# The Kinetic Study of Ligand Substitution Reaction Using Lead as Catalyst

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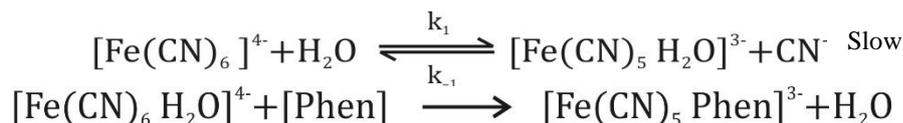University of Lucknow , Lucknow(UP)

**ABSTRACT**

The Kinetic study of Pb (II) catalyzed exchange reaction between hexacyanoferrate (II) and phenanthroline (Phen) were studied as ligand substitution reaction which followed a dark coloured complex $[Fe(CN)_4 Phen]^{3-}$ at 528 nm, pH=3.0±0.02, temperature =25±0.5⁰ C. The effect of various parameters like Concentration of [Phen] and $[Fe(CN)_6]^{4-}$ on the rate of reaction rate were also seen and explained in detail. The reaction rate showed variable order dependence in $[Fe(CN)_6]^{4-}$ . The effect of water , dielectric constant, ionic strength, temperature were also considered to arrive at a possible interchange dissociative mechanism for the catalysed reaction. Activation parameters of the reaction under study was calculated with the help of Erying and Arrhenius equation and given in support of proposed mechanism.

## INTRODUCTION

Out of the complex compound of transition metal series the Potassium hexacyanoferrate (II) is known to be the least labile cyano complex. A large number of sparingly soluble salts of formula $K_2M^{II}Fe(CN)_6$ or $KM^{III} Fe(CN)_6$ are obtained due to fixation of alkali, alkaline earth or transition metal ions in the outer sphere of $Fe(CN)_6^{4-}$ [1-3]. The adducts of $K_4 Fe(CN BX_3)_6$ (B = Boron, X = F,Cl) type are formed very slowly [4,5] and are suggested to contain cyano bridges recognised by shift in CN stretching band by about $100cm^{-1}$ towards higher frequency side [4].

A number of researches have been carried out for kinetic study of the ligand exchange reactions of low spin iron (II) complex compounds, however most of these reactions involved pentacyanoferrate (II) complex compounds [6-16].

To further augment our knowledge about the mechanism of these reactions a number of researches have been done in micellar [13,14] media or in concentrated aqueous solution of electrolyte [12] .Many research groups have also studied the kinetics of oxidation reactions of the hexacyano ferrate (II) complex compounds by many reagents, in different kinds of medium like neutral or acidic [17-19] but the information about the kinetics and mechanistic study of the substitution [20-24] is very less. Moreover many of these findings have already been taken up to solve different types of problems relating to analysis[20-23], instead of making a comprehensive study of the various aspects of the mechanism of these replacement reactions of hexacyanoferrate (II) [24].Therefore there are several unsolved mysteries of the mechanistic and and kinetic study of these replacement reactions of hexacyanoferrate (II) that are still left to be answered.

The hexacyanoferrate (II) undergoes aquation under the influence of near ultraviolet light in acidic medium synthesising $[Fe(CN)_5H_2O]^{3-}$ and $CN^-$[25]. A great amount of research of complexes substituted with P-,O-, N- and P- donar ligands have been formed from labile $[Fe(CN)_5H_2O]^{3-}$ ion [26, 27]. The thermal decomposition of hexacyano ferrate (II) ion is an extremely slow process that is reversible in nature in accordance to Eqn(1). The penta aqua cyanoferrate(II) complex produced has been reported to react with nitroso R-salt [28] and N-Methyl pyrazinium [29] ion. Thus the reaction of hexacyanoferrate (II) with phenanthroline is also believed to proceed through following Equations in conformity with the above investigated systems.

$$[Fe(CN)_6]^{4-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5 H_2O]^{3-} + CN^- \text{ Slow}$$

$$[Fe(CN)_6 H_2O]^{4-} + [Phen] \longrightarrow [Fe(CN)_5 Phen]^{3-} + H_2O$$

The uncatalysed reaction takes several hours to complete but metals like lead[28, 29], silver [30] catalyse the reaction and bring down the required time of the reaction.Lead is used as catalyst in the reaction between hexacyanoferrate (II) and phenanthroline was under our invesyigation (31). We are trying to develop a method using lead as catalyst for the reaction between hexacyanoferrate (II) and 1,10 phenanthroline. The

stoichiometry of the formed product of in the reaction under study was recorded as as 1:1 by mole and slope ratio methods [32]

Lead has been found to catalyse the breakage of hexacyano ferrate(II) bonds, in the manner[23,24,28,29] via the above two equations.In this paper we have tried our level best to study the above mentioned reaction and draw the most possible mechanism and to derive the kinetic aspects of the reaction.

