be of limiting dissociative type, based on the positive volume of activation for these reactions[37].

The positive entropy of activation of the dissociation of $Fe[CN]_5PNP^{3-}$ and $Fe[CN]_5PNA^{3-}$, and the rate pattern are conclusive evidence of a limiting D-mechanism. The enthalpy and entropy of activation are very similar to the range reported by other workers [25, 14]. The enthalpy and entropy of activation are both higher for PNA than PNP, while the limiting rate is higher for PNP. The overall rate and entropy of activation suggest a stronger bond with PNA than with PNP. This seems logical, because the dimethyl amino group in the 4-position of the benzene ring should confer a higher basicity on the nitroso-nitrogen, as compared to the electron withdrawing phenolic group in PNP. The higher entropy of activation for the dissociation of $Fe[CN]_5PNA^{3-}$ is in conformity with the bulky nature of PNA as compared to PNP. Since the removal of both

PNA and PNP under the conditions of this experiment do not involve a change in electrostriction of the activated complex, it is expected that the removal of the bulkier PNA should result in higher $\Delta S^{\neq}$. A word of caution may, however, be in order, while drawing a parallel between dissociating ligands of widely varying types and particularly with π-bonds, which have been shown to influence rates and activation parameters [14].

The earlier reactions studied were generally monitored by the appearance of the exchanged complexes of DMSO, py, Pyrazine, Methyl pyrazine, *etc.*, all of which have very low molar absorbitivities. The present study has the advantage of being monitored by the disappearance of the PNA and PNP complexes which have a very high molar absorbitivities in spectral region far removed from those of the entering or leaving ligands and $Fe[CN]_5H_2O^{3-}$ and avoid any overlap patterns. These can be used as model experiments for graduate courses in Inorganic Chemistry dealing with mechanism of dissociation of inorganic complexes.

The limiting D mechanism is relatively rare for inorganic substitutions. It is not often that loss of a ligand from a complex leaves a species stable enough to persist long enough to discriminate between leaving and potential entering groups. In the case of the pentacyanoferrates(II), the very high ligand field of the cyanides seems to be just enough for five of them to confer limited life on $[Fe[CN]_5]^{3-}$. It is interesting to note that the next metal, cobalt, forms only a pentacyano-complex in the 2+ oxidation state - $[Co[CN]_5]^{3-}$ and not $[Co[CN]_6]^{4-}$. The D mechanism does operate in a number of important biochemical systems. Such entities as haem have iron

with four very strongly bound nitrogen atoms from a macrocyclic yyring. If the fifth coordination position has another firmly bound ligand, such as histidine-nitrogen from another part of the enveloping protein, then the ligand replacement reaction may take place at the sixth coordination site by the D-mechanism. Several instances are known at this type of iron site, and others at other metals such as cobalt [10]. The difference in C.F.S.E. for a penta coordinated square pyramidal and trigonal bipyramidal intermediate for Fe(II) is ~ 4.5 kcal $mole^{-1}$ in favour of the former. However, the π-bonding ligands like CN^- may stabilize the latter, due to better π-bonding overlap [5].

4.4 Kinetics of the Hg(II) promoted dissociation of $Fe[CN]_5PNA^{3-}$

RESULTS

4.4.1 Nature of the Product

Aliquots of $2x10^{-4}$ M $Fe[CN]_5PNA^{3-}$ and 10^{-2} M $HgCl_2$ were mixed to give a series of solutions containing $[HgCl_2]$ and $[Fe[CN]_5PNA^{3-}]$ in the ratio of 20:1 to 5:1. The spectrum of the mixture showed that the abstraction of CN^- and PNA were complete within 30 minutes. The final product of the reaction was Fe^{2+}(aquo). This was confirmed by adding bipy and phen, after the reaction is over, which resulted in the formation of intense red and orange red coloured tris-Bipyridine and trisiphenantroline Fe[II] complexes, respectively.

On mixing $Fe[CN]_5PNA^{3-}$ and mercuric chloride solutions, a dusty green product was formed immediately which changed colour very fast to almost the original colour. At temperatures > 8 °C, the product could not be scanned as the colour change was very fast. At 1 °C, a spectral scan was possible within 30 - 60 seconds after mixing. The spectra are given in Fig. 8. This clearly established the formation of a transient adduct between $HgCl_2$ and $Fe[CN]_5PNA^{3-}$ which undergoes a fast change, before the abstraction of CN^- takes place. The transient adduct formation and its change was also indicated by an initial increase in absorbance at low temperature at 650 nm, before the decomposition started.

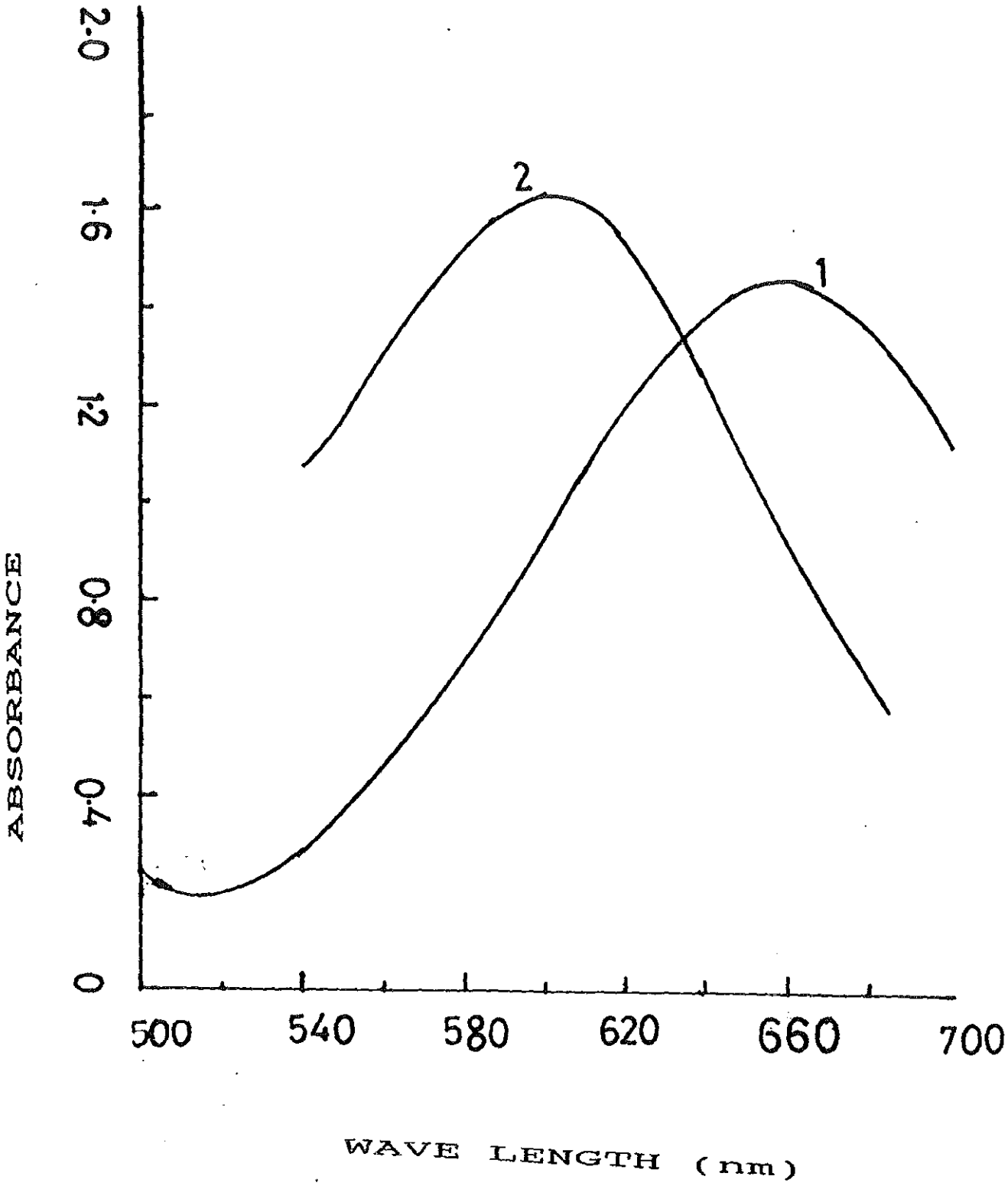


Fig.8. Spectra of:

1. $5x10^{-5}$ M $Fe(CN)_5PNA^{3-}$ at 1 °C
2. $5x10^{-5}$ M $Fe(CN)_5PNA^{3-}$ + $2x10^{-4}$ $HgCl_2$ at 1 °C

4.4.2 Kinetics

The rate of the reaction was measured from the rate of disappearance of $Fe[CN]_5PNA^{3-}$. For this, the decrease in absorbance with time at 650 nm was monitored. Kinetics was observed for more than three half lives in all cases and under pseudo first order condition with excess $HgCl_2$.

The first order rate constants obtained as the slope of plot of $-\ln(A_\infty - A_t)$ versus time for different concentrations of $HgCl_2$ are given in Table 9.

The kinetic data showed that the rate constants increased initially with an increase in $HgCl_2$ concentration and reached a limiting value when about 10 fold excess of $HgCl_2$ is present, Fig. 9. The attainment of a limiting rate for $HgCl_2 > 10$, clearly indicated the presence of a strong equilibrium formation of an adduct between $Fe[CN]_5PNA^{3-}$ and Hg(II) prior to the abstraction of PNA and CN^-. The rate data were therefore analyzed for the probable formation of a 1:1 adduct and a 2:1 adduct between Hg(II) and $Fe[CN]_5PNA^{3-}$ prior to abstraction. The calculated limiting rate agreed closely with that experimentally found for a 2:1 adduct, Table 10. The rate constant k_1 was obtained as reciprocal of the intercept and K as the (intercept/slope) of the plot of $1/k_{ob}$ versus $1/[HgCl_2]^2$.

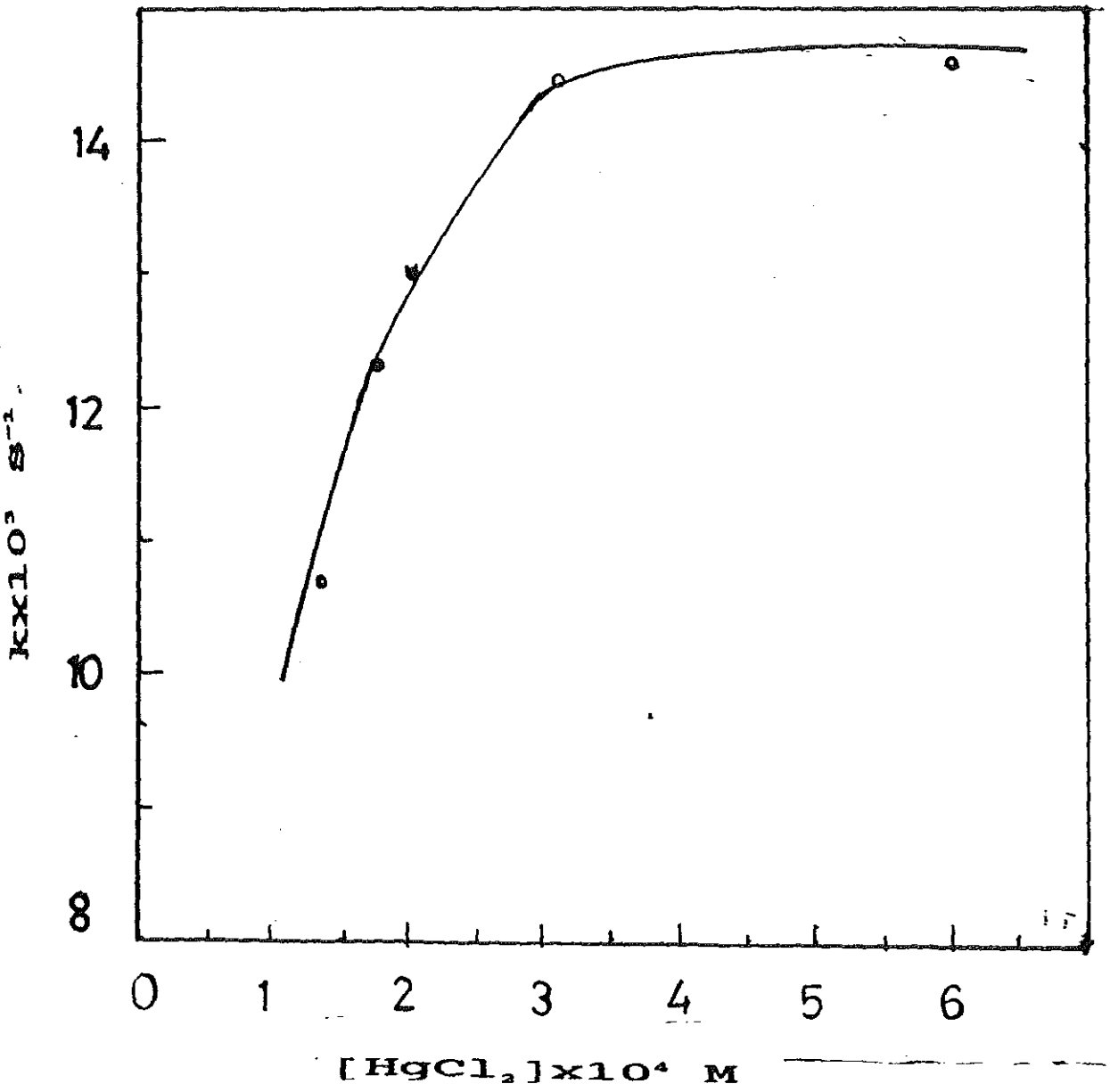


Fig.9. Rate Constants Vs. [$HgCl_2$]

4.4.3 Activation parameters

Rate constants at different temperatures are given in Table 11. The entropy and enthalpy of activation for the reaction as calculated from the absolute reaction theory from ln(k/T) versus 1/T (Fig. 10) are given in Table 12.

