JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

KINETICS OF SILVER CATALYZED LIGAND EXCHANGE REACTION BETWEEN HEXACYANOFERRATE (II) AND DPQ

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ABSTRACT

This study investigates the kinetics and mechanism of the Ag(I)-catalyzed substitution of coordinated cyanide in hexacyanoferrate(II) by dipyrido [3,2-d∶2′,3′-f] quinoxaline (Dpq), monitored spectrophotometrically via the formation of the dark green complex $[Fe(CN)_5bpy]^{3-}$ at 547 nm. Experimental conditions were maintained at 25 ± 0.1°C and pH 2.5 ± 0.02. The reaction rate was examined as a function of pH, $[Fe(CN)_6]^{4-}$, and [dpq], revealing variable order dependence on the ferricyanide concentration. Effects of dielectric constant, solvent composition, temperature, and ionic strength were analyzed to suggest a polar transition state and an interchange dissociative (Id) mechanism. The catalytic behaviour of Ag^+ across various concentrations was also explored. Activation parameters were derived using Arrhenius and Eyring equations to support the proposed mechanistic pathway.

Keywords: Dpq, Kinetics, hexacyanoferrate, dissociative, silver catalysed.

INTRODUCTION

Potassium hexacyanoferrate(II), $[Fe(CN)_6]^{4-}$, is recognized for its kinetic inertness among cyano complexes of transition metals. Various sparingly soluble salts with formulations like $K_2MII[Fe(CN)_6]$ and $KMIII[Fe(CN)_6]$ form via outer-sphere coordination involving alkali or transition metal ions. Adducts of the form $K_4Fe(CN\cdot BX_3)_6$ (B = boron; X = F, Cl) develop slowly and are identified by a ∼100 cm^{-1} shift in CN stretching frequencies[1-4].

While extensive literature exists on ligand exchange kinetics in pentacyanoferrate(II) systems, limited information is available for reactions involving hexacyanoferrate(II) complexes [5-16], particularly in highly ionic or micellar environments. Moreover, oxidation kinetics of this complex have been broadly studied [17-19], but its substitution kinetics remain underexplored. Previous investigations focused more on analytical applications rather than mechanistic insights[20-24].

Upon photolysis or thermal activation, $[Fe(CN)_6]^{4-}$ slowly forms $[Fe(CN)_5H_2O]^{3-}$, a reactive intermediate that can undergo ligand exchange. Substitution by dipyrido proceeds via this aquated species [25-29]. While the uncatalyzed reaction is sluggish [30-32], the presence of transition metals like silver accelerates the substitution process considerably as per following equations 1-3.

$$[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_5(H_2O)]^{3-} + CN^- \quad (1)$$

$$[Fe(CN)_5(H_2O)]^{3-} + dpq \rightarrow [Fe(CN)_5dpq]^{3-} + H_2O \quad (2)$$

$$[Fe(CN)_6]^{4-} + dpq \rightarrow [Fe(CN)_5dpq]^{3-} + CN^- \quad (3)$$

Recent kinetic and mechanistic studies in coordination chemistry have seen a significant shift toward environmentally friendly catalytic systems. The substitution of hazardous heavy metals with greener alternatives, such as Ag(I), has received attention due to silver's lower toxicity and comparable catalytic efficiency. For example, Liu et al. (2021) demonstrated that Ag^+ ions exhibit catalytic behavior in cyanide exchange reactions similar to Hg^{2+}, albeit through slightly different electronic interactions and coordination geometries [33]. Their study employed time-resolved UV-Vis spectroscopy and proposed an associative intermediate stabilized by Ag–CN interactions.