## EXPERIMENTAL
### Materials

Double distilled water was taken to prepare all of the reactant solutions. Moreover, the reagents used in this particular reaction were of analytical grade. The solution of $K_4[Fe(CN)_6] \cdot 3H_2O$ (AR,E. Merck, Germany) was prepared by weighing a required amount and was taken in brown bottles. The fresh solutions of Phenanthroline (AR,E. Merck, Germany) was taken in HPLC grade water. It was diluted everyday before starting the reaction for kinetic study. A stock solution of $PbCl_2$ (A.R. Glaxo BDH) was synthesized by taking the required amount in water. This stock solution was Diluted everyday to stop the loss of adsorption on glasswares. $KNO_3$ (A.R. Qualigens Fine chemicals)was utilized to adjust ionic strength of the reaction under study. The pH of the reaction under study was kept as required by taking buffer solutions synthesized by adjusting HCl to potassium hydrogen phthalate or KCl (BDH) and NaOH/ HCl according to literature [33].

### Procedure

$$Hg^{2+} + [Fe(CN)_3]^{4-} + H_2O \longrightarrow [Fe(CN)_5 + H_2O]^{3-} + HgCN^+$$
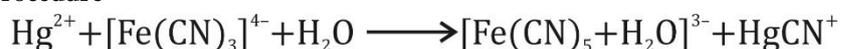
The equilibration of the reaction was done inside the environmental chamber at 25°C. The make an modal of UV-Visible spectrophotometer used to study this reaction is Genesis model No. 10UV. Sio-global pH meter was used to record the

$$HgCN^+ + H^+ \longrightarrow Hg^{2+} + HCN$$

pH of the reaction.

Once the equilibration was done the 2ml of the reactants, were mixed in the sequence one after the other as phenanthroline then buffer then adding lead (II) chloride but The reaction could start only by mixing 2 ml of hexacyanoferrate (II) to the above reaction sequence. This was thoroughly shaken and transferred quickly to a 10 mm cuvette, the temperature was controlled in the cell compartment of the UV-Visible spectrophotometer. The progress of the reaction could be monitored by seeing the absorbance grow at 528 n.m. most probably due to the appearance of the product $[Fe(CN)_4Phen]^{3-}$ (Fig.1).
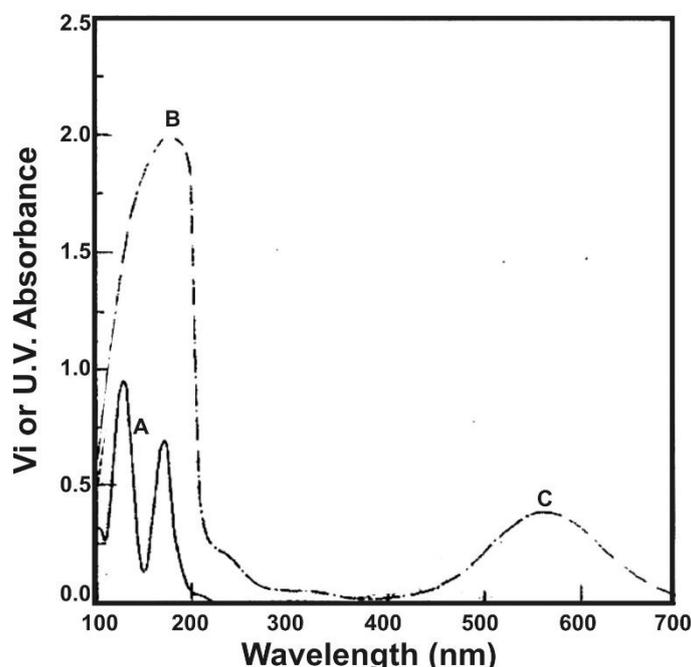


**Fig. 1 Absorption spectras of the reactants and products**
(C) Product, (B) $[Fe(CN)_6]^{4-}$ ,(A) [Phen]

Under conditions: $[Fe(CN)_6]^{4-}=5.5X10^{-4}M$, $[Phen]=5.5X10^{-3}$, $[Pb^{2+}] = 7.5x10^{-7}M$ and pH = $3.0\pm 0.02$ (after one hour).

## RESULTS AND DISCUSSION
### Effect of pH on the rate of reaction

To see the effect of various pH on the rate of reaction between $[Fe(CN)_6]^{4-}$ and phenanthroline as catalysed by $[Pb]^{2+}$, fixed time procedure was followed and the chosen pH range was 1.0-11.0. It is to be noted that the values of absorbance, $A_t$ was measured at (time equal to 5 and 10 minutes ) as a function. of lead, all the other values were fixed as at optimum and were measured closer to initial rate of reaction in this experiment .