4.4.4 Attempts to characterize the adduct

At high $HgCl_2$ concentrations, a dark green precipitate was formed which is probably the adduct of $Fe[CN]_5PNA^{3-}$ and $HgCl_2$. The precipitate was filtered out at 4^0C decomposed with concentrated HNO_3 and analyzed for Fe(II) and Hg(II) as given in chapter 3. The results indicate a 1:2 Fe:Hg(II) ratio.

Table 9. Pseudo-first order rate constants ($kx10^3$, s^{-1}) at different concentrations of $HgCl_2$

Conc. of $HgCl_2$ x 10^4(M)	Rate Constant ($kx10^3$)*, s^{-1}
1.30	10.06 ± 0.06
1.72	12.30 ± 0.04
2.00	13.00 ± 0.05
2.40	14.30 ± 0.08
3.10	14.47 ± 0.02
6.00	14.60 0.06

* Average of minimum of three replicates;

$[Fe[CN]_5PNA^{3-}] = 5x10^{-5}$ M; T = 292.15 k.

Table 10. Equilibrium constants and limiting rates for Hg(II) promoted dissociation of $Fe[CN]_5PNA^{3-}$

Temp., K	$K[M^{-2}]x10^7$ [2:1]	Exptl., $kx10^3$, s^{-1}	Caltd., $kx10^3$, s^1 [2:1]
292.15	12.57 ± 0.9	14.56 ± 0.07	15.60 ± 0.32

Table 11. Rate constants $(kx10^3)^*$ at different temperatures

Temperature, K	295.15	288.65	282.15
Rate constant,	14.47 ± 0.01	8.53 ± 0.08	2.71 ± 0.00

* Average of at least four replicates; $[HgCl_2] = 1x10^{-3}M$; $[Fe[CN]_5PNA^{3-}] = 5x10^{-5}M$.

Table 12. Activation parameters for Hg[II] promoted dissociation of $Fe(CN)_5PNA^{3-}$

$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
104 ± 3	71 ± 6

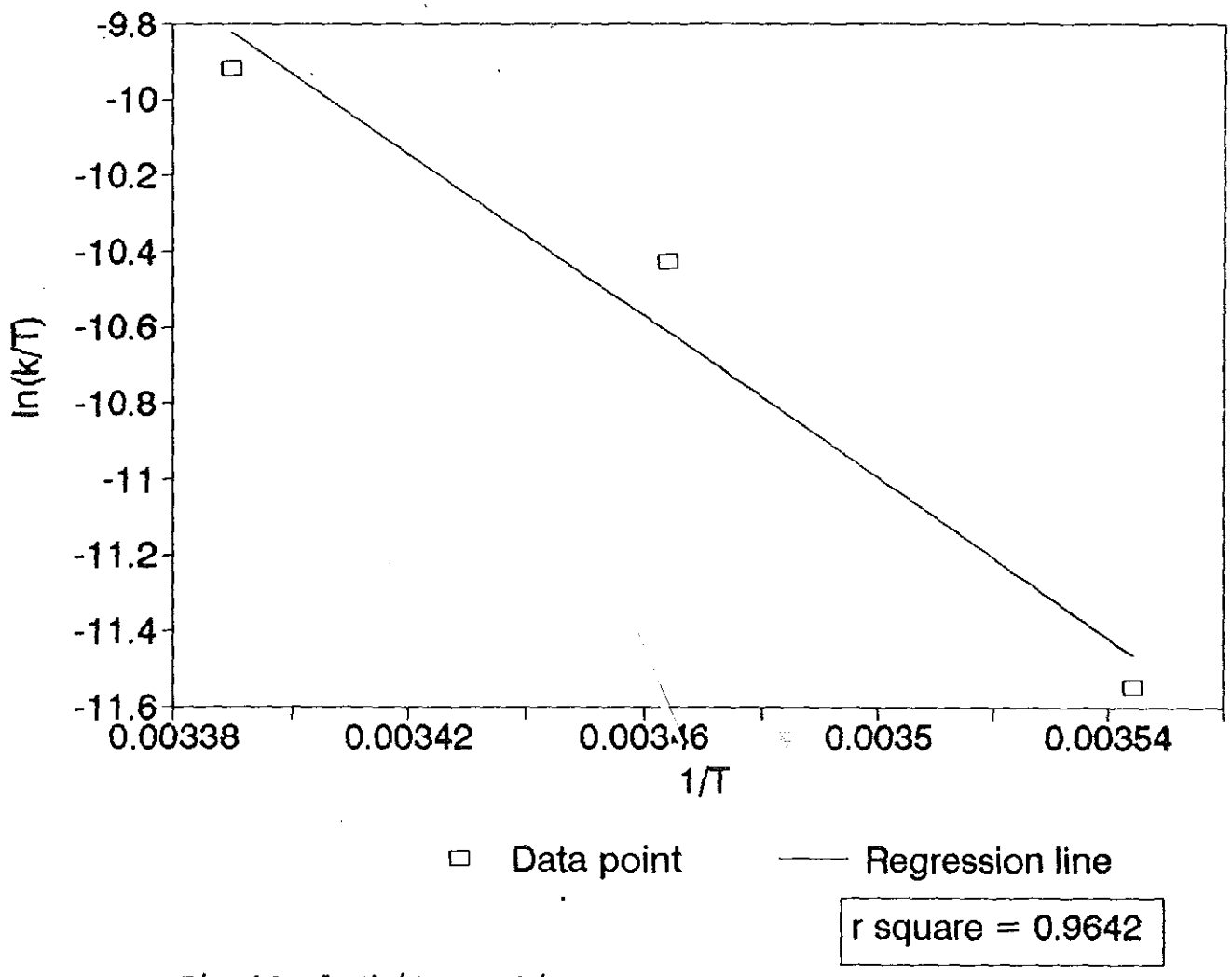


Fig.10. ln(k/T) vs 1/T

4.5 Kinetics of the Hg(II) promoted dissociation of $Fe[CN]_5PNP^{3-}$ complex

RESULTS

4.5.1 Nature of the product

Aliquots of 10^{-2} M $HgCl_2$ and $2x10^{-4}$ M $Fe[CN]_5PNP^{3-}$ were mixed to give a series of solutions containing $[HgCl_2]$ and $Fe[CN]_5PNP^{3-}$ in the ratio of 20:1 to 5:1. The spectra of the mixtures were scanned with time, the maximum absorption band of $Fe[CN]_5PNP^{3-}$ disappeared within 20 min. Addition of bipyridine and phenantroline, confirmed the complete abstraction of $Fe[CN]_5PNP^{3-}$ under these conditions.

On mixing $Fe[CN]_5PNP^{3-}$ and mercuric chloride solutions, a pink product was formed which changed colour very fast to almost the original colour, intense blue. At temperatures > 8 °C, the product could not be scanned as the colour change was very fast. At 1 °C, spectral scan are given in Fig. 11. This clearly established a transient adduct between $HgCl_2$ and $Fe[CN]_5PNP^{3-}$ which undergoes a fast change before the abstraction of CN^- takes place. The transient adduct formation and its change was also indicated by an initial increase in absorbance at low temperatures at 575 nm, before the decomposition started.

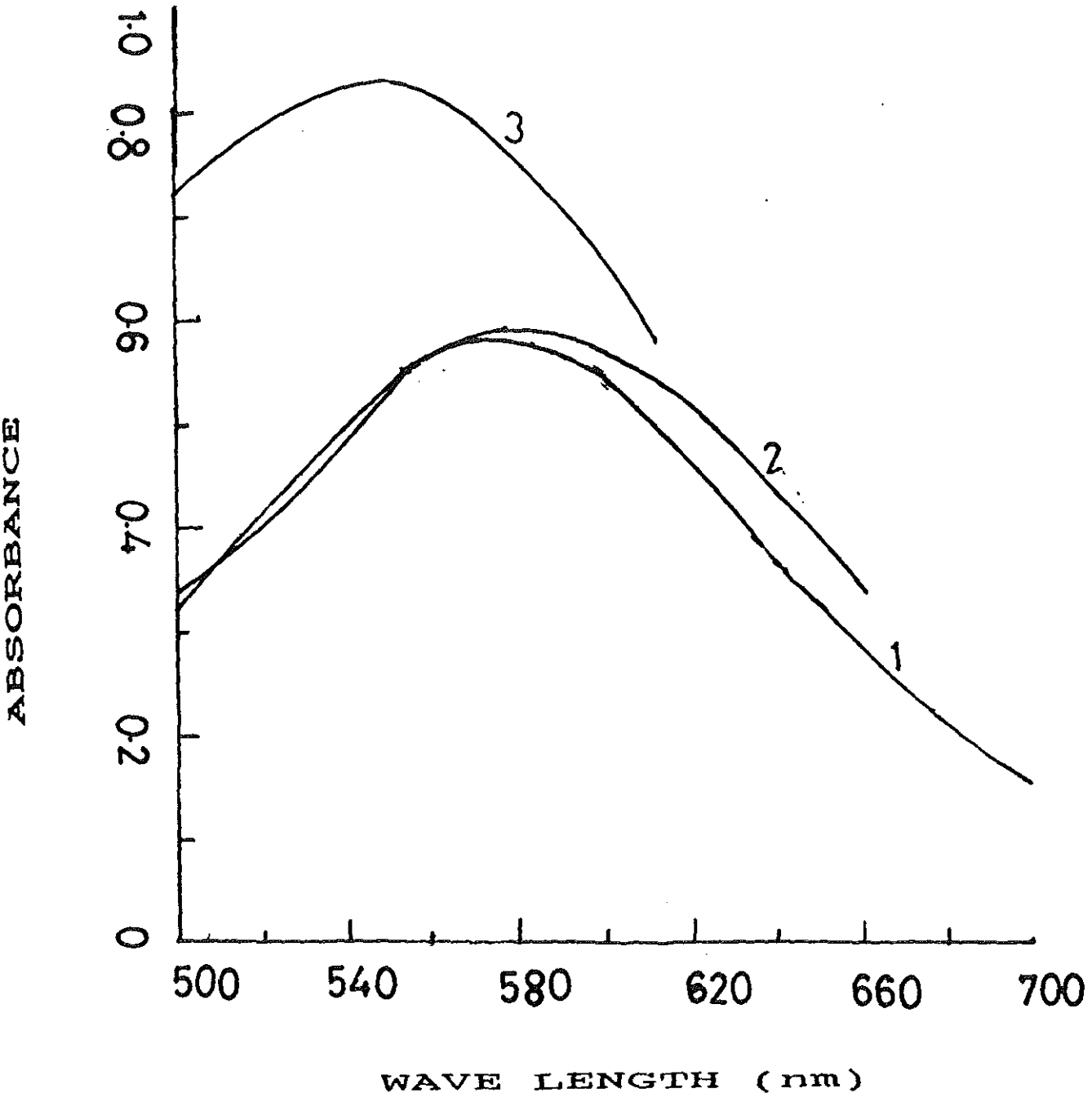


Fig. 11. Spectra of:

1. $5x10^{-5}$ M $Fe[CN]_5PNP^{3-}$ at 1 °C
2. $5x10^{-5}$ M $Fe[CN]_5PNP^{3-}$ + $2x10^{-4}$ $HgCl_2$ at 20 °C
3. $5x10^{-5}$ M $Fe[CN]_5PNP^{3-}$ + $2x10^{-4}$ $HgCl_2$ at 1 °C

4.5.2 Kinetics

The rate of the reaction was measured from the rate of disappearance of $Fe[CN]_5PNP^{3-}$. For this, the absorbance at 575 nm was monitored at suitable time intervals.

The data gave very good correlation for $-\ln(A_\infty - A_t)$ versus time for 80% of the completion of the reaction. The pseudo first order rate constants increased continuously with an increase in $HgCl_2$ concentration and reached a limiting value for $([HgCl_2]:[Fe[CN]_5PNP^{3-}]) > 8$, Fig. 12.

First order rate constants at different concentrations of $HgCl_2$ are give in Table 13. Since the limiting value for first order rate constant indicates a pre-equilibrium step with the formation of an adduct which dissociates later, the rates were analyzed for the formation of a 1:1 and 2:1 binuclear complexes. The rates agreed closely with that experimentally found for a 2:1 adduct, Table 14.

4.5.3 Activation parameters

The rate constants at different temperatures are given in Table 15. The entropy and enthalpy of activation for the reaction as calculated from the absolute reaction theory from $\ln(K/T)$ versus $1/T$, Fig. 13, are given in Table 16.

4.5.4 Attempt to characterize the adduct

As in the case of PNA complex, at high $HgCl_2$ concentration, there was a precipitate of a dark blue product which probably is the adduct. The precipitate was isolated, decomposed with concentrated HNO_3 and analyzed for Fe and Hg(II) as given in chapter 3. The results were indicative of a 2:1 Hg(II):Fe ratio.