Another notable study by Sharma et al. employed DFT calculations to examine the ligand substitution mechanism in pentacyano complexes using bipyridyl and its derivatives [34]. Their results suggested that electron-donating substituents on the ligand backbone reduce the activation barrier, facilitating faster substitution. This has direct implications for designing more effective ligands for substitution chemistry.Furthermore, Patel et al. [35,36] explored the kinetics of dpq (dipyridoquinoxaline) complexes in mixed aqueous-organic media and found that the presence of Ag^+ significantly enhanced substitution rates, supporting an interchange dissociative (I_d) mechanism similar to earlier findings with Hg^{2+} [37].Studies also reflect a strong trend toward mechanistic modeling using Eyring and Arrhenius frameworks, with modern adaptations including ionic strength and solvent polarity variables [35]. The shift in research priorities toward silver-based systems underscores not only scientific innovation but also a commitment to sustainability in coordination chemistry [38-40].

$$[Fe(CN)_6]^{4-} + dpq \rightarrow [Fe(CN)_5dpq]^{3-} + CN^- \quad (4)$$

$$[Fe(CN)_6]^{4-} + Ag^+ \rightleftharpoons [Fe(CN)_6 \cdot Ag]^{3-} \quad (5)$$

This chapter details the kinetic study of Ag^+-catalyzed substitution of cyanide by dipyrido in $[Fe(CN)_6]^{4-}$, with mechanistic analysis and derivation of kinetic parameters.

EXPERIMENTAL

Materials

All reagents were of analytical grade. Aqueous solutions were prepared using double-distilled water. Stock solutions of $K_4[Fe(CN)_6]\cdot 3H_2O$ (Merck, Germany) were stored in amber bottles to prevent photodecomposition. Fresh solutions of dipyrido (Dpq) (SD Fine)and $AgNO_3$ (BDH) were prepared daily. Ionic strength was maintained using KNO_3(AR Glaxo). pH adjustments were made using potassium hydrogen phthalate buffers and controlled with HCl or NaOH as reported in literature[49].

Procedure

Reactants were pre-equilibrated at 25°C. In sequence, 2 mL each of dipyrido, buffer, and $AgNO_3$ solutions were mixed, followed by 2 mL of $[Fe(CN)_6]^{4-}$ to initiate the reaction. The mixture was rapidly transferred to a 10 mm pathlength quartz cuvette, and absorbance was recorded at 547 nm using a Genesis 10UV spectrophotometer to track formation of $[Fe(CN)_5dpq]^{3-}$ (Fig.1).

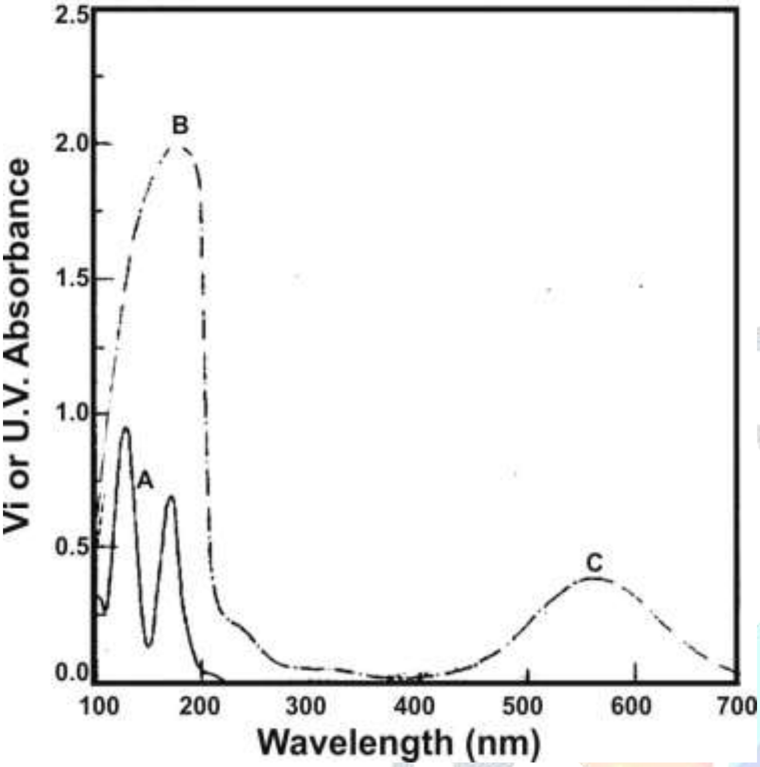


Fig. 1. **Absorption spectra of reactants and products**

(A)[Dpq] = $3.5x10^{-4}$M, (B) $[Fe(CN)_6]^{4-}$ = $6.5x10^{-4}$M, (C) Product
Under Conditions: $[Fe(CN)_6]^{4-}$ = 6.5 X 10^{-4}M, [Dpq] = 3.5 X 10^{-3}, $[Ag^{1+}]$ = $8.5x10^{-7}$M and pH = 2.5$\underline{+}$ 0.02 (after one hour).