Various variables were kept constant to select a pH value for the optimum reaction rate. The pH upto 6 was varied using potassium hydrogen phthalate / NaOH or HCl buffer, however, for higher pH all the working solutions were maintaned using 5M NaOH. The plot of variations of absorbance, $A_t$ (measured at time equal to 5 and 10 minutes) after mixing the reactants vs the pH of the reaction is plotted in Fig. 2.
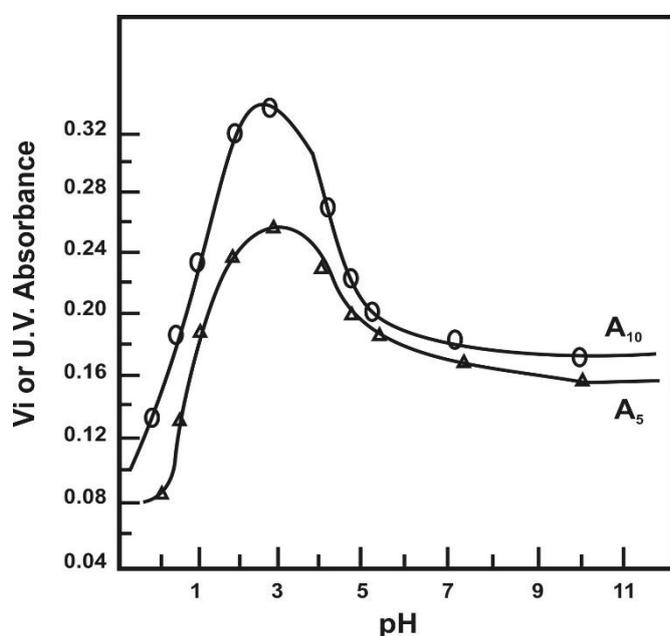


**Fig.2. The substitution of phenanthroline in hexacyanoferrate (II) in presence of lead as Catalyst Vs pH**
Under conditions : I = 0.1 M ($KNO^3$ , Temp. $25.0\pm0-1^0C$ , [Phen] = $5.5x10^{-5}M$ $[Fe(CN)_6]^{4-} = 5.5x10^{-3}$, $[Pb^{+2}] = 2.5x10^{-5}$ M

The plot reveals that the reaction rate is slow at lower pH but maximizes between pH values of 2.8 and 3.2 and then falls off again. The reaction rate is slower at low values of pH most probably due to synthesis of protonated forms of $[Fe(CN)_6]^{4-}$ being formed[34]. The downfall of rate pH of higher values may be attributed due to the deficiency of protons that are required to reproduce the catalytic species. In addition to the above reason, the decrease in reaction rate may be explained by the decrease hydrolytic precipitation of lead.

**Dependence of initial rate of reaction on the concentration of $[Fe(CN)_6]^{4-}$ and [Phen]**

The initial rate is defined as the measurement of rate in first 15 minutes after the start of the reaction. It is not at time equal to is measured as a function of Phenanthroline ranging the concentration from $2.5x10^{-2}$ to $7.5x10^{-6}$ M keeping other variables reaction constant at $[Pb^{2+}] = 1.5x10^{-5}$ M, pH = $3.0\pm 0.02$, temp. =$25\pm 0.1^oC$ and I = 0.16 M ($KNO_3$).

The plot of initial rate Versus. Phenanthroline is plotted in Fig.3. The plot reveals the increase in rate at the starting of the reaction, becoming constant in the range $5.0 \times 10^{-5}$M – $5.0 \times 10^{-4}$M and then decreasing at still more higher concentrationof the reagents. The possibility of any complexation between $Pb^{2+}$ ions and phenanthroline can be ruled out under these condition.
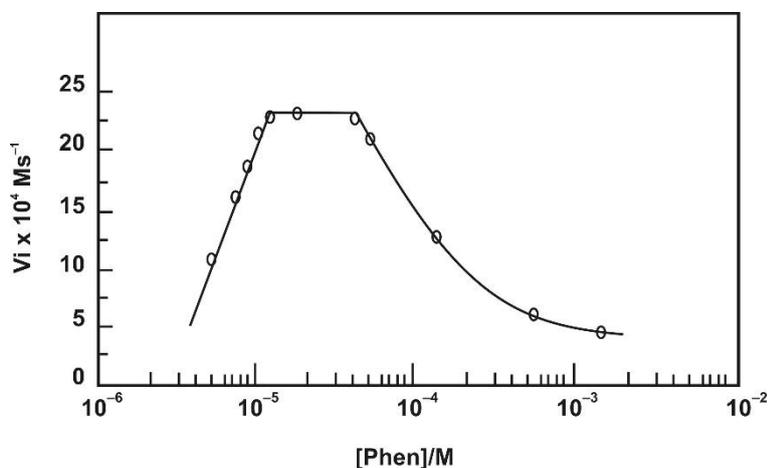


**Fig 3 : Effect of concentration of [Phen] on initial rate**
**Under Conditions:** $[Fe(CN)_6]^{4-}$ = $2.0 \times 10^{-2}$M, $[Pb^{+2}]$ = $1.5 \times 10^{-5}$ M, pH = $3.0 + 0.02$, Temp. $25.0 \pm 0.1^{\circ}$C and I=0.15M (KNO$_3$).