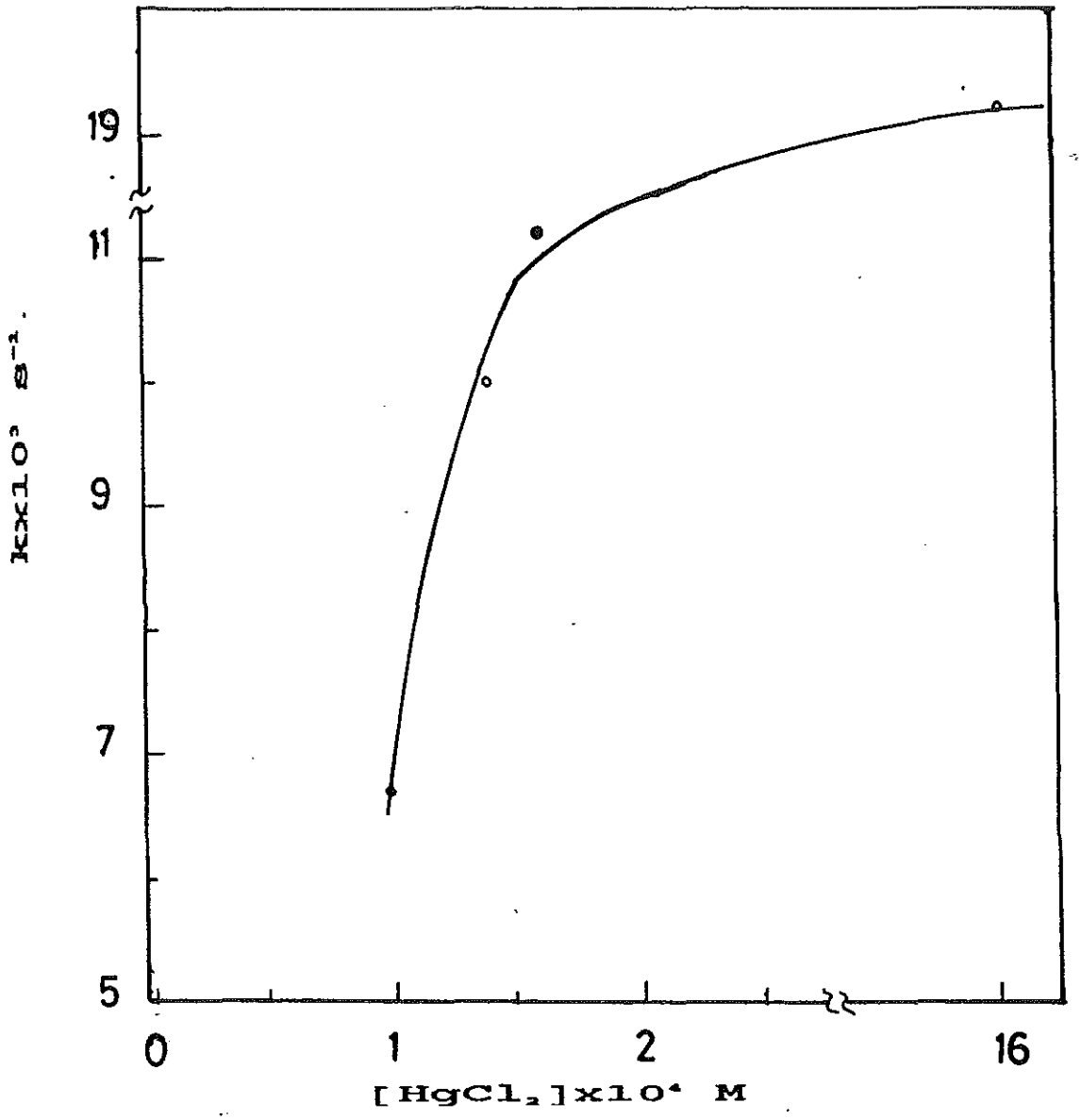


Fig. 12. Rate Constants Vs [$HgCl_2$]

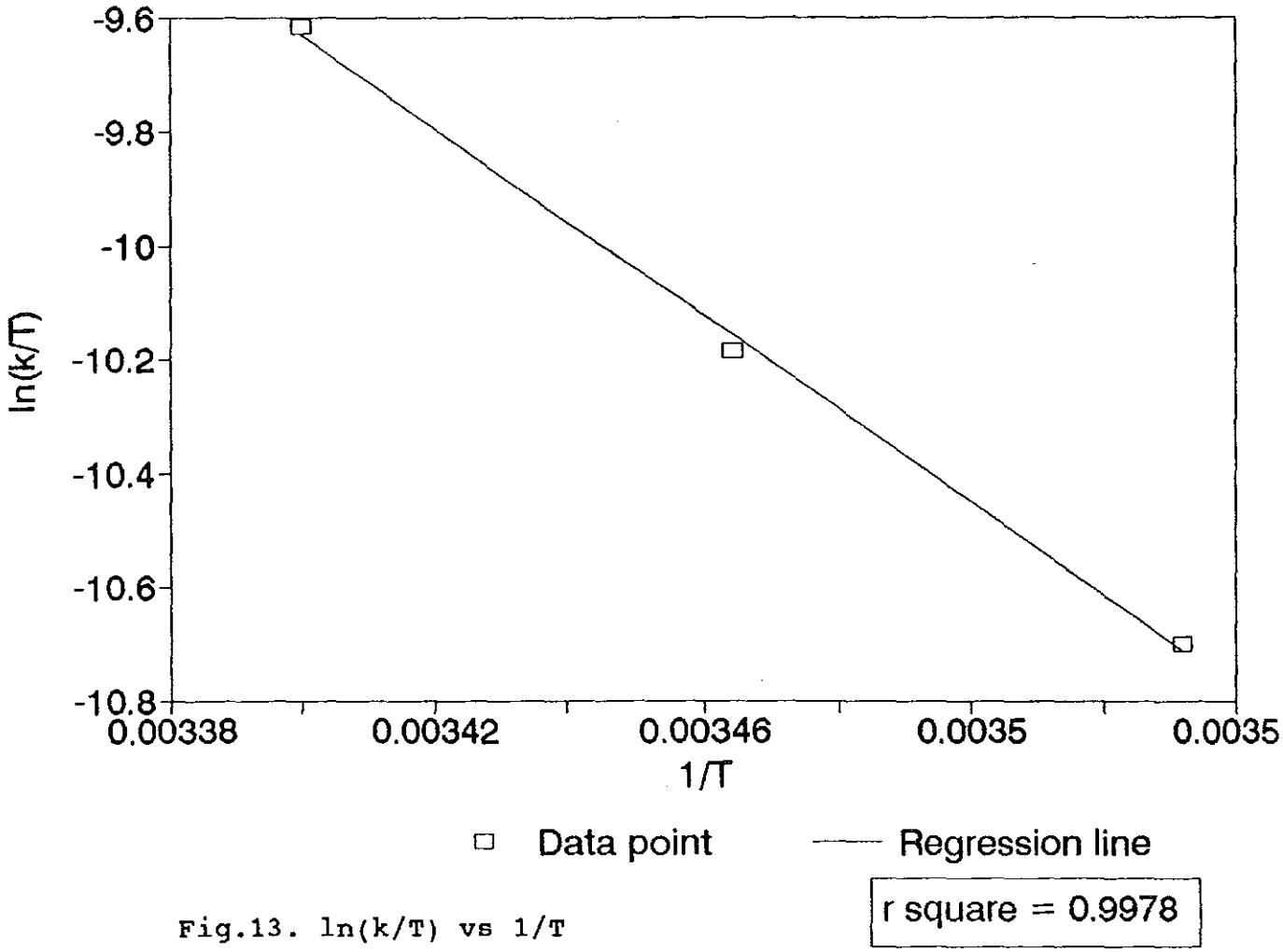


Fig.13. ln(k/T) vs 1/T

Table 13. Rate constants ($Kx10^3$, s^{-1})* at different concentrations of $HgCl_2$

Conc. of $HgCl_2$ x10^2 M	0.5	1.0	1.4	1.6	16
Rate conts.	2.50 ± 0.02	6.69 ± 0.05	10.00 ± 0.03	11.20 ± 0.05	19.58 ± 0.06

* Average of at least three replicates; Temp. = 293.15 K; $[Fe[CN]_5PNP^{3-}]$ = $5x10^{-5}$ M.

Table 14. Equilibrium constants and limiting rates for Hg(II) promoted dissociation of $Fe[CN]_5PNP^{3-}$

$K[M^{-2}]x10^{-7}$ 2:1 Adduct	Calctd., $kx10^3$, s^{-1}	Exptl.$kx10^3$, s^{-1}
6.49 ± 0.90	19.61 ± 0.05	19.58 ± 0.17

Temp. = 293.15 K; $[Fe[CN]_5PNP^{3-}]$ = $4x10^{-5}$ M.

Table 15. Rate constants ($kx10^3$ s^{-1})* at different temperatures

Temp., K	294.15	288.65	283.15
Rate const.	19.58 ±0.06	10.88 ±0.09	7.06 ±0.05

* Average of at least 3 replicates.

Table 16. Activation parameters

$\Delta H^{\ddagger}$ (kJ/mole)	$\Delta S^{\ddagger}$ (J/K mole)
86 ± 1	16 ± 3

DISCUSSION

It is well known that Hg(II) being a class "b" metal ion (soft acid) exhibits high affinity for ligands (soft bases) like halides (Cl^-, Br^-, I^-), sulphide, CN^-, SCN^-, *etc.*, and is thus capable of abstracting these when coordinated to Fe(II), Co(III), Rh(III), Ru(III), *etc.*

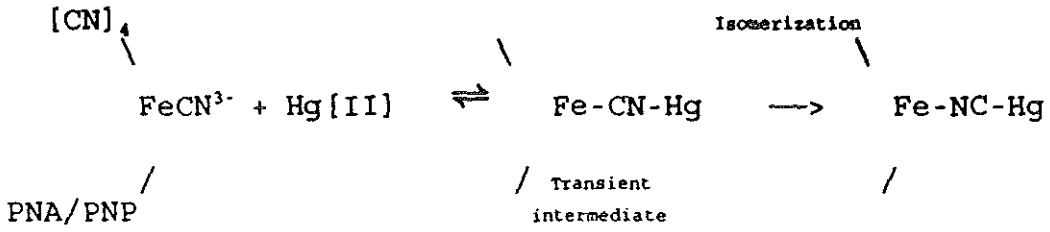
The quantitative formation of $Fe[bipy]_3^{3+}$ or $Fe[phen]_3^{2+}$ when $Fe[CN]_5PNP/PNA^{3-}$ is reacted with excess $HgCl_2$ shows that the abstraction of CN^- is complete and the reaction proceeds as follows

$$5Hg(II) + 2Fe[CN]_5PNP/PNA^{3-} \longrightarrow 5Hg[CN]_2 + 2Fe^{2+} + 2PNP/PNA$$

It is seen from the results that the pseudo first order rate reaches a limiting value in both $Fe[CN]_5PNP^{3-}$ and $Fe[CN]_5PNA^{3-}$. This indicates that strong adducts are formed prior to the abstraction of CN^- in both cases.

The formation of adducts between $HgCl_2$ and $Fe[CN]_5PNP/PNA^{3-}$ is confirmed by the formation of products with completely different spectral characteristics as shown in the results. The formation of pink product for $Fe[CN]_5PNP^{3-}$ and $HgCl_2$, and the dusty green adduct for $Fe[CN]_5PNA^{3-}$ and $HgCl_2$ are definite intermediates before cyanide abstraction. These are transient and revert very quickly to blue black and green colours similar to that of the original complexes. Since the change is so fast, an isosbestic point could not be obtained with existing facilities. The half life for the change of these transient products is of the order of a few seconds even at 5 °C. The transient change is further indicated by a small initial increase in absorbance after mixing at 575 nm and 650 nm for $Fe[CN]_5PNP^{3-}$ and $Fe[CN]_5PNA^{3-}$ respectively, at lower temperature.

In this connection, it is interesting to note that there are reports about mercury(II) catalyzed linkage isomerization for the reaction of $HgCl_2$ and $CrSCN^{2+}$, where $Hg\text{-}CNSCr^{4+}$ is first formed as intermediate which changes to HgSCN[47]. Similarly in the oxidation of $Fe[CN]_5SCN^{4-}$ with $Fe[CN]_6^{3-}$ a transient purple intermediate at λ = 550-560 nm of the form $Fe[CN]_5SCN^{3-}$ is formed which undergoes fast isomerization to blue $[CN]_5FeNCS^{3-}$ [72]. Hence it is possible that the transient intermediate in the case of $Fe[CN]_5PNP/PNA^{3-}$ are N-bonded-Hg isomers which change to the more stable C-bonded-Hg adducts as follows



The kinetic data were analyzed for the probable formation of a 1:1 adduct and 2:1 adduct between $HgCl_2$ and $Fe[CN]_5PNP^{3-}$, $HgCl_2$ and $Fe[CN]_5PNA^{3-}$ prior to CN^- and PNP/PNA abstraction.

The calculated limiting rates for both complexes correspond closely to the experimentally found rates, for 2:1 adducts, prior to CN^- abstraction.

$$Fe[CN]_5PNA/PNP^{3-} + 2Hg(II) \overset{K_e}{\rightleftharpoons} [\ Hg(II)\text{-}Fe[CN]_5PNA/PNP^{3-}Hg(II)\ ]$$

$$\downarrow k_1$$

$$Fe^{2+} + 2Hg[CN]_2 + CN^- + PNA/PNP$$

The rate law for the above mechanism is

$$k_{ob} = \frac{k_1 K_e [HgCl_2]^2 [Fe(CN)_5 x]}{1 + K_e [HgCl_2]^2}$$

At high $[HgCl_2]$, $k_{ob} = k_1$, for both cases.