RESULTS AND DISCUSSION

Effect of pH on reaction rate

In order to investigate the effect of pH on the rate of reaction between $[Fe(CN)_6]^{4-}$ and Dpq catalysed by $[Ag]^{1+}$, fixed time procedure was followed and the chosen pH range was 1.0-11.0. It is to be noted that the absorbance values ,A_t is measured at (t = 5,10 minutes) as a function of $[Ag]^{!+}$,keeping all other experimental values fixed at optimum, are treated as a closer measure of initial rate as given in Table 1. Thus Eqn 14 predicts a linear relationship between initial rate and absorbance values.

Table 1
Effect of variation of pH on intiial rate of catalysed substitution rate.

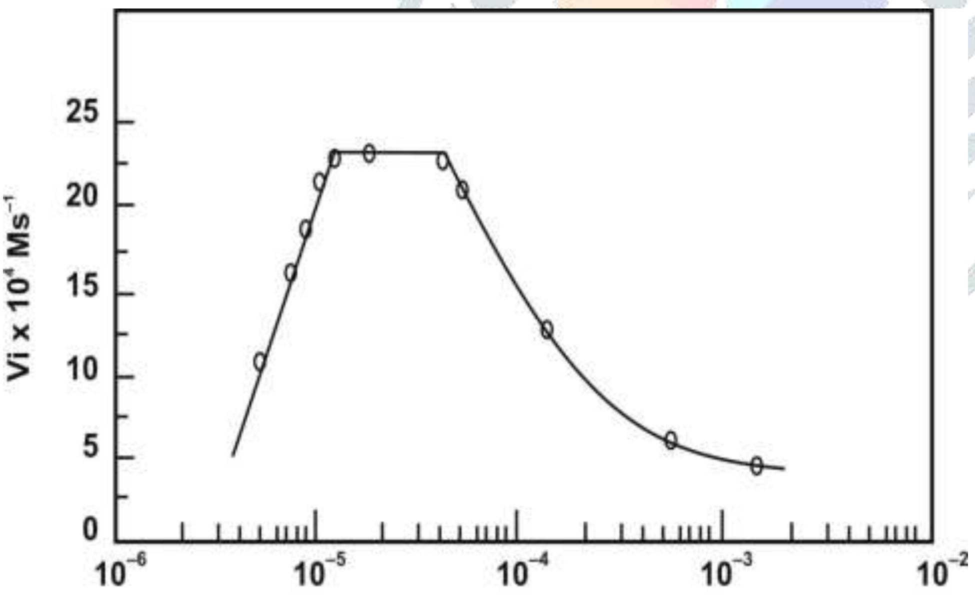
pH	A_5	A_{10}
0.5	0.080	0.136
1.0	0.122	0.168
1.5	0.181	0.185
2.0	0.238	0.222
2.5	0.261	0.345
3.0	0.223	0.267
4.0	0.198	0.215
6.0	0.180	0.198
7.5	0.163	0.175
9.5	0.158	0.165

Under Conditions : $[Fe(CN)_6]^{4-}$ = 2.8 x 10^{-3} M, [Dpq] = 6.5 x 10^{-5} M $[Ag]^{1+}$= 2.5 x 10^{-5} M, Temp. = 25 ± 0.1°C and I = 0.05 M $(KNO)_3$

All the other variables were kept constant in order to select a pH value corresponding to the optimum rate of reaction. 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 table shows that the rate is slow at low pH values reaches to a maximum value between 2.0 and 3.0 and subsequently falls again. The rate is slow at low pH values due to formation of various protonated forms of [Fe(CN)$_6$]$^{4-}$ itself [50]. The decrease in rate at higher pH values may be due to the deficiency of protons required to reproduce the catalytic species. In addition to the above reason, the decrease in rate may be attributed due to decrease in [Ag]$^{1+}$ because of its hydrolytic precipitation.