On the other hand ,complex formation of the adduct type may take place between $Pb^{2+}$ ions and phenantholine ligand when phenanthroline concentration is very much higher than $[Pb^{2+}]$. This would eventually inhibit thecatalytic activty of $[Pb^{2+}]$. Keeping all of the reaction parameters constant at values of optimisation values, the rate of dependence on $[Fe(CN)_6]^{4-}$ was studied in the range of concentration between, $4.6 \times 10^{-4}$M to $2.6 \times 10^{-2}$M.The plot of logof intial rate (Vi) Vs. Log of concentration value of $[Fe(CN)_6]^{4-}$ is plotted in Fig. 4, which clearly shows a variable order dependence starting from first order at lower concentrations of $[Fe(CN)_6]^{4-}$ to a lower fractional order at a stil higher concentrations but certainly never going towards zero.
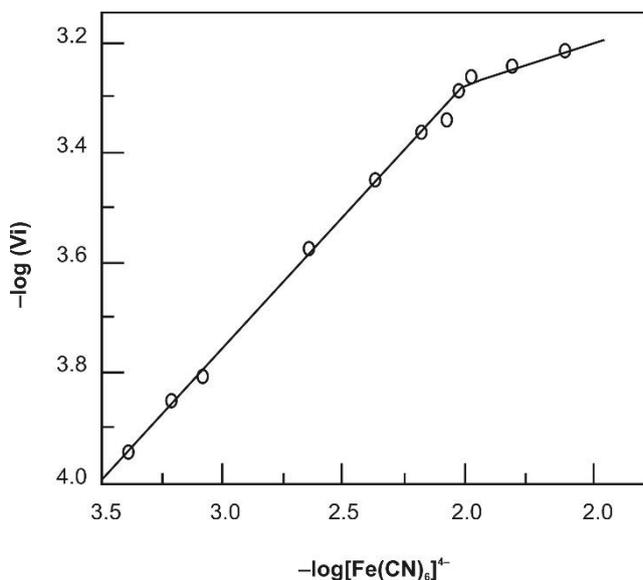


**Fig4. $Pb^{+2}$ presence to vary of the initial rate of $[Fe(CN)_6]^{4-}$**
**Under conditions:** I = 0.15 M (KNO$_3$), Temp. $25.0 \pm 0.1^0$C, $[Pb^{+2}]$ = $8.0 \times 10^{-6}$ M
$[Phen]$ = $6.0 \times 10^{-5}$ M, pH = $3.0 \pm 0.2$

**Variation of lead concentration on the reaction rate**

The concentration of $[Pb]^{2+}$ was changed from $1.5 \times 10^{-7}$M to $2.8 \times 10^{-1}$M while concentrations of phen. and $[Fe(CN)_6]^{4-}$ were constant at optimum value at pH $=3.0 \pm 0.02$, temp. $= 25 \pm 0.1$°C., I = 0.1M (KNO₃). This variation range for $[Pb]^{2+}$ was taken to check the linear relatioship between initial rate and $[Pb]^{2+}$ for analytical application due to its catalytic effect and also to see the differing role of $Pb^{+2}$ as a function of concentration. The results are graphically represented in Fig. 5. where the value of the absorbance changes after 5 min ($A_2$) versus $[Pb^{2+}]$ increases linearly in the beginning reaches to a maximum value at still higher concentrations in a non-linear manner until $[Pb]^{2+}$ becomes equal to Ferrocynide, the rate finally starts declining. The intercept got from the curve of initial lined portiongives us the rate due to uncatalysed path.
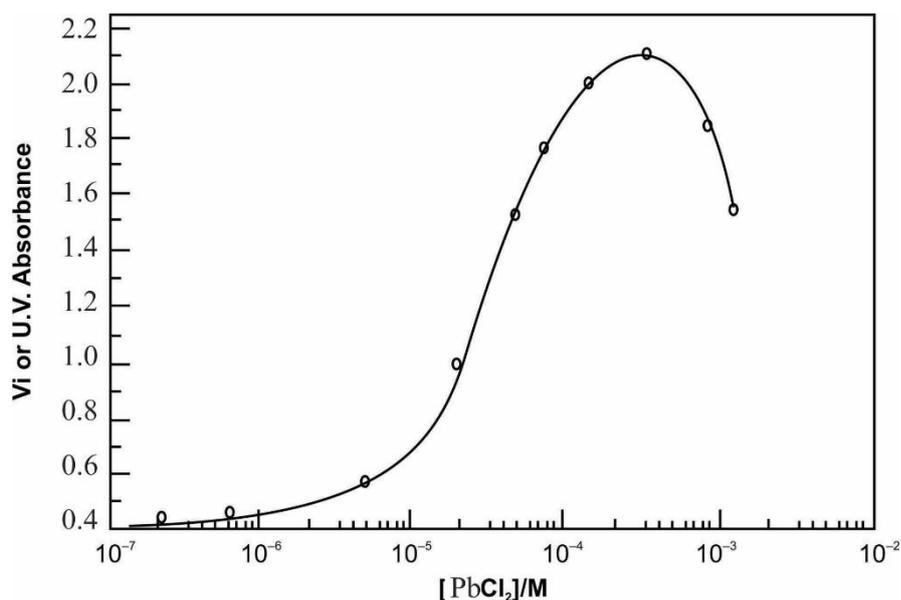