The formation of stable adducts prior to abstraction of soft ligands by Hg(II) has been shown to occur in almost all cases of abstraction of CN^- from $Fe[CN]_6^{4-}$ [50,59,63,51] and even when both Hg(II) and the complexes decomposed are cationic [64,44,47,40,65].

Positive entropy of activation support a D type of dissociation of the intermediate in the rate determining step. The enthalpy and entropy of activation are both higher for $Fe(CN)_5PNA$ than for $Fe(CN)_5PNP$; as in the case of simple ligand

dissociation.

4.6 Kinetics of acid catalyzed dissociation of $Fe[CN]_5PNA^{3-}$

RESULTS

4.6.1 Nature of the complex in acidic media

It was shown earlier that the complex was stable for more than 24 h. in neutral medium. Preliminary investigation showed that the dissociation of the complex was accelerated by acids. In order to see if this was a case of general acid catalysis (aquation) of the complex or a specific case of proton catalyzed dissociation of the complex, a detailed study of the nature of the complex in the presence of acid was undertaken. The spectrum of the free ligand and the complex at different acid concentrations are given in Fig. 14 and Fig. 15, respectively.

The λ_{max} for the free ligand shifted from 440 nm in neutral media to 347 nm in acidic medium, due to protonation. The spectrum remained unchanged from $[H^+] = 10^{-3}$ to 1 M indicating that only a monoprotonated species was formed at all these acid concentrations. This is in conformity with an earlier investigation which gave a pKa of 4.1 ± 0.05 for PNA[52].

The spectrum of the complex under the same conditions showed that its λ_{max} shifted from 650 nm in neutral medium to 750 nm in 0.001 M acid. It was also seen that the dissociation of the complex at this acid concentration was much faster than in neutral medium but still quite low to make too much difference in the life span of spectral scan.

The spectrum of the complex was scanned at low (3 °C) temperatures for [H⁺] = 0.01 to 1 M acid, Fig. 15, because the dissociation was fast. There was a small but gradual shift in the λ_{max} from 750 nm at 0.001 M acid to about 735 nm at 1 M acid. This together with a very marked increase in the rate of dissociation indicated a second stage protonation of the complex at [H⁺] ≥ 0.01 M. Hence detailed kinetic studies were taken up at these acid concentrations for the dissociation of the complex.

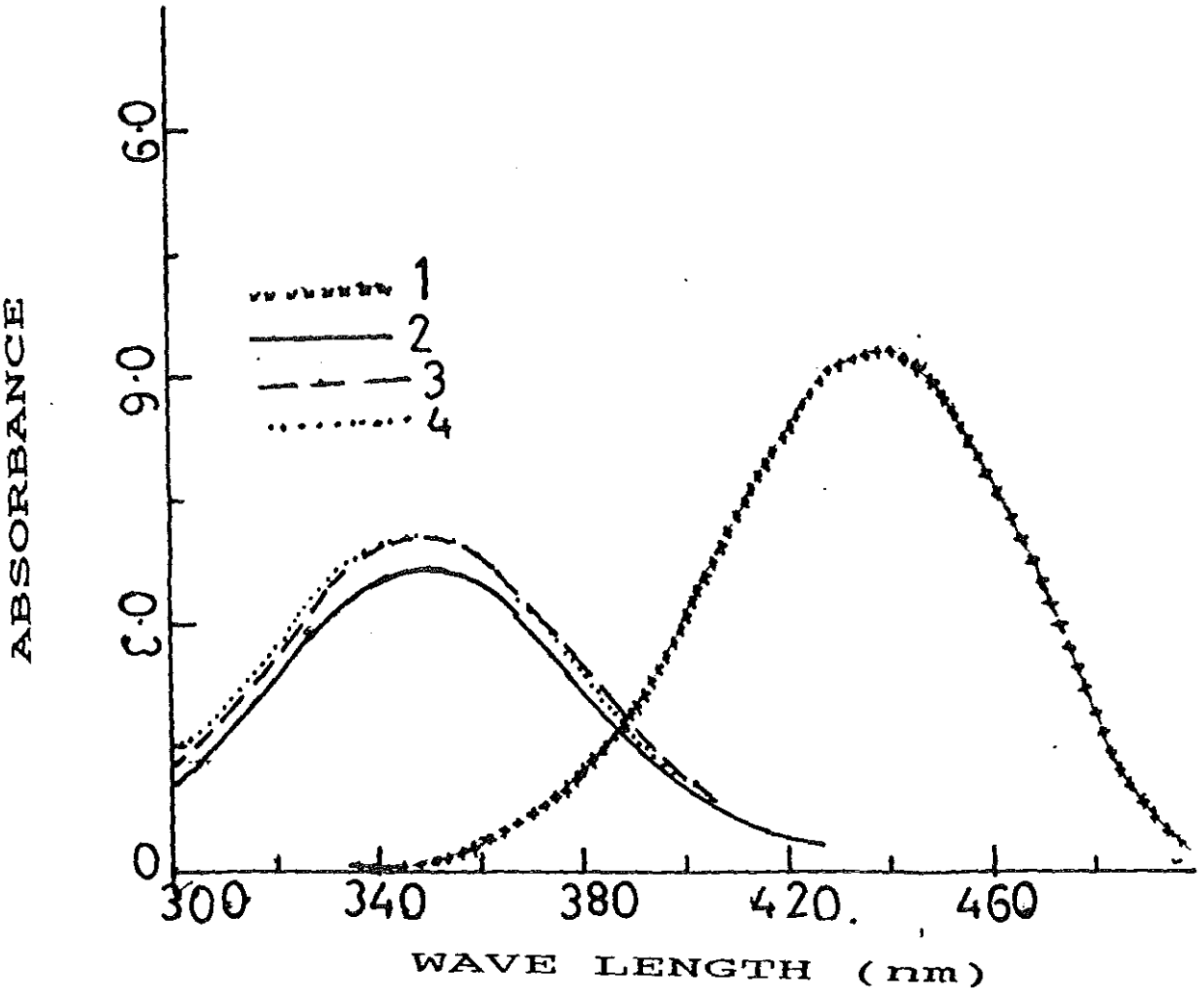


Fig. 14. Spectra of:
1. 1.10^{-4} M PNA ligand
2. 2.10^{-4} M PNA in 1 M acid
3. 3.10^{-4} M PNA in 0.1 M acid
4. 4.10^{-4} M PNA in 0.01 M acid

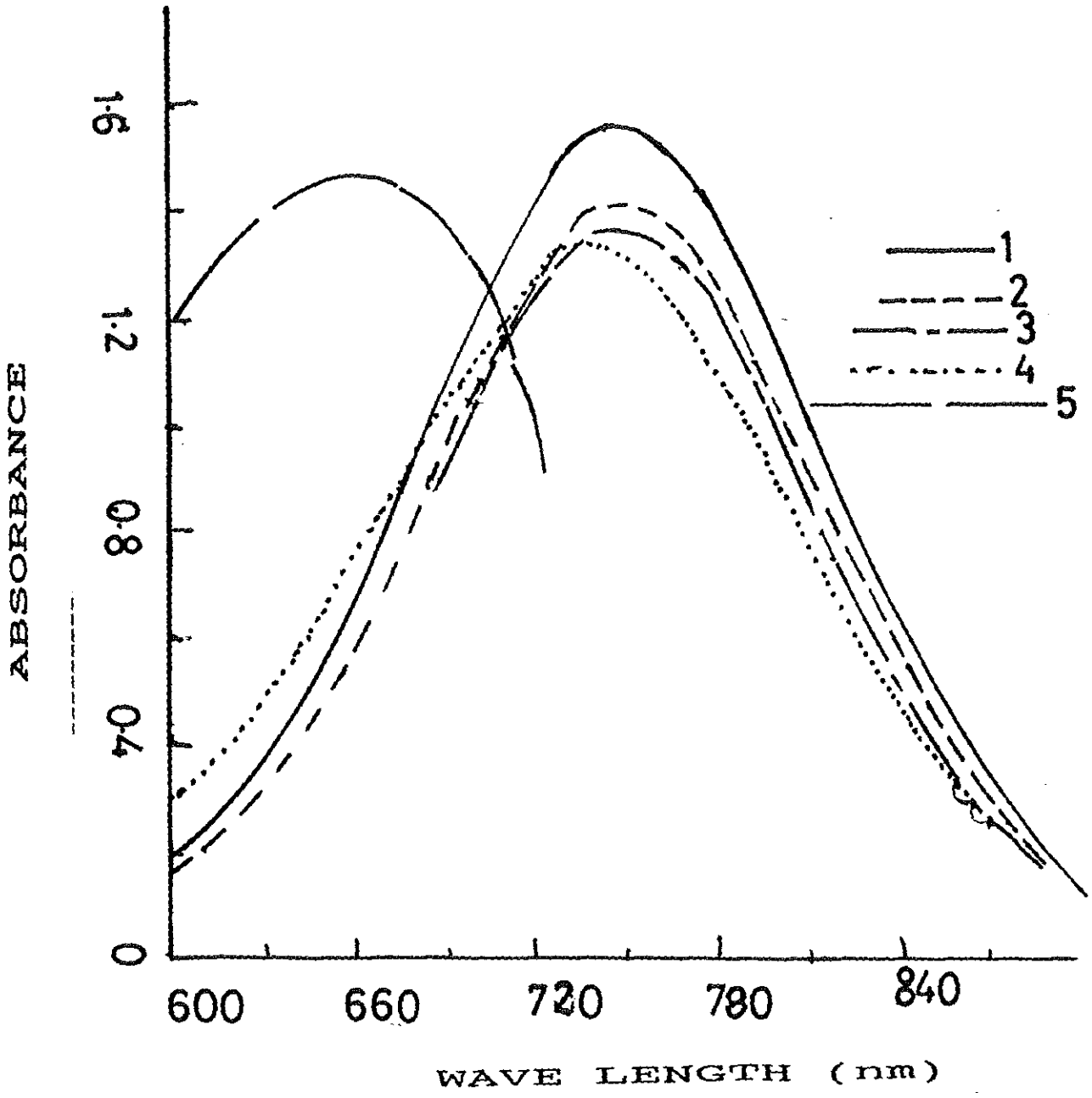


Fig. 15. Specua of:

1. $5x10^{-5}$ M $Fe[CN]_5PNA^{3-}$ + 10^{-3} M acid at 3 °C
2. $5x10^{-5}$ M $Fe[CN]_5PNA^{3-}$ + 10^{-2} M acid at 3 °C
3. $5x10^{-5}$ M $Fe[CN]_5PNA^{3-}$ + 10^{-1} M acid at 3 °C
4. $5x10^{-5}$ M $Fe[CN]_5PNA^{3-}$ + 1 M acid at 3 °C
5. $5x10^{-5}$ M $Fe[CN]_5PNA^{3-}$ at 3 °C

4.6.2 Kinetics

The rate of the reaction was measured from the rate of disappearance of the protonated complexes at 0.001 to 1 M $HClO_4$. For this the decrease in absorbance at 750 nm with time was monitored.

Kinetic data showed that there was excellent linearity for log[A] versus time at 0.001 M acid, indicating a pseudo first order kinetics. The pseudo first order rate constants at different temperatures for the dissociation the complex in 0.001 M acid are given in Table 17. The activation parameters were calculated (Fig. 16) and are given in Table 18.

At 0.01 to 0.1 M acid concentrations there is a fast initial rate of dissociation followed by a much slower step. The plot of log[A] versus time gave two distinct straight lines, one with a much steeper slope than the other, indicating two first order kinetic steps for the dissociation. The rate constants for these biphasic kinetics steps were resolved by extrapolating the slower rate plot to zero time. The faster rate was obtained from the difference slope of the initial and the extrapolated lines. The rate constants for dissociation were 3.4×10^{-2} s^{-1} for the fast step and 2×10^{-4} s^{-1} for the slower step.

In 1 M acid, the rates were very fast and showed only one step dissociation by pseudo first order kinetics. The rates at different temperatures are given in Table 19 and the activation parameters at Table 20. Figure 18 shows the plot of ln(k/T) vs. 1/T.