Dependence of initial rate on [Dpq] and [Fe(CN)$_6$]$^{4-}$

The initial rate which is defined as the rate measured within 15 minutes of the start of the reaction and not at t = 0, were determined as a function of [Dpq] by varying its concentration from 3.8x10^{-2} to 8.8x10^{-6} M ,plotted in Fig. 2, keeping the concentrations of other reaction variables constant at Ag^{1+} = 3.5x10^{-5} M, pH = 2,5± 0.02, temp. =25± 0.1^{o}C and I = 0.05 M (KNO$_3$).The plot of initial rate Vs. [Dpq] is shown in Figure 2. This plot shows that the rate increases in the beginning, becomes constant in the range 5 X 10^{-5}M to
5 X 10^{-4}M and finally decreases at still higher concentration. The possibility of any complexation between Ag1+ ions and phenanthroline can be ruled out under these conditions.



[Dpq]/M

Fig 2 : Effect of [Dpq] on initial rate at [Fe(CN)$_6$]$^{4-}$

Under Conditions: [Fe(CN)$_6$]$^{4-}$ = 2.0x10^{-2}M, [Ag]$^{1+}$ = 1.5x10^{-5} M, pH = 2.5±0.02, Temp. = 25.0±0.1^{o}C and I=0.05M (KNO$_3$).

On the other hand ,complex formation of the adduct type may take place between Ag^{1+} ions and Dpq ligand when dipyrido concentration is very much higher than [Ag $^{1+}$]. This would eventually inhibit the catalytic activty of [Ag $^{1+}$]. Keeping all experimental parameters constant at optimum values, the dependence of rate on [Fe(CN)$_6$]$^{4-}$ was studied in the concentration range, 7.5x10^{-4}M to 4.5x10^{-2}M. The plot of log (Vi) versus Log [Fe(CN)$_6$]$^{4-}$ is shown in Figure 3, which indicates a variable order dependence ranging from first order at its low concentration to a low fractional order at higher concentrations but certainly not tending towards zero.