**Fig.5. Variation of the initial rate of replacement of CN⁻ in $[Fe(CN)_6]^{4-}$ by [Phen] when lead is present as catalyst**

Required conditions: $[Fe(CN)_6]^{4-} = 8.0 \times 10^{-4}$M, [Phen] $= 7.5 \times 10^{-5}$ M, pH $= 3.0 \pm 0.2$, Temp $= 25.0 + 0.1$°C and I = 0.15M (KNO₃).

The fall in the reaction rate at higher concentration of leadis because of binary product $[Fe(CN)_6^{4-} \cdot PbCl_2]$ being formed. In a different experiment it was seen that a white ppt. is being made in the starting just after mixing lead and $[Fe(CN)_6]^{4-}$ in the molar ratio of 2:1. At higher $[Fe(CN)_6]^{4-}$ it quickly changed into blue showing the synthesis of a binuclear complex. Beck. [35] also proposed the same type of complex between $[Pb(CN)_2]$ and $[Fe(CN)_6]^{4-}$.

**Influence ofionic strength and temperature on rate of reaction**

The effect of temperature on the initial rate for the exchange of cyanide from $[Fe(CN)_6]^{4-}$ by phen. was considered at different temperatures between 25°C-45°C.

Due to the possibility of decomposition of $[Fe(CN)_4Phen]^{3-}$ complex compound Higher temperature were avoided .The catalysed as well as uncatalysed reactions both follow, the Erying and Arrhenius equations through which activation parameters have been measured.

The values of a activation parameter for catalysed reaction are found to be Ea=58. 29 $\pm$ 4.2K J Mol⁻¹ , $\Delta H^{\neq} = 56.27 \pm 3.8$ KJMol⁻¹, $\Delta S^{\neq} = 43.79 \pm 8.4$JK⁻¹ Mol⁻¹.

The values of a activation parameter for uncatalysed reaction are found to be Ea=63. 82 $\pm$ 2.8K J Mol⁻¹ , $\Delta H^{\neq} = 60.21 \pm 3.2$ KJMol⁻¹, $\Delta S^{\neq} = -36.41 \pm 6.4$JK⁻¹ Mol⁻¹(Fig. 6).
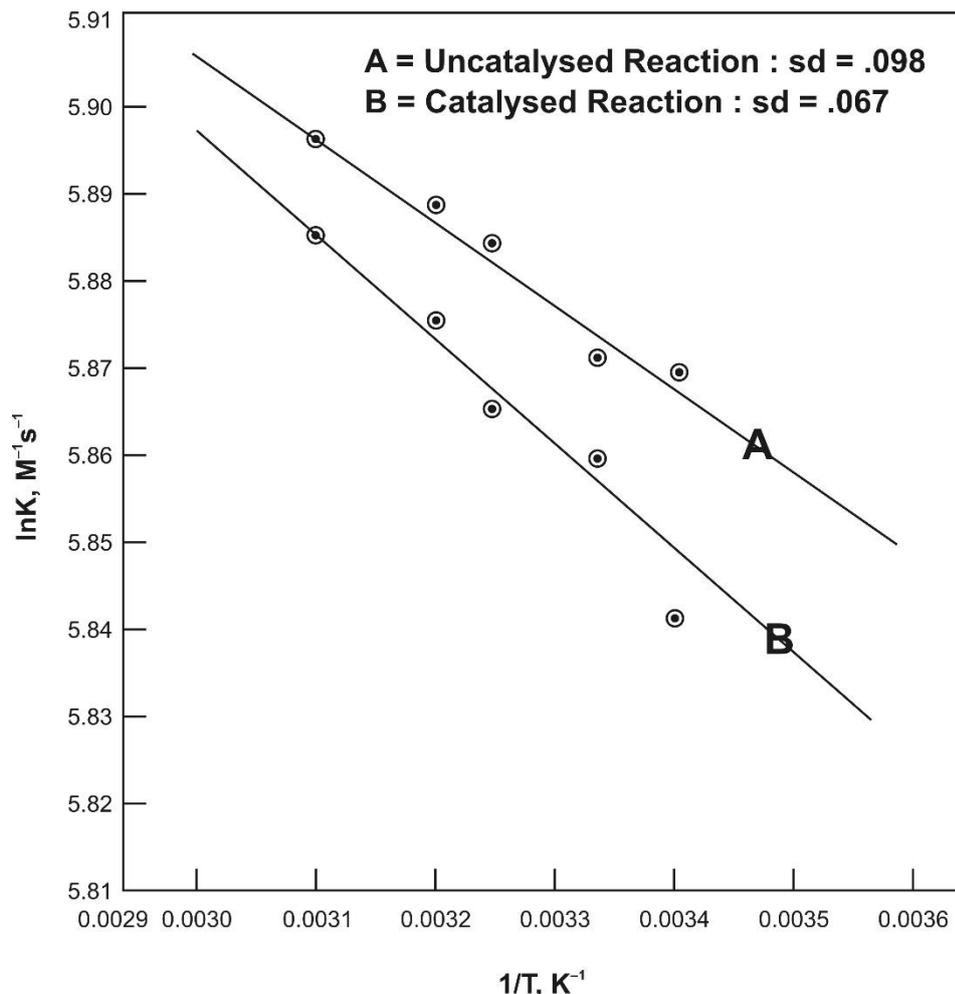
**Fig.6. Effect of temperature on catalysed and uncatalysed reaction**
Required conditions: $I = 0.05M$ (KNO$_3$), pH = $3.0 \pm 0.02$, [Phen]=$5.5 \times 10^{-4}$M [Fe(CN)$_6$]$^{4-}$ = $5.5 \times 10^{-5}$M, Pb$^{2+}$ = $2.5 \times 10^{-4}$M.