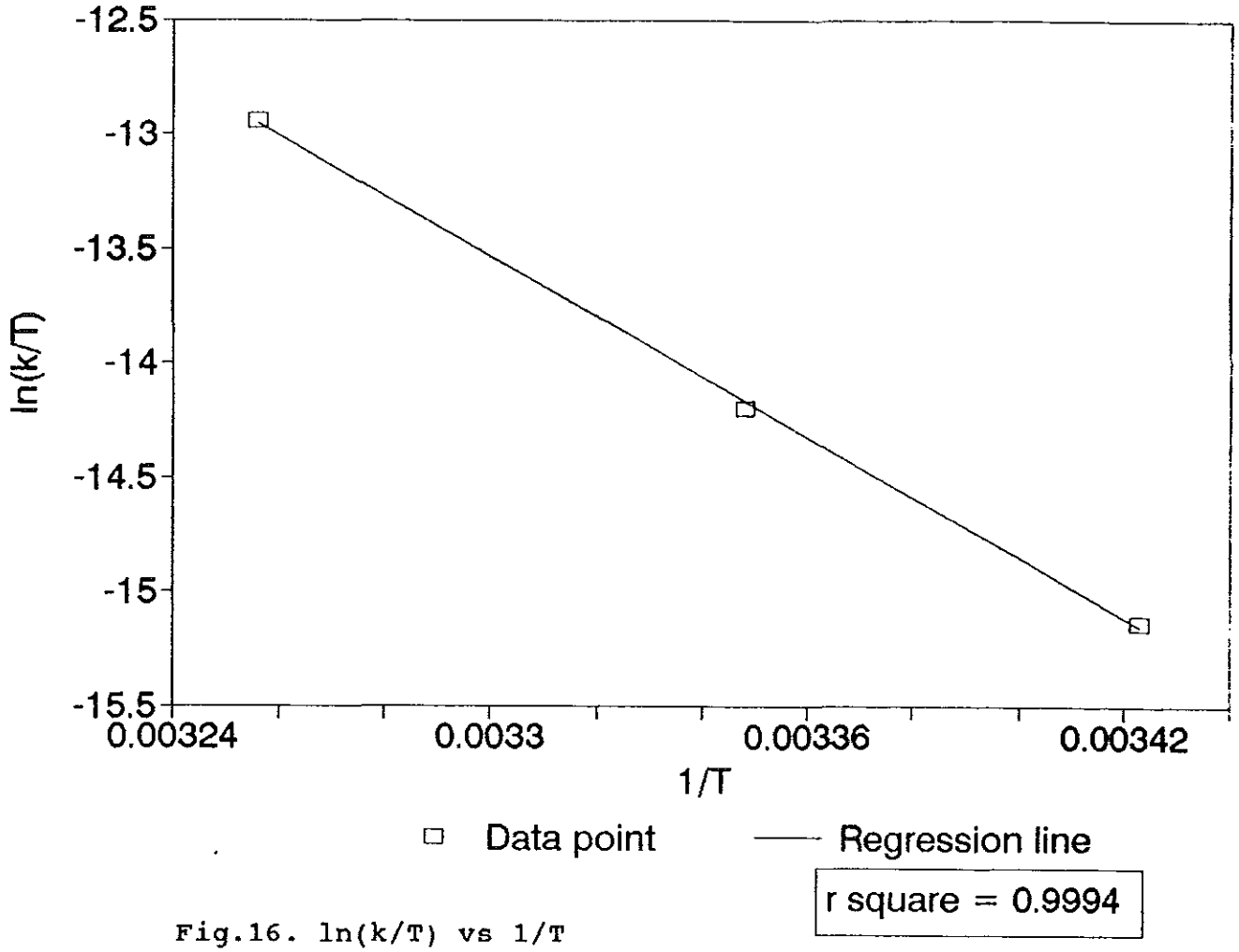


Fig.16. ln(k/T) vs 1/T

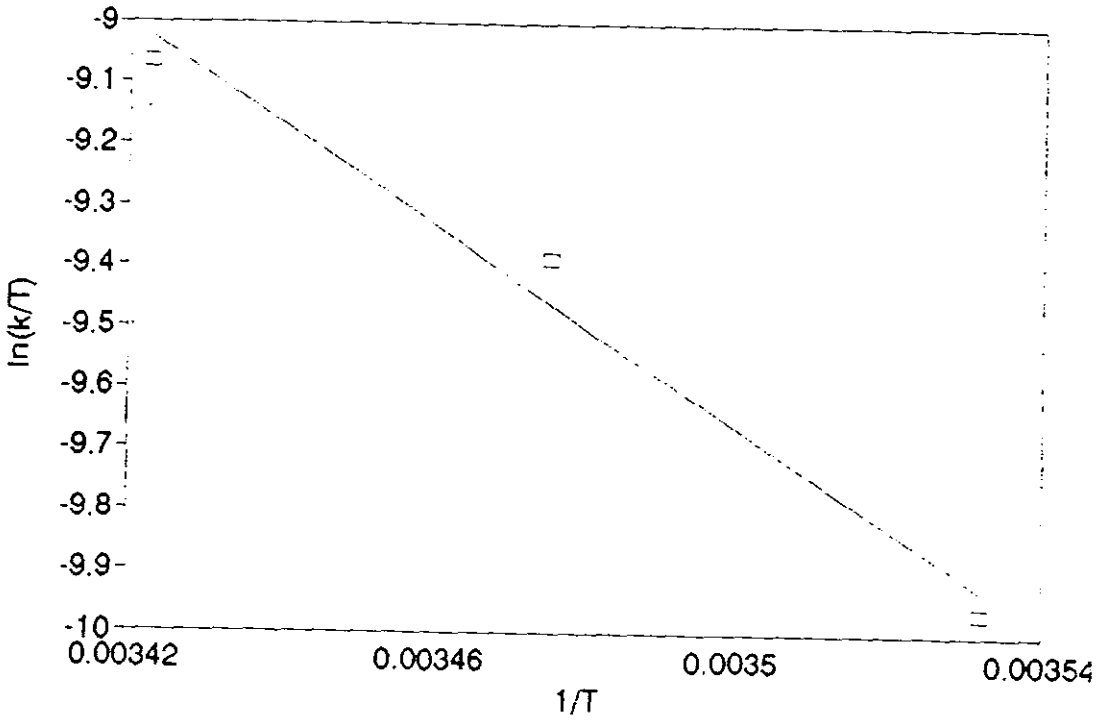


Fig.17. ln(k/T) vs 1/T

Table 17. Rate constants ($kx10^4$, s^{-1})* for acid catalyzed dissociation of $Fe(CN)_5PNA$ at different temperatures; $[Fe[CN]_5PNA^{3-}] = 2x10^{-5}$ M; $[HClO_4]$ = 0.001 M

Temp., K	292.15	298.65	307.15
Rate const.	0.78 ±0.02	2.04 ±0.03	7.36 ±0.02

* Average of at least 3 replicates.

Table 18. Activation parameters for the acid catalyzed dissociation of $Fe(CN)_5PNA$ in $[H^+]$ = 0.001M HCl.

$\Delta H^{\#}$ (kJ/mole)	$\Delta S^{\#}$ (J/mole K)
113 ± 2	65 ± 5

Table 19. Rate constants ($kx10^2$, s^{-1})* for the dissociation of $Fe(CN)_5PNA^{3-}$ at different temperatures

$[Fe[CN]_5PNA^{3-}] = 3.2x10^{-5}$ M; $[HClO_4]$ = 1 M.

Temp., K	292.15	287.65	283.15
Rate const.	3.38 ±0.04	2.41 ±0.05	1.33 ±0.07

* Average of at least 3 replicate.

Table 20. Activation parameters for the dissociation of $Fe[CN]_5PNA^{3-}$ in 1 M $HClO_4$

$\Delta H^{\ddagger}$ (kJ/mole)	$\Delta S^{\ddagger}$ (J/mole K)
86 ± 2	22 ± 4

DISCUSSION

$Fe[CN]_5PNA^{3-}$ has a tertiary amine substituent (N,N-Dimethyl amine) which is a base. Hence it should be protonable in acidic medium. The spectral characteristics of the free ligand and that of the complex confirm the protonation of the ligand in the free state and in the complex. These results are in conformity of the earlier investigation which assigned pKa of 4.1 ± 0.05 to the PNA and 4.3 ± 0.1 to the complex [52]. The protonation equilibrium can be written as follow for the free ligand and the complex

$$PNA + H^+ \rightleftharpoons PNAH^+$$

$$Fe[CN]_5PNA^{3-} + H^+ \rightleftharpoons [Fe[CN]_5PNAH]^{2-}$$

The protonation of some pentacyano ferrate(II) complexes, $Fe[CN]_5X$ with bases where X ≡ pyridine, isonicotineamide, and N-methyl-pyrazinium ion ($Me(pyr)^+$) was reported earlier by Toma and Malin [14], who found the pKa values to be 2.1, 1.9, and 0.73, respectively at = 0.10 M. They, however, attributed the protonation to the protonation of CN^- group. Later, Malin and Koch [24] studied also the protonation of $Fe[CN]_5H_2O^{3-}$ by complexing with $Me[pyr]^+$ at different pH and gave a value of pka = 2.63 ± 0.12 at 25 °C and = 1.0 M. The same was later confirmed by McAuley [34].

There are reports on pentacyanoferrate(II) complexes with acidic ligands ($HL \rightleftharpoons H^+ + L^-$) like cysteine, glutathione, penicillamine [34], nicotine acid and isonicotinohydrazide [22], HCN and HSO_3^- [66] and some highly basic amines like hexane-1,6-diamine [23], ethylene diamine [21], 2-mercapto ethyl amine [34] for which the pKa is 8 - 11 . The acid dissociation constant has been determined for these complexes and pK_a value of the free and the metal coordinated ligands have been found to be quite similar.

4.6.3 Dissociation of $Fe[CN]_5PNA^{3-}$ at $[H^+] = 10^{-3}$ M

The protonation in the present work of the PNA complex at pH = 3 is attributed to the protonation of the PNA which is a

weak base rather than at CN^-. Further confirmation is also available from the kinetics of dissociation of the complex at 0.001 M acid which gave a single rate for dissociation.

In view of these observations the following mechanism is suggested for the dissociation at low acid concentration:

$$Fe[CN]_5PNA^{3-} + H^+ \rightleftharpoons^{K_e} [Fe[CN]_5PNAH]^{2-} \rightarrow^{k_1} Fe[CN]_5H_2O^{3-} + PNAH^+$$

Thus, we have

$$k_{ob} = \frac{k_1 K_e [H^+]}{1 + K_e [H^+]} .$$

Since K_e for the complex is about 2×10^4 at $[H^+] = 0.001$ M, $k_{ob} = k_1$.

The enthalpy and entropy of activation are both higher than for the dissociation of the free ligand reported earlier. This indicates a greater strengthening of the metal-protonated ligand bond. This is expected in view of the high negative charge of the $Fe[CN]_5^{3-}$ moiety. Positive entropy of activation is in consonance with a limiting D-mechanism as indicated earlier for the monoprotonated complex. The dissociation of $PNAH^+$, in the activated complex, leaves a more negative transition state which results in a positive entropy of activation due to greater electrostriction.

4.6.4 Dissociation of $Fe[CN]_5PNA$ at $[H^+] > 10^{-3}M$

At 0.01 M and 0.1 M acid concentrations, there is fast step of initial rate of dissociation followed by a slower step.

At 0.1 M, almost 60% of the complex dissociated by fast step. The slower rate of the resolved biphasic kinetics corresponds to the rate at 0.001 M and the faster one corresponds to the rate at 1 M acid concentrations. It is therefore clear that at $[H^+] \geq 0.01$ M, second stage protonation of the complex occurs which leads to very fast dissociation.

The second stage protonation is also confirmed from the shift in λ_{max} from 750 nm to 735 nm. Since the dissociation is very fast, the spectral scans were obtained with difficulty at very low temperature, 3°C. In comparison with the protonation of $Fe[CN]_5H_2O^{3-}$ by Malin and Koch [24], the second stage protonation is suggested to occur at the CN^- group and the following equation is suggested:

$$[CN]_5FePNAH^{2-} + H^+ \rightleftharpoons^{K_{e2}} H[CN]_5FePNAH]^{1-}$$

In view of the very fast decomposition of the complex, it was difficult to determine the pK_{a2}. From the kinetics and spectral data it is estimated to be about 1 ± 0.5. At 1 M acid, no biphasic kinetics was observed which indicates dissociation through complete second stage protonation. In view of these the following mechanism is proposed for dissociation through second stage protonation:

$$[CN]_5FePNAH^{2-} + H^+ \rightleftharpoons^{K_{e2}} H[CN]_5FePNAH]^{1-} \rightarrow^{k_2} H[CN]_5FeH_2O^{2-} + PNAH^+$$

The $\Delta H^{\#}$ for this step is lower than that for the dissociation of free ligand and the protonated ligand. This shows that the Fe-L bond is destabilized due to the cyanide protonation which

will render metal-cyanide back bonding difficult. The positive entropy of activation is in conformity with a D-mechanism for the dissociation and also with the separation of the positively charged PNA in the transition state.

4.7 Kinetics of acid catalyzed dissociation of $Fe[CN]_5PNP^{3-}$

RESULTS

4.7.1 Nature of the complex in acid media

Preliminary investigation showed that in contrast to neutral media where the complex was stable for more than 24 hs., the dissociation of the complex was accelerated by acids.

The spectrum of the free ligand and the complex at different acid concentrations are given in Fig. 18 and Fig. 19 respectively. The λ_{max} for the free ligand in neutral media is 300 nm, this value remains unshifted in acidic medium from $[H^+]$ = 0.001 to 1 M.

The spectrum of the complex in 1 M acid shifted by a small amount from the neutral media (575 nm to 580 nm) indicating the possibility of protonation.

4.7.2 Kinetics

The rate of the reaction was measured from the rate of disappearance of the protonated complex. For this the absorbance at 575 nm was monitored.

Kinetic data showed that there was excellent linearity for log[A] versus time, at 0.001 M acid to 1 M acid concentrations indicating pseudo first order kinetics.

The pseudo first order rate constants at different concentrations of acid for the dissociation of the complex are given in Table 21.

The rate of dissociation increased from 0.001 to 1 M and

reached a plateau after this.

The rates at different temperatures for 1 M and 0.01 M acid concentrations are given in Table 22. The activation parameters were calculated (Fig. 20) for 1 M acid concentrations and are given in Table 23.