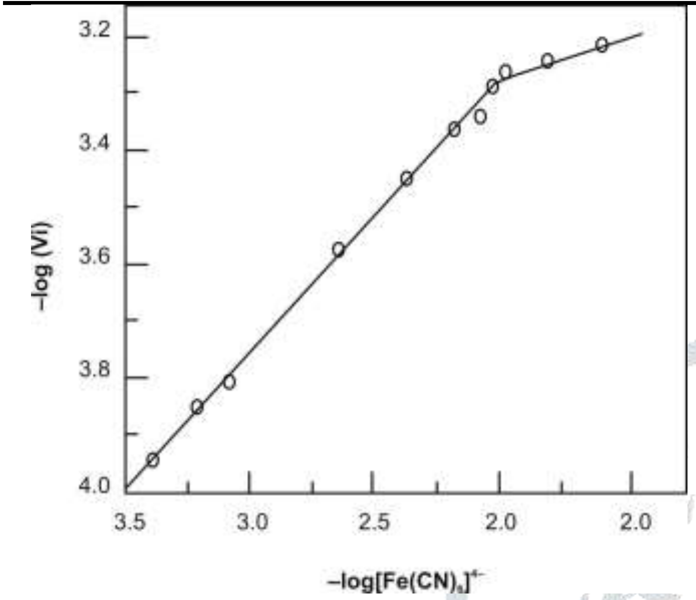
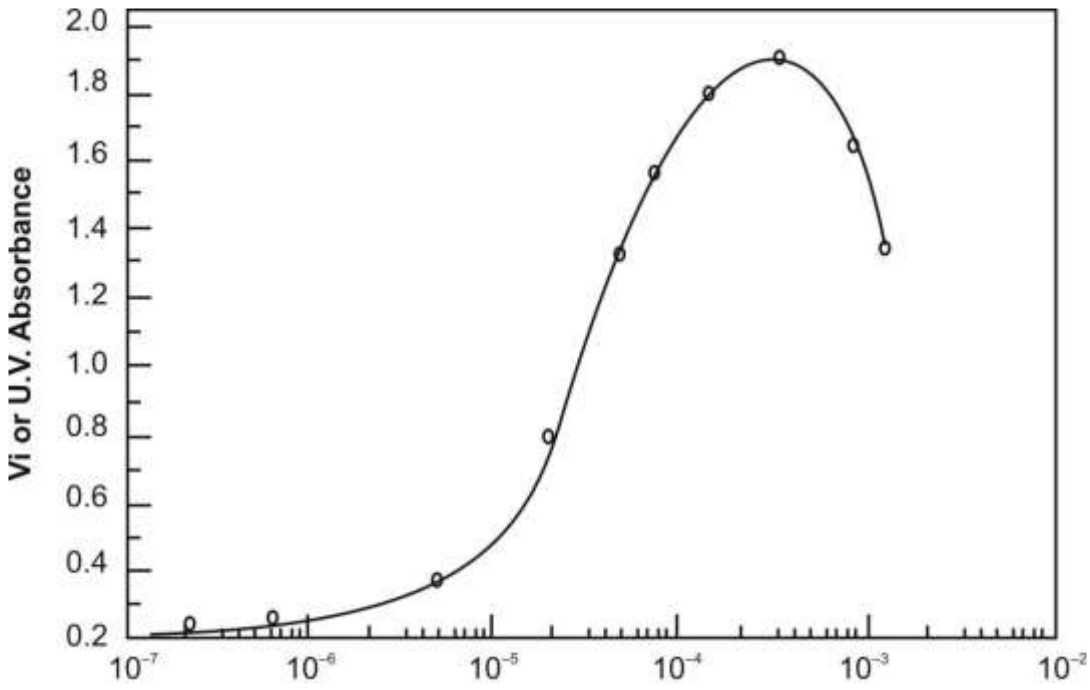


Fig.3. Dependence of the initial rate on $[Fe(CN)_6]^{4-}$ in presence of $[Ag^{1+}]$.
Under Conditions [Dpq] = 6.0×10^{-5} M, $[Ag^{1+}]$. = 8.0×10^{-6} M, pH = 2,5$\pm$0.2 Temp. 25.0$\pm$0.1^{0}C and I = 0.05 M (KNO_3)

Influence of Ag^{1+} concentration on reaction rate

The concentration of $[Ag^{1+}]$. was varied from 1.5×10^{-7}M to 3.5×10^{-1}M keeping concentrations of $[Fe(CN)_6]^{4-}$ and dipyrido constant at an optimum value at pH =2,5±0.02, I = 0.05M (KNO_3) and temp. = 25± 0.1°C .This variation range for $[Ag^{1+}]$. $^+$ was selected in order to test the linearity between initial rate and $[Ag^{1+}]$ for analytical application due to its catalytic effect and also to know the changing role of Silver as a function of concentration. The results are shown in Fig.4. where the plot of the absorbance change after 5 min (A_2) versus $[Ag^{1+}]$ increases linearly in the beginning reaches to a maximum value at still higher concentrations in a non-linear manner until $[Ag^{1+}]$ becomes equal to $[Fe(CN)_6]^{4-}$, the rate finally starts declining. The intercept obtained from the initial linear portion of the curve provides the rate due to uncatalysed path.



$[Ag^{1+}]$/M

Fig.4. Dependence of the initial rate of substitution of CN^- in $[Fe(CN)_6]^{4-}$ by [Dpq] in presence of $[Ag^{1+}]$.

Under Conditions: $[Fe(CN)_6]^{4-}$ = 8.0 x10^{-4}M, [Dpq] =7.5x10^{-5} M, pH = 2.5±0.2, Temp. = 25.0 +0.1^{0}C and I = 0.05M (KNO_3)

The decline in the rate at higher [Ag $^{1+}$] is probably due to the formation of a binary adduct $[Fe(CN)_6^{4-}$. $AgNO_3]$. In a different experiment it was observed that a white precipitate is formed in the beginning immediately after mixing $[Fe(CN)_6]^{4-}$ and [Ag $^{1+}$]in 1:2 molar ratio at higher $[Fe(CN)_6]^{4-}$ it rapidly turned into pale blue confirming the formation of a binuclear complex. [43].