On the catalysed reaction The effect of Ionic strength was also observed in the range 0.05-0.40M using KNO$_3$.As the ionic strength of the medium increases in The initial rate decreased indicating a negative salt effect. In place of KNO$_3$ if, KCl for maintaining ionic strength the rate decreases to an appreciable extent. This may be attributed to subsequent decrease in [Pb]$^{+2}$ or [PbCl$^+$] along with the formation of "ion-pair complex" between [Pb]$^{2+}$ and [Fe(CN)$_6$]$^{4}$[19].

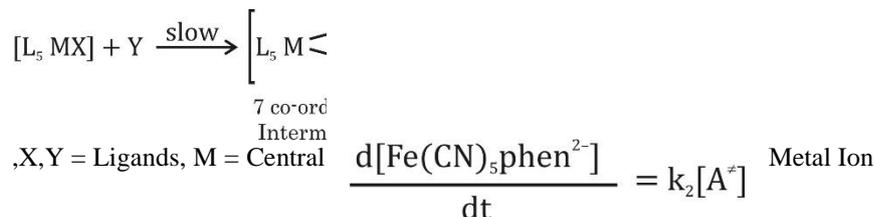**Effect of concentration of water**

The results observed till now show that the reaction follows either a D or an I$_d$ mechanism. The ligand substitution reactions may follow two extreme conditions-Dissociative (D) mechanism- It occurs through 5 membered transition state.[36,37]
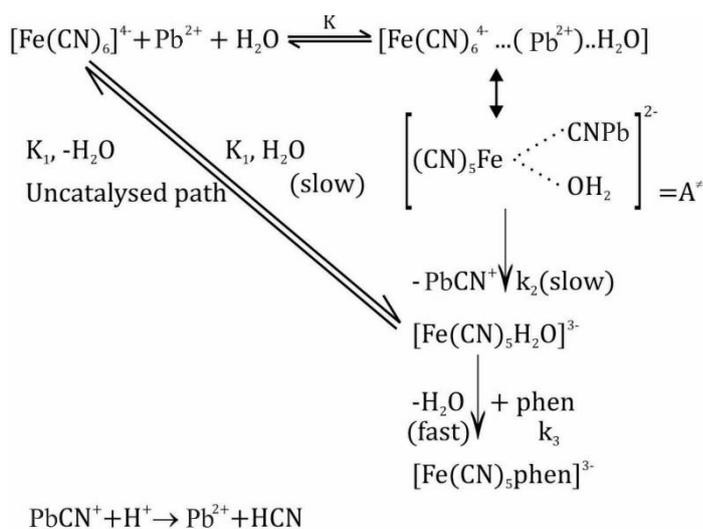
$$[L_5\,MX] \xrightarrow{\text{slow}} X + [L_5\,M] \xrightarrow[\text{fast}]{+Y} [L_5\,MY]$$

5 co-ordinated
Intermediate
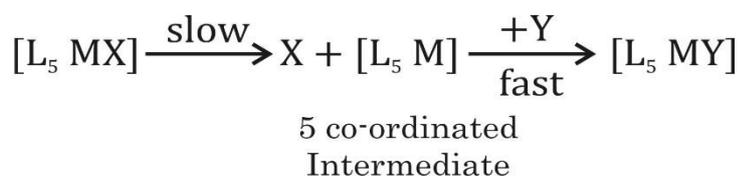
Assosiative(A) mechanism – It occurs through 7 membered transition state.

$$[L_5\,MX] + Y \xrightarrow{\text{slow}} \Big[ L_5\,M \Big\langle$$

7 co-ord
Interm
,X,Y = Ligands, M = Central $\dfrac{d[Fe(CN)_5phen^{2-}]}{dt} = k_2[A^{\neq}]$   Metal Ion

Instead of 5 or 7 membered transition state ,a transition state may be reached in which some degree of bond breaking accompanies a given degree of bond making. The interchange of the ligands X and Y could be accomplished mostly by formatiom of bond of the incoming ligand i.e. involving interchange dissociative $I_d$ mechanism or by breakage the bond of the outgoing ligand (interchange dissociative $I_d$)[ 38,39] but in both cases both ligands are bound to the metal to some extentI[40].