Table 21. Rate constants ($kx10^4$, s^{-1})* for the dissociation of $Fe(CN)_5PNP^{3-}$ at different acid concentrations

$[Fe[CN]_5PNP^{3-}] = 4x10^{-5}$ M; Temp. = 292.15 K

Acid Conc., M	1	0.10	0.010
Rate const.	9.37 ±0.060	6.61 ±0.08	1.76 ± 0.03

* Average of at least 3 replicates.

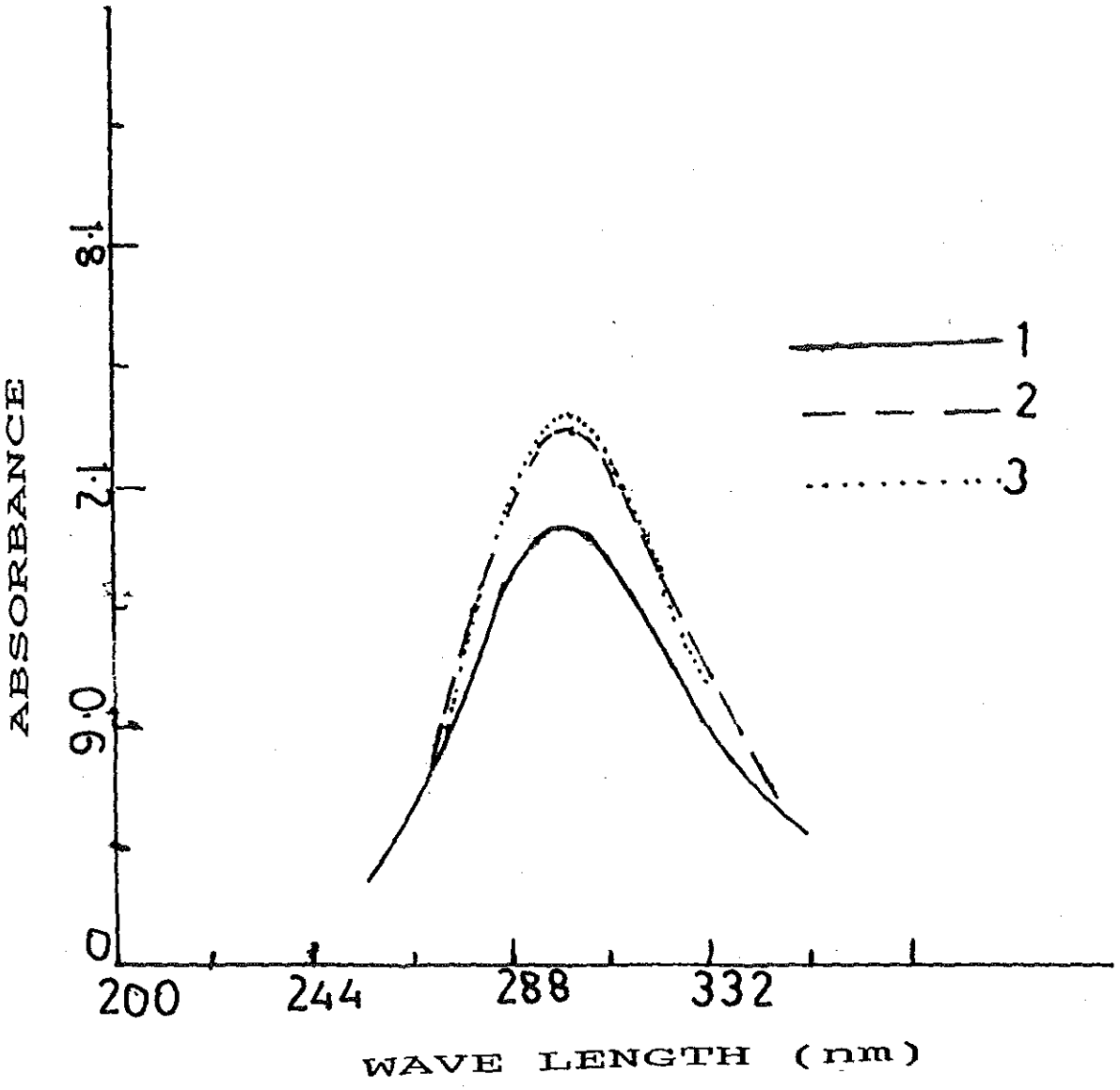


Fig. 18. Spectra of:
1. 10^{-4} M PNP ligand
2. 10^{-4} M PNP in 1 M acid
3. 10^{-4} M PNP in 10^{-2} M acid

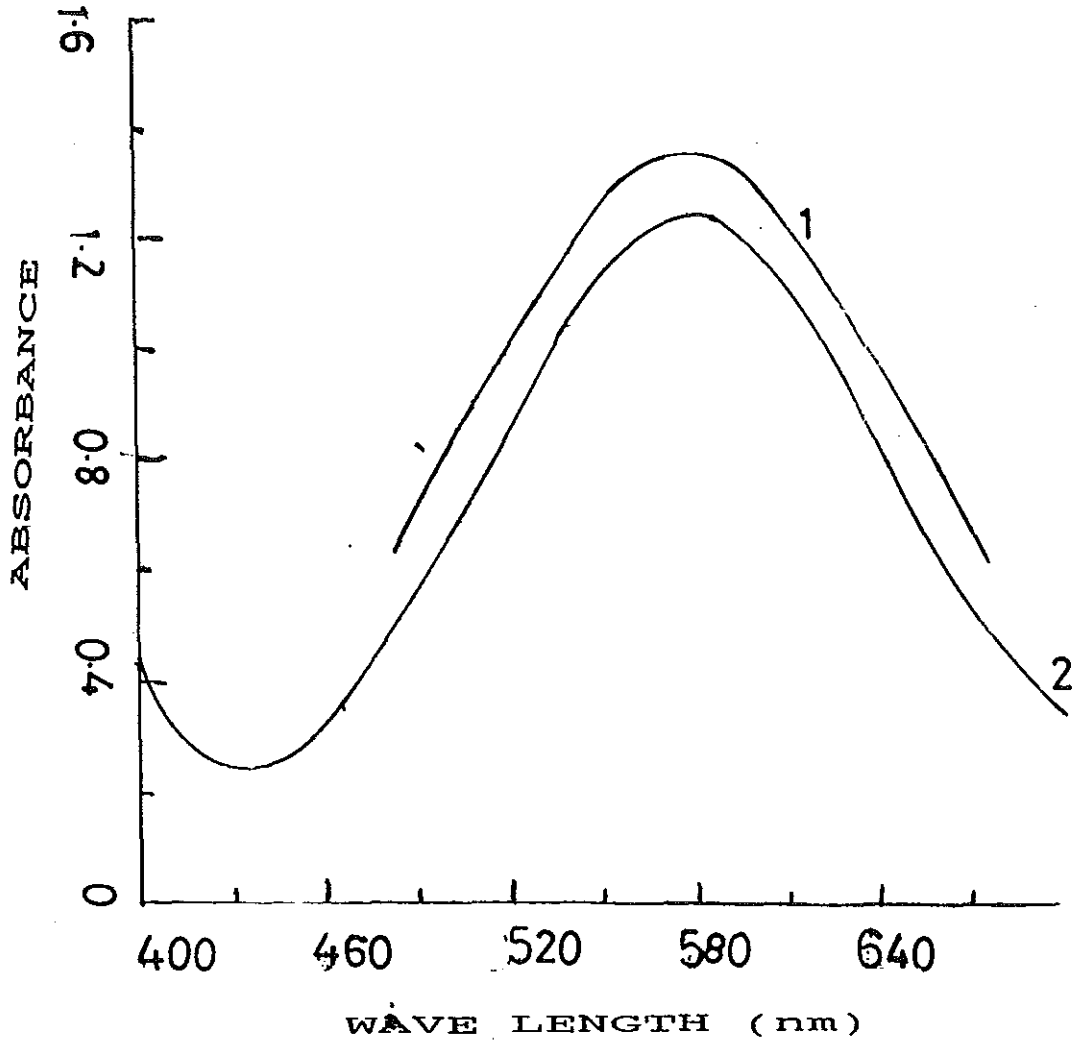


Fig. 19. Spectra of :
1. $5x10^{-5}$ M $Fe[CN]_5PNP^{3-}$
2. $5x10^{-5}$ M $Fe[CN]_5PNP^{3-}$ + 1 M acid

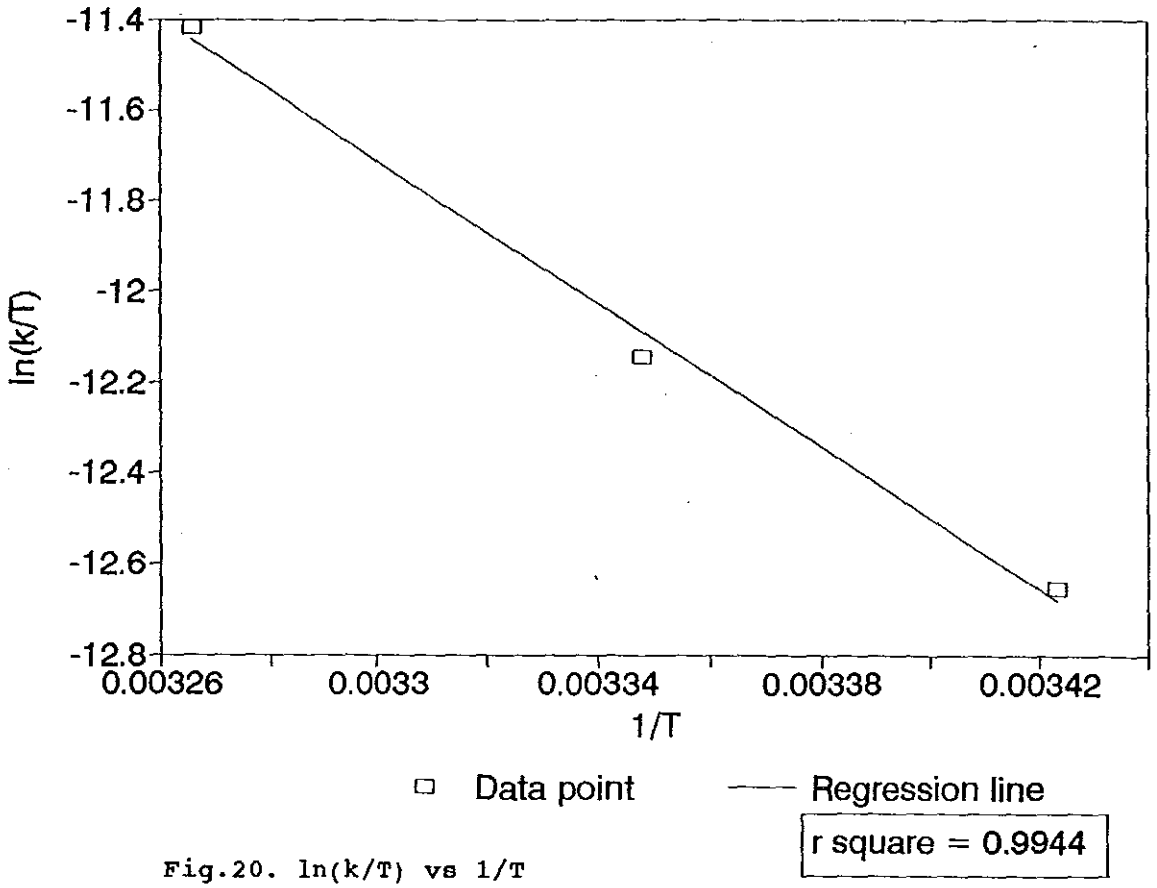


Fig.20. ln(k/T) vs 1/T

Table 22. Rate constants ($kx10^4$, s^{-1})* for the dissociation of $Fe(CN)_5PNP^{3-}$ at different temperatures in 1 M and 0.01 M acids.

Temp., K	292.15	298.65	306.15
Rate const. in 1 M acid	9.37 ± 0.06	15.90 ± 0.02	33.60 ± 0.09
Rate const. in 0.01 M acid	1.76 ± 0.05	7.50 ± 0.01	10.76 ± 0.02

* Average of at least 3 replicates; $[Fe[CN]_5PNP^{3-}] = 4x10^{-5}$ M.

Table 23. Activation parameters

$\Delta H^{\ddagger}$ (kJ/mole)	$\Delta S^{\ddagger}$ (J/mole K)
91 ± 3	10 ± 5

DISCUSSION

The spectrum of the ligand at different pH shows that it does not undergo any change in the range of neutral to 1 M

acid. This is expected for p-nitrosophenol, which has a faintly acidic phenolic group and no other basic centre for protonation. Hence, in the complex, it is expected that protonation of the ligand should not occur. The spectral data of the complex is indicative of this.