Effect of temperature and ionic strength on reaction rate

The influence of temperature on the initial rate for the substitution of co- ordinated cyanide from $[Fe(CN)_6]^{4-}$ by dipyrido was studied at different temperatures in the range 25ºC-45ºC (Table 2).

Table 2. Effect of Temperature on Initial Rate $[Fe(CN)_6]^{4-}$

Temperature (^{0}K)	Vi x 10^4 M sec^{-1}
293	0.740
298	0.883
303	1.157
308	1.226
313	1.361

Under Conditions: $[Fe(CN)_6]^{4-}$ = 5.5 × 10^{-5}M], [Dpq] = 5.5 × 10^{-1}, $[Ag^{1+}]$= 2.5 × 10^{-4} M, pH = 3.0±0.02, I = 0.05 M (KNO_3**)**

Higher temperature were avoided due to the possibility of decomposition of $[Fe(CN)_4Dpq]^{3-}$ complex. The catalysed as well as uncatalysed reactions both follow, the Arrhenius and Eyring equation from which activation parameters have been calculated. The values of a activation parameter for catalysed reaction are found to be Ea = 57. 28 ± 2.6K J Mol^{-1} , Δ H $^{\neq}$ = 51.72 ± 4.9 $KJMol^{-1}$, $\Delta S^{\neq}$ = -44.97 ± 5.7JK^{-1} Mol^{-1}. The values of a activation parameter for uncatalysed reaction are found to be Ea = 65.92 ± 2.5 $KJmol^{-1}$, Δ H $^{\neq}$ = 64.32 ± 2.9 $KJmol^{-1}$, $\Delta S^{\neq}$ = -38.99± 5.8 $KJmol^{-1}$ (Fig.5).

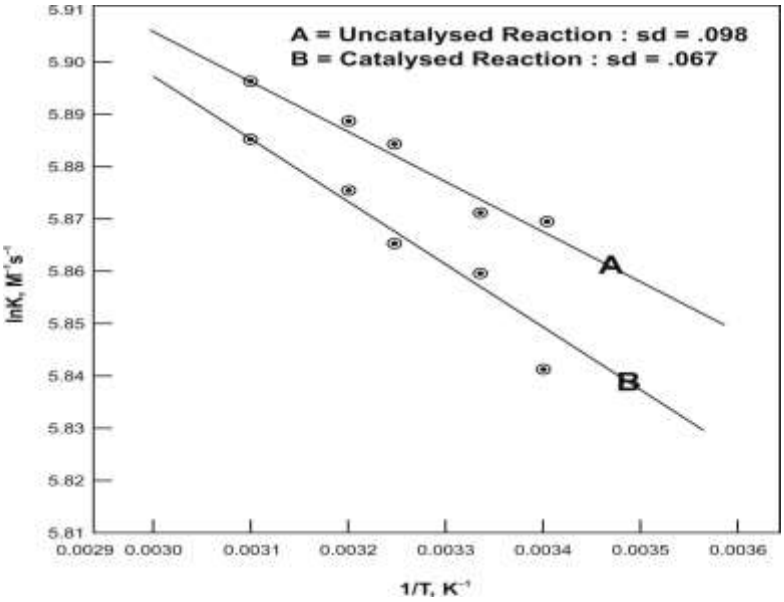
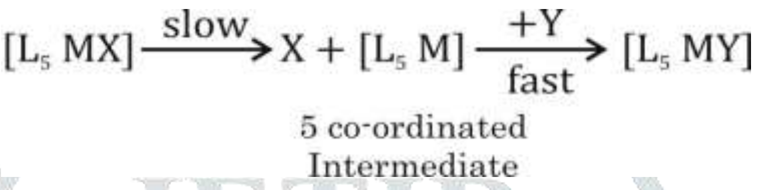