In order to make a distinction between these two, the concentration of water content concentration of the medium was reduced from 55.00M to 35.00 M by adding different amount of ethanol content. The reaction rate decreased with the decrement in the content of water which proved an Id as the most plausible mechanism. However, if someone argues in favour of the D mechanism , the reaction rate would have been indifferent to the varying amounts of water content [38].

The effect of lead, phen. and ferrocyanide concentration were considered and all together they pointed towards the Id mechanism as depicted below-

$$[Fe(CN)_6]^{4-} + Pb^{2+} + H_2O \rightleftharpoons[\;]{K} [Fe(CN)_6^{4-}...(\,Pb^{2+})..H_2O]$$

$K_1, -H_2O$    $K_1, H_2O$
Uncatalysed path    (slow)

$$\Big[ (CN)_5Fe \underset{\cdots OH_2}{\overset{\cdots CNPb}{\cdots}} \Big]^{2-} = A^{\neq}$$

$- PbCN^+ \downarrow k_2(slow)$

$[Fe(CN)_5H_2O]^{3-}$

$-H_2O \downarrow + phen$
(fast)    $k_3$

$[Fe(CN)_5phen]^{3-}$

$PbCN^+ + H^+ \rightarrow Pb^{2+} + HCN$

The rate equation for the complex formed during the reaction i.e. $[Fe(CN)_5\,Phen]^{3-}$ via the catalysed reaction is given by Eqn (1)

(1)

The rate corresponding to uncatalysed reaction can be expressed by Eqn (2) where k' is a constant of composite rate.

Uncatalysed   Rate =    $k'[Fe(CN)_6]^{4-}$    (2)
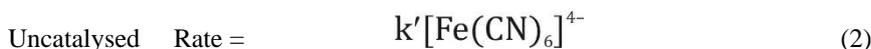
The proposed mechanistic scheme explains the activity of $Pb^{2+}$ as catalyst at lower concentrations of the rate determing step of the path is assumed to be decomposition of the activated complex. The overall reaction, both catalysed and uncatalysed in presence of non-rate limiting amounts of [Phen] can be written by Eqn (3).

Rate=

$$\frac{d[Fe(CN)_5phen^{2-}]}{dt} = k_2[Fe(CN)_6]^{4-} + \frac{k_2K[Fe(CN)_6]^{4-}[Hg]^{2+}[H_2O]}{1+K[Fe(CN)_6]^{4-}} \quad (3)$$

The Second term in Eqn. 3 tells us about catalyzed rate of reaction and which shows the variable order dependence with respect to $[Fe(CN)_6]^{4-}$. The equilibrium constant K is observed from the above equation for addition of $[Fe(CN)_6]^{4-}$ and lead (II) in aqueous media.

When K>I, the equilibrium in the above proposed mechanism is observed to lie on the right side. Moreover, if $[Fe(CN)_6]^{4-}$ is present in smaller concentration then $K[Fe(CN)_6]^{4-} << I$. Then, in this case water is taken in excess, therefore Eqn (3) transforms to Eqn (4)-

$$\text{Rate} = k'[Fe(CN)_6]^{4-} + k'_2K[Hg]^{2+}[Fe(CN)_6]^{4-} \quad (4)$$

Eqn (4) gives us the value of the observed rate constant and $k_2'$ becomes equal $k_2[H_2O]$.

When high concentrations of $[Fe(CN)_6]^{4-}$ are taken

$K[Fe(CN)_6]^{4-} >> 1$ Eqn (3) transforms to Eqn (5).