The small shift in the spectra of the complex at high acid concentrations, 1 M and 0.1 M, indicates a protonation, most probably at the CN^-, because the ligand is not protonable. This is supported by the enhancement in the rate of dissociation of the complex with increase in H^+ concentration. Hence the following equation is suggested:

$$[CN]_5FePNP^{3-} + H^+ \rightleftharpoons [H[CN]_5FePNP]^{2-}.$$

As can be seen from the kinetic data (Table 21) the rate increases from 0.001 to 1 M non linearly with tendency to reach a plateau. This denotes dissociation via protonation. Based on this and activation parameters the following mechanism is proposed:

$$Fe[CN]_5PNP^{3-} + \overset{k_e}{\rightleftharpoons} HFe[CN]_5PNP^{2-} \overset{k_1}{\rightarrow} H[CN]_5FeH_2O^{2-} + PNP\ .$$

The rate law is then is

$$-\frac{dFe(CN)_5PNP^{3-}}{dt} = k_{ob}[Fe(CN)_5PNP]$$

where

$$k_{ob} = \frac{k_1 k_e [H^+]}{1 + k_e [H^+]} \quad .$$

From the available data pKa for the protonation of the complex was estimated to be 1.6 ± 0.2. The estimated pK_a is lower than 2.63 ± 0.12 [24] for $Fe[CN]_5H_2O^{3-}$ by an order of magnitude and is higher than that for the CN^- protonation of $Fe[CN]_5PNA^{3-}$ complex, indicating a CN^- basicity in the order $Fe[CN]_5H_2O^{3-}$ > $Fe[CN]_5PNP^{3-}$ > $Fe[CN]_5PNAH^{2-}$. PNA and PNP are aromatic ligands with π-bonds which are different from H_2O. The possibility of charge transfer from metal to low energy π^* orbitals of the ligand are thus possible. This is evident from the spectrum also. This will naturally have the effect of lowering the CN^- back-bonding and its basicity in both of the cases. The protonation of PNA further lowers the basicity of CN^- as compared to PNP where no protonation occurs.

The $\Delta H^{\#}$ is similar to the dissociation of PNP from the unprotonated complex, indicating that the Fe-PNP bond is not very much different in the protonated complex. $\Delta S^{\#}$ is, however, higher for the protonated form. $\Delta S^{\#}$ is positive and shows a D-mechanism.

4.8 Kinetics of Hg(II) promoted dissociation of $Fe[CN]_5PNA^{3-}$ in acidic medium

It was shown in the acid-catalyzed dissociation of $Fe[CN]_5PNA^{3-}$, that dissociation occurs through monoprotonation or diprotonation, or both depending on the concentration of the acid used. In this part a detailed kinetic study of Hg(II) promoted dissociation of the complex in different acid concentrations has been taken up.

RESULTS

4.8.1 Kinetics

The rate of the reaction was measured from the rate of disappearance of the protonated complex. For this the decrease in absorbance at 750 nm was monitored.

Kinetic data showed that there was excellent linearity for log[A] versus time, at 0.001 M acid in different concentrations of $HgCl_2$ indicating a pseudo first order kinetics.

The pseudo first order rate constants at different concentrations of $HgCl_2$ for the dissociation of the complex in 0.001 M acid concentration are given in Table 24. The kinetic data showed that the rate constant increased initially with an increase in $HgCl_2$ concentration and reached a limiting value when $HgCl_2$ is present in large excess.

At 0.1 M acid concentrations biphasic kinetics was observed when concentration of $HgCl_2$ is low, with fast rate equal 7.8×10^{-2} s^{-1} for 0.001 M $HgCl_2$. In the other concentrations of $HgCl_2$ there was excellent linearity for

log[A] versus time indicating a pseudo first order kinetics as given in Table 25. A saturation kinetics with respect to the concentration of $HgCl_2$ is observed.

In 0.001 M acid also, the rate dissociation showed a tendency to reach a limiting value at lower Hg(II) concentration, than in 0.1 M acid.

Table 24. Rate constants ($kx10^3$)* for the dissociation of $Fe(CN)_5PNP^{3-}$ at different $HgCl_2$ concentrations in 0.001M acid.

$HgCl_2$ x 10^3	0	1	2	3	4
Rate Const.	0.078	13.81	14.86	15.42	15.90

* Minimum of three replicates; Temp. = 292.15 K;
$[Fe[CN]_5PNA^{3-}] = 4x10^{-5}$; [HCl] = 0.001 M.

Table 25. Rate constants ($kx10^3$)* for the dissociation of $Fe(CN)_5PNA^{3-}$ at different $HgCl_2$ concentrations in 0.1M acid; $[Fe[CN]_5PNA^{3-}] = 4x10^{-5}$; [HCl] = 0.1 M

$HgCl_2$ $x10^3$, M	Rate constant
0	0.284
1	4.22
2	6.70
4	9.00
6	10.00
8	10.55
10	10.58

* Minimum of three replicates; Temp. = 292.15 K.

DISCUSSION

The general pattern of Hg(II) promoted dissociation of $Fe[CN]_5PNA^{3-}$ was similar in both neutral and acidic media, except that in acidic medium, the rate saturation is reached at much higher concentration of $HgCl_2$.

As seen under acid catalyzed dissociation, $Fe[CN]_5PNA^{3-}$ undergoes two protonation stages between $[H^+] = 10^{-4}$ M and 10^{-1} M, the ligand protonation taking place at lower acid concentration and the protonation of CN^- at H^+ concentration. The dissociation of Hg(II) promoted dissociation of $Fe(CN)_5PNA^{3-}$

in acidic media, is therefore complicated by these protonation equilibria also. However, the attainment of a limiting rate shows the formation of strong adduct as in the case of neutral medium. The limiting rate constants in 0.1 M acid is quite similar to that in neutral medium, showing that the equilibrium for adduct formation with Hg(II) is much stronger than that with the acid. This is reasonable because the proton association constant for CN^- is of the order of only 10. The limiting rate in 10^{-3} M and is also similar though slightly higher. Contrary to the $Fe[CN]_5PNP^{3-}$, where the lack of colour change indicated a weak equilibrium for $Fe[CN]_5PNP^{3-}$ and $HgCl_2$ in acid medium, the same colour (dusty green) obtained in neutral medium is also seen in acid medium for $Fe[CN]_5PNA^{3-}$, confirming the formation of a strong adduct. This is also borne out by the fact that Hg(II) catalyzed decomposition takes preference over the proton catalyzed dissociation in 0.1 M and at higher $HgCl_2$ concentration, as indicated by the lower rate of dissociation. At low $HgCl_2$ concentration the kinetics is biphasic, showing that both proton and Hg(II) catalyzed reactions take place.

A similar scheme as shown for the dissociation $Fe[CN]_5PNP^{3-}$ can also be considered for $Fe[CN]_5PNA^{3-}$.

$$
\begin{array}{ccccc}
 & & \overset{K_1}{\rightleftharpoons} & & \overset{K_2}{\rightleftharpoons} \\
Fe[CN]_5PNA^{3-}+H^+ & & Fe[CN]_5PNAH^{2-}+H^+ & & HFe[CN]_5PNAH^{1-} \\
\downarrow\uparrow K_3[Hg] & & \downarrow\uparrow K_4\ Hg(II) & & \downarrow k_3 \\
[Hg\text{-}Fe[CN]_5PNA]^{1-} & & [Fe[CN]_5PNAH\text{-}Hg] & & HFe[CN]_5H_2O^{2-} \\
 & & & & +\ PNAH^+ \\
\downarrow k_1 & & \downarrow k_2 & & \\
Fe^{2+} + Hg[CN]_2 + 3CN^- & & Fe^{2+} + Hg[CN]_2 & & \\
+\ PNA & & +\ 3CN^- + PNAH^+ & &
\end{array}
$$

4.9 Kinetics of Hg(II) promoted dissociation of $Fe[CN]_5PNP^{3-}$ in acid medium.

RESULTS

4.9.1 Nature of the complex in acidic medium in presence of Hg(II).

The spectrum of the complex at different acid concentrations in presence of Hg(II) are given in Fig. 21.

The spectrum of the complex in 0.1 M acid and 0.01 M acid in presence of Hg(II) shifted by a small amount from the neutral media (*i.e.*, 575 nm to 580 nm) as in the case of acid only spectra of the complex.

4.9.2 Kinetics.

The rate of the reaction was measured from the rate of disappearance of the complex. For this the absorbance at 575 nm was monitored.

All the runs were carried under pseudo first order conditions with excess $HgCl_2$ in 0.1 M and 0.001 M acid concentrations. The data gave very good correlation for $-\ln[A_\infty - A_t]$ versus time for 80% of the completion of the reaction in 0.1 M and 0.001 M acid concentrations indicating a pseudo first order kinetics.

The pseudo first order rate constants at different concentrations of Hg(II) for the dissociation of the complex in 0.1 M and 0.001 M acid concentrations are given in Table 26 and Table 27.

The kinetic data showed that the rate constants increased

linearly with an increase in $HgCl_2$ in the range of $HgCl_2$ concentrations studied in 0.1 M and 0.001 M acid concentrations. This showed that the reaction is first order with respect to complex and $HgCl_2$. The observed second order rate constants are 0.621 s^{-1} M^{-1} and 1.925 s^{-1} M^{-1}, Fig. 22 and Fig. 23.

Table 26. Rate constants ($kx10^3$, s^{-1})* at different $HgCl_2$ concentrations in 0.1M $HClO_4$

$HgCl_2x10^3$, M	0	1	2	4	6	8	10
Rate Const.	0.58	1.97	2.45	3.68	4.88	5.60	7.56

* Average of minimum of three replicates; Temp. = 292.15 K; $[Fe[CN]_5PNA^{3-}] = 2x10^{-5}$.

Table 27. Rate constants ($kx10^3$, s^{-1})* at different $HgCl_2$ concentrations in 0.001M HCl

$HgCl_2x10^3$, M	3	4	5
Rate Const.	5.55	7.34	9.53

* Average of minimum of three replicates; Temp. = 292.15 K; $[Fe[CN]_5PN^{3-}] = 2x10^{-5}$

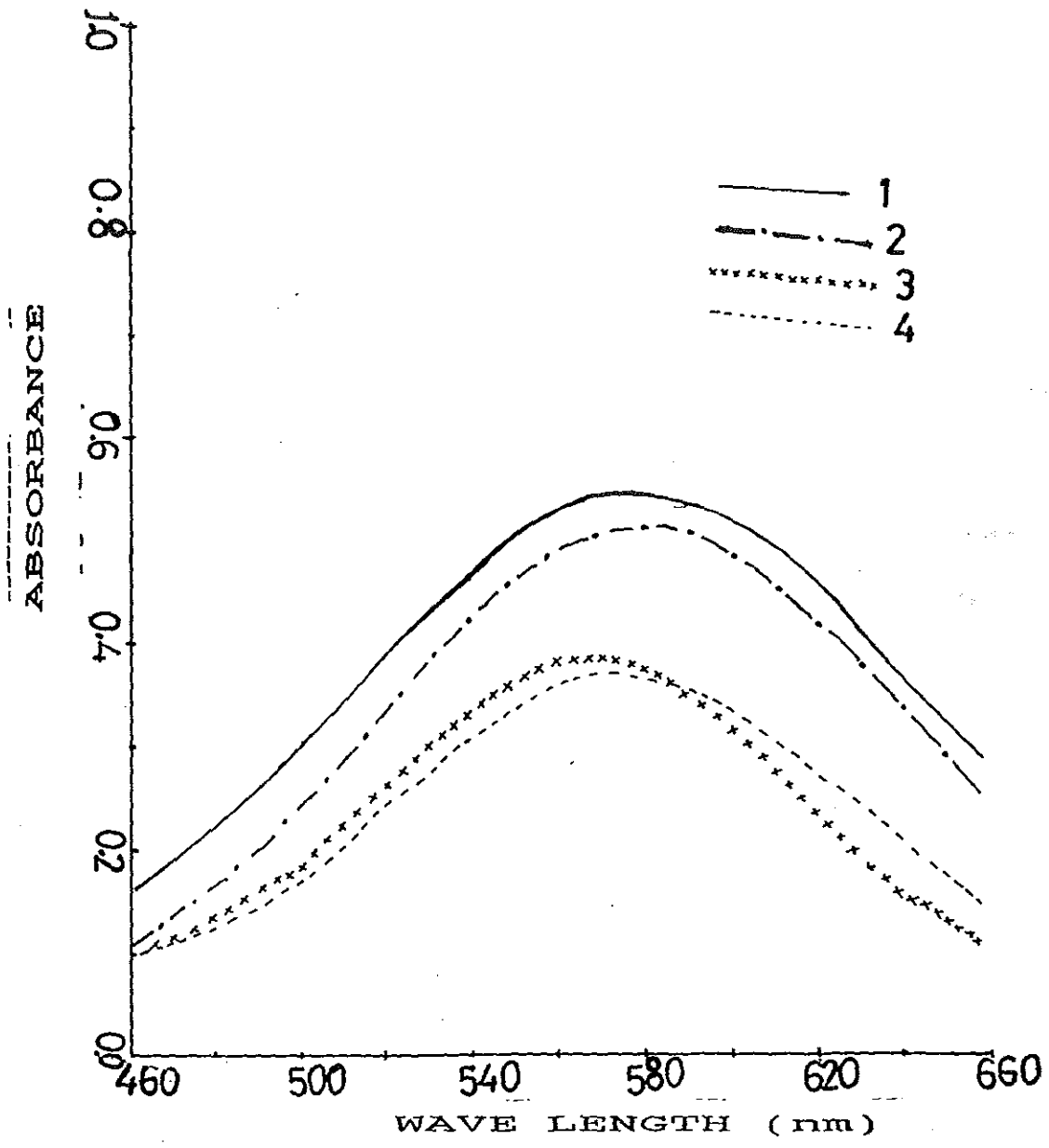


Fig. 21. Spectra of:

1. $5x10^{-5}$ M $Fe[CN]_5PNP^{3-}$
2. $5x10^{-5}$ M $Fe[CN]_5PNP^{3-}$ + 0.1 M acid
3. $5x10^{-5}$ M $Fe[CN]_5PNP^{3-}$ + 0.1 M acid + $HgCl_2$
4. $5x10^{-5}$ M $Fe[CN]_5PNP^{3-}$ + 10^{-2} M acid + $HgCl_2$

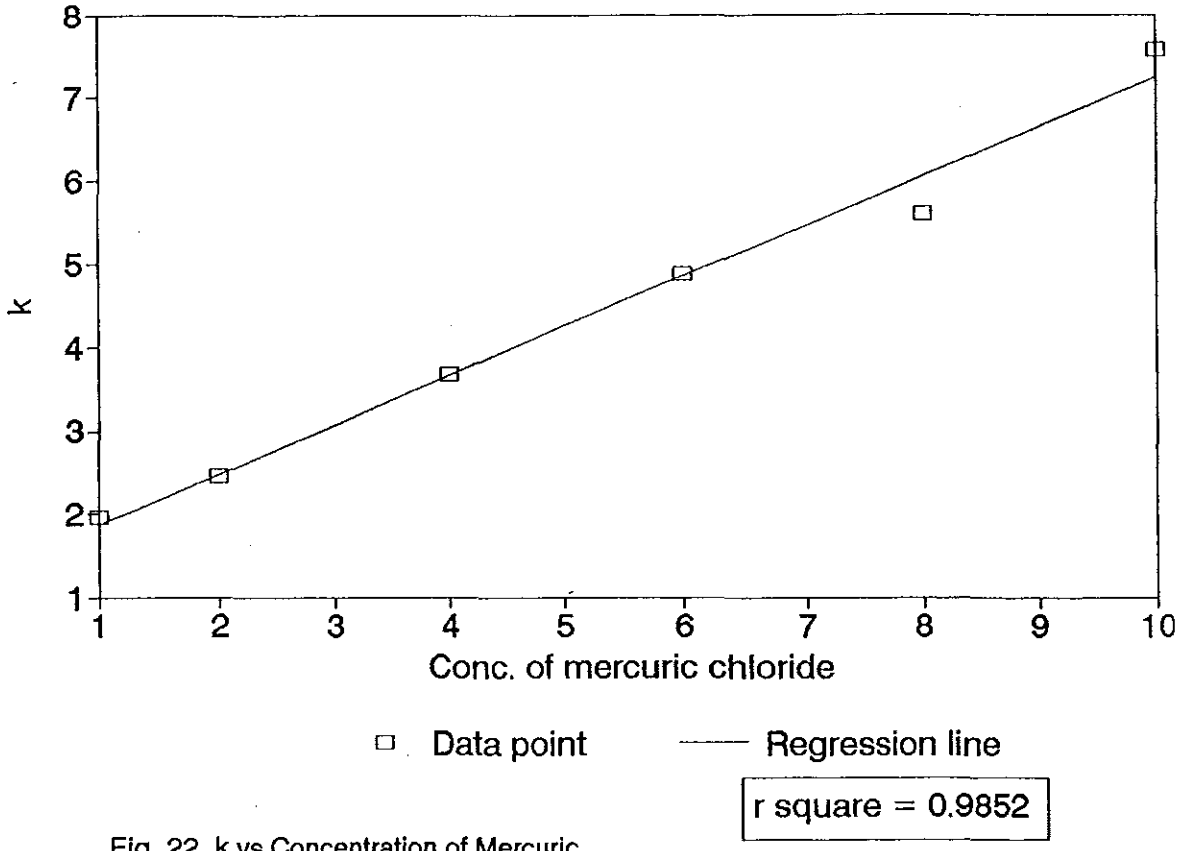


Fig. 22. k vs Concentration of Mercuric Chloride in 0.1 M Acid

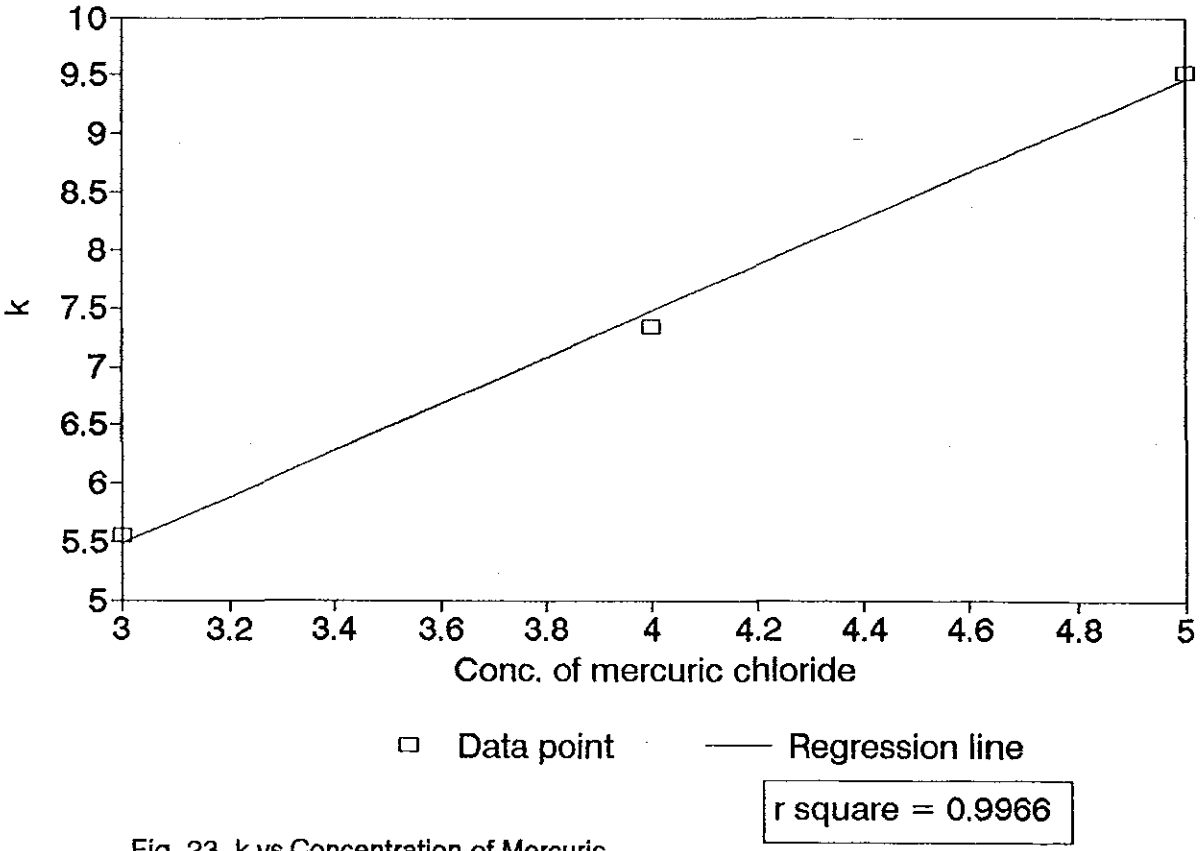


Fig. 23. k vs Concentration of Mercuric Chloride in 0.001 M Acid

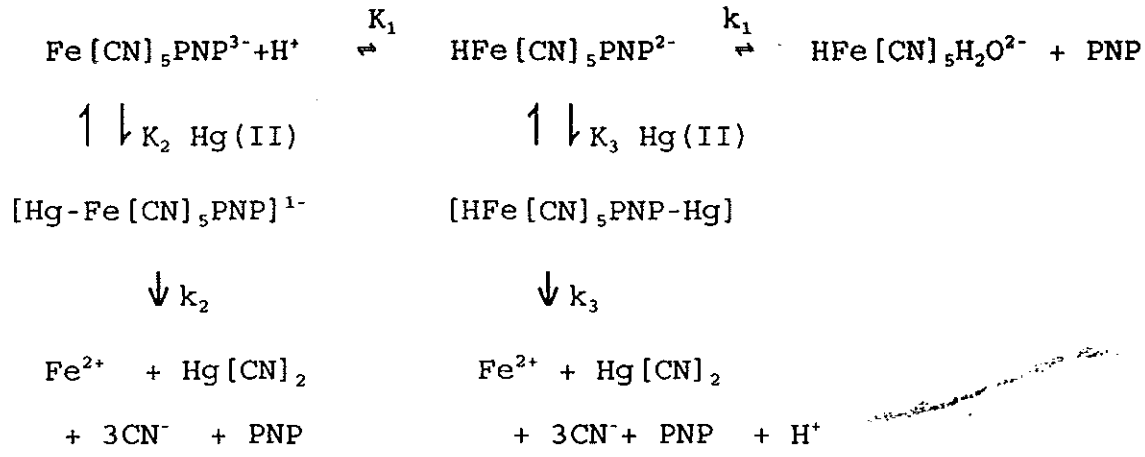
DISCUSSION

There is a very small shift in the spectra of the complex in presence of Hg(II) in acidic media which is similar to the spectra of the complex in acidic medium.

The fact that the rate increases linearly with $HgCl_2$ concentration shows that the reaction is second order with respect to [Hg] and $Fe[CN]_5PNP^{3-}$ with a possible weak equilibrium for the adduct formation as seen in neutral medium. The prominent pink colour that was observed in neutral medium was absent in acidic medium. This suggests at best, an equilibrium with a low equilibrium constant.

In acids, specially at 0.1 M, as seen from the study on the acid dissociation of PNP complex, a protonation equilibrium pKa with an estimated value of 1.6 ± 0.2 exists. Thus there will be a competition between the protonated and neutral forms of the complex to react with $HgCl_2$. The acid catalyzed decomposition rate is also approximately one tenth of the composite rate observed at $1x10^{-3}$ M $HgCl_2$. In view of these several possibilities, the composite rate in 0.1 M acid has to be attributed to all these competing reactions. This is borne out by the fact that the rates of dissociation at 0.1 M acid are lower than the dissociation in neutral medium with $HgCl_2$.

The following mechanistic scheme is proposed, taking into consideration the above points:



At 10^{-3} M acid, the protonation of $Fe[CN]_5PNP^{3-}$ is largely ruled out. Even so, the rates are linear with $HgCl_2$ concentration and the rates are much higher than at 0.1 M for the same $HgCl_2$ concentrations and practically passing through the origin, showing that the acid catalyzed dissociation is negligible. This gives a value of $k_2Ke_2 = 1.9$. Assuming k_2 to be similar to that found under neutral conditions, $Ke_2 \approx 190$ which is very much smaller than that estimated under neutral conditions. The composite k_2Ke_2 in 0.1 M acid is 0.63, giving an estimate of 63 for Ke.

CONCLUSION

$Fe(CN)_5PNA^{3-}$ and $Fe(CN)_5PNP^{3-}$ complexes exhibited a limiting D-mechanism for the exchange of PNA and PNP by pyridine. Thus, although the aromatic nitroso ligands are quite different from other basic nitrogen ligands or sulphur bonding ligands, the mechanism of dissociation is governed by the initial formation of $Fe(CN)^{3-}_5$ intermediate, as in the case of the other $Fe(CN)_5X$ complexes. The reactions could be very conveniently monitored because of the high molar absorptivity of the complexes in the visible spectrum. These are suitable as model experiments for Graduate Courses in Inorganic Labs.

Excess Hg(II) prompted complete aquation of $Fe[CN]_5PNP^{3-}$ and $Fe[CN]_5PNA^{3-}$ by the abstraction of CN^-. Intermediate adducts were formed in both cases, prior to aquation. The adducts were confirmed from their characteristic spectra. Saturation kinetics, leading to limiting rate, independent of Hg(II) concentrations, indicated very strong equilibrium between the complexes and Hg(II). The entropy of activation is supportive of a limiting D-mechanism.

The kinetics of aquation by Hg(II) in acidic medium is more complex due to the simultaneous presence of the protonation and the Hg(II)-Complex equilibrium. For $Fe[CN]_5PNA^{3-}$, the rates indicated that the $Fe[CN]_5PNA^{3-}$-Hg(II) was more dominant than the protonation equilibrium. For $Fe[CN]_5PNP^{3-}$, the rate was linear with $HgCl_2$ in acids, indicating a weak equilibrium between the complex and $HgCl_2$ and the rate was therefore k_1Ke as explained.

Decomposition of $Fe[CN]_5PNA^{3-}$ in acidic medium took place

through two stage protonation, via that of PNA and then CN^-. The rates of dissociation was very much faster for the diprotonated form. $Fe[CN]_5PNP^{3-}$ undergoes proton catalyzed dissociation, by protonation at the CN^- only. The pK_a is 1.6 ± 0.2.

From the limiting D-mechanism seen for all the three types of ligand substitution, taken up in this investigation, it is clear that $Fe(CN)^{3-}_5$ species are stable enough to form, as steady state intermediate in the dissociation $Fe(CN)_5X$ complexes.

It is therefore clear that the π-bonding CN^- ligand with large crystal field stabilization energy, is capable of stabilizing the penta coordinated intermediate $Fe(CN)^{3-}_5$, possibly through a trigonal bipyramidal configuration which favours better π-bonding overlap.

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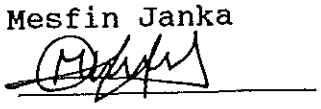
DECLARATION.

I, the undersigned, declare that this thesis is my original work and has not been submitted for a degree to any other university. All sources of materials used for the thesis have duly acknowledged.

Name. Mesfin Janka

Signature. 

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