$$\text{Rate} = k'[Fe(CN)_6]^{4-} + k'_2K[Hg]^{2+}[Fe(CN)_6]^{4-} \quad (5)$$

The value of rate constants $k'$ and $k_2$ are calculated from the intercept and slope respectively from the graph between initial rate vs $[Pb^{2+}]$ under conditions specified for Eqn (5). The rate constants at I = 0.4M, Temp. = $25^0C$, pH = 3.0 are k' = $(6.1 \pm 0.25) \times 10^{-3}s^{-1}$, $k_2 = 4.31 \pm 0.1s^{-1}$. The rate constants k' and $k_2$ obtained above were kept in Eqn (4) and the values that correspond to equilibrium constant K are calculated, at different concentrations of lead at lower concentrations of $[Fe(CN)_6]^{4-}$. It was seen that the calculated value of log K as $2.55 \pm 0.08$ (table 1) is in good agreement with the value as reported by Beck [35] as 2.38. The values of $k_2$ were calculated for higher concentrations of $[Fe(CN)_6^{4}]$, it was equally valid for low $[Fe(CN)_6]^{4-}$ concentrations, by reframing Eqn (4) to Eqn (6)

$$k_2 = \frac{\text{rate} - k'[Fe(CN)_6]^{4-}}{K[Fe(CN)_6]^{4-}[Hg]^{2+}[H_2O]} \quad (6)$$

**Table 1 Calculation of K**
**Variation $[Pb^2+]$ at lower concentration of $(Fe(CN)_6)^{4-}$**

| $10^7[Pb^{+2}](M)$ | $10^4Vi(Ms^{-1})$ | K[Calculated using Eq. (14)] |
|---|---|---|
| 2.5 | 1.0 | 356.12 |
| 4.5 | 2.0 | 340.44 |
| 6.5 | 3.5 | 349.05 |
| 8.5 | 4.5 | 354.20 |
| 10.5 | 6.5 | 358.07 |
| | | Av. $351.58 \pm 8.01$ |

Under conditions: I =0.1 M(KNO$_3$, pH =$3.0 \pm 0.02$, Temp. = $25 \pm 0.1°C$, [Phen]=$7 \times 10^{-5}$M, $[Fe(CN)_6]^{4-}$ =$7 \times 10^{-3}$M.

Utilising the values of rate, concentration terms and K , $k_2$ was calculated to be $4.12+0.1s^{-1}$, this is in excellent agreement with the experimentally observed value $4.01+0.1s^{-1}$. The complex behaviour of $[Pb^{+2}]$ on initial rate at higher concentration needs to be discussed at length. The rapid enhancement in rate at $[Pb^{+2}] > 2.1x10^{-5}$ M may be expressed by taking into consideration a 28% character that is ionic in nature for the Pb-Cl bond in $PbCl_2$ [42] along with the following equilibrium.

$$Hg^{2+} + Cl^- \underset{K_1}{\rightleftharpoons} HgCl^+$$

$$HgCl^+ + Cl^- \underset{K_2}{\rightleftharpoons} HgCl_2$$
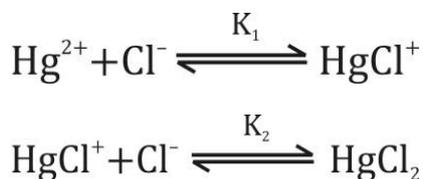
Although the values of $K_1$ and $K_2$ are not known for this condition, in this experiment but the values [43] of log $K_1 = 6.62$ and log $K_2 = 6.36$ at I = 0.5 ($NaClO_4$) and $[H^+] = 0.1M$ have been used to obtain the distribution of three possible species i.e. $Pb^{2+}$, $PbCl^+$ and $PbCl_2$ in a hydrated solution of $PbCl_2$ as a function of Log $[PbCl_2]$ (Figure 6). It is evident from the species distribution that the species $PbCl^+$ exists in appreciable concentration at $[PbCl_2] > 10^{-6}$ M, though PbCl exists in considerable concentrations while $PbCl_2$ predominates at still higher concentrations. Therefore the formation of an ion-pair between $[Fe(CN)_6]^{4-}$ and $PbCl^+$ is highly expected (log $K_{PbCN-Cl}=10.52$) [44], (log $K_{PbCN}=17$) [45]. However, this adduct is weaker in comparison to the corresponding adduct formed with $Pb^{2+}$. The most suitable explanation is lower polarizing power that facilitates the faster decomposition of the complex. It has been seen that at $[Fe(CN)_6^{4-}] = 6.4 x 10^{-4}M$ and with $[Pb^{2+}] > 6.4 x10^{-4}$ M , there is a rapid fall in the rate of reaction that may be because of the complex formed between $[Fe(CN)_6]^{4-}$ and $PbCl_2$ in the ratio of 1:1 and subsequently the species $Pb^{2+}$ and $PbCl^+$ have been removed from the catalytic cycle.[35]

### 3.5. Conclusion

Hence, the supposition about the catalytic role of Pb(II) in the given mechanism sounds possible. After first combination of $Pb^{2+}$ and $[Fe(CN)_6]^{4-}$ , the ion pair quickly isomerizes which finally decomposes, relatively slowly forming $[Fe(CN)_5(H_2O)]^{3-}$ and Pb $CN^+$. After this, water molecule in $[Fe(CN)_5H_2O]^{3-}$ is replaced quickly by phenanthroline forming our required compound $[Fe(CN)_5 Phen]^{3-}$ by replacing the cyanide ion present in ferrocyanide [46, 47, 48] .

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