Fig.5. Effect of temperature on catalysed and uncatalysed reaction

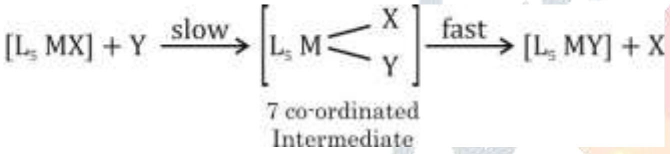
Under Conditions: $[Fe(CN)_6]^{4-}$ = 5.9 x 10^{-5}M, [Dpq] = 5.7 x 10^{-4}M, Ag^{1+}= 2.5 x 10^{-4}M, pH = 2.5 ± 0.02, I = 0.05M (KNO_3)

Effect of water concentration.

The results discussed till now indicate operation of 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.[51,52,53]



Assosiative(A) mechanism – It occurs through 7 membered transition state.



X,Y = Ligands, M = Central 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 breaking the bond of the leaving group (interchange dissociative I_d)[54,55] [or by making the bond of the entering group(interchange associative I_a) but in both cases both ligands are bound to the metal to some extentI[48]

In order to make a distinction between these two, the water concentration of the medium was reduced from 55.00 to 35.00 M by addition of varying amounts of ethanol. The rate of reaction decreases with decrease in water content and suggest to an Id mechanism. If the D mechanism is obeyed, the rate of reaction would have been insensitive to the variations observed in binary aqueous medium. [54].

The effect of concentrations of $[Fe(CN)_6]^{4-}$, Dipyrido and Ag^{+1}as catalyst and other observations reported above lead us to propose the following mechanistic scheme.

Uncatalysed reaction

(6) $[Fe(CN)_6]^{4-} + H_2O \xrightleftharpoons[k_{-1}]{k_1} [Fe(CN)_5H_2O]^{3-} + CN^-$

Catalysed reaction

$[Fe(CN)_6]^{4-} + Ag^{+1} + H_2O \ \ k \rightarrow \ [[Fe(CN)_6]^4 …. Ag^{+1} ….. H_2O]$ (7)

$[[Fe(CN)_6]^4 …. Ag^{+1} ….. H_2O]\ k_2 \rightarrow \ [Fe(CN)_5H_2O]^{3-} + AgCN$ (8)

$[Fe(CN)_5H_2O]^{3-} + [Dpq]\ \ k_3 \rightarrow \ [Fe(CN)_5dpq]^{3-} + H_2O$ (9)

$AgCN + H+ \rightarrow Ag+ + HCN$ (10)

The rate expression for the formation of complex $[Fe(CN)_5 Phen]^{3-}$ through catalysed path can be expressed by Eqn (11)

$$\frac{d[Fe(CN)_5\ dpq\ ]^{3-}}{dt} = k_2[A^{\neq}] \qquad (11)$$

The rate corresponding to uncatalysed path can be given by Eqn (12) where k' is a composite rate constant.

Uncatalysed $\quad$ Rate = $k'[Fe(CN)_6]^{4-}$ $\quad$ (12)

The proposed mechanistic scheme explains the catalytic activity of Ag^{1+} at low concentration if 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 [Dpq] can be written by Eqn (13).

$$\text{Rate} = \frac{d[Fe(CN)_5\ dpq\ ]^{3-}}{dt} = k'[Fe(CN)_6]^{4-} + \frac{k_2K[Fe(CN)_6{}^{4-}][Ag^{+}]}{1+K[Fe(CN)_6{}^{4-}]}$$

(13)

The Second term in Eqn.13 refers to the rate of catalysed reaction and explains the variable order dependence in $[Fe(CN)_6]^{4-}$. The K is defined as equilibrium constant for association of silver and water with $[Fe(CN)_6]^{4-}$.

If K > 1, the equilibrium in Eqn (7) is assumed to lie on the right hand side. However, if $[Fe(CN)_6]^{4-}$ is small then $K[Fe(CN)_6]^{4-} << 1$. Since the water concentration is in large excess, therefore Eqn (13) reduces to Eqn (14)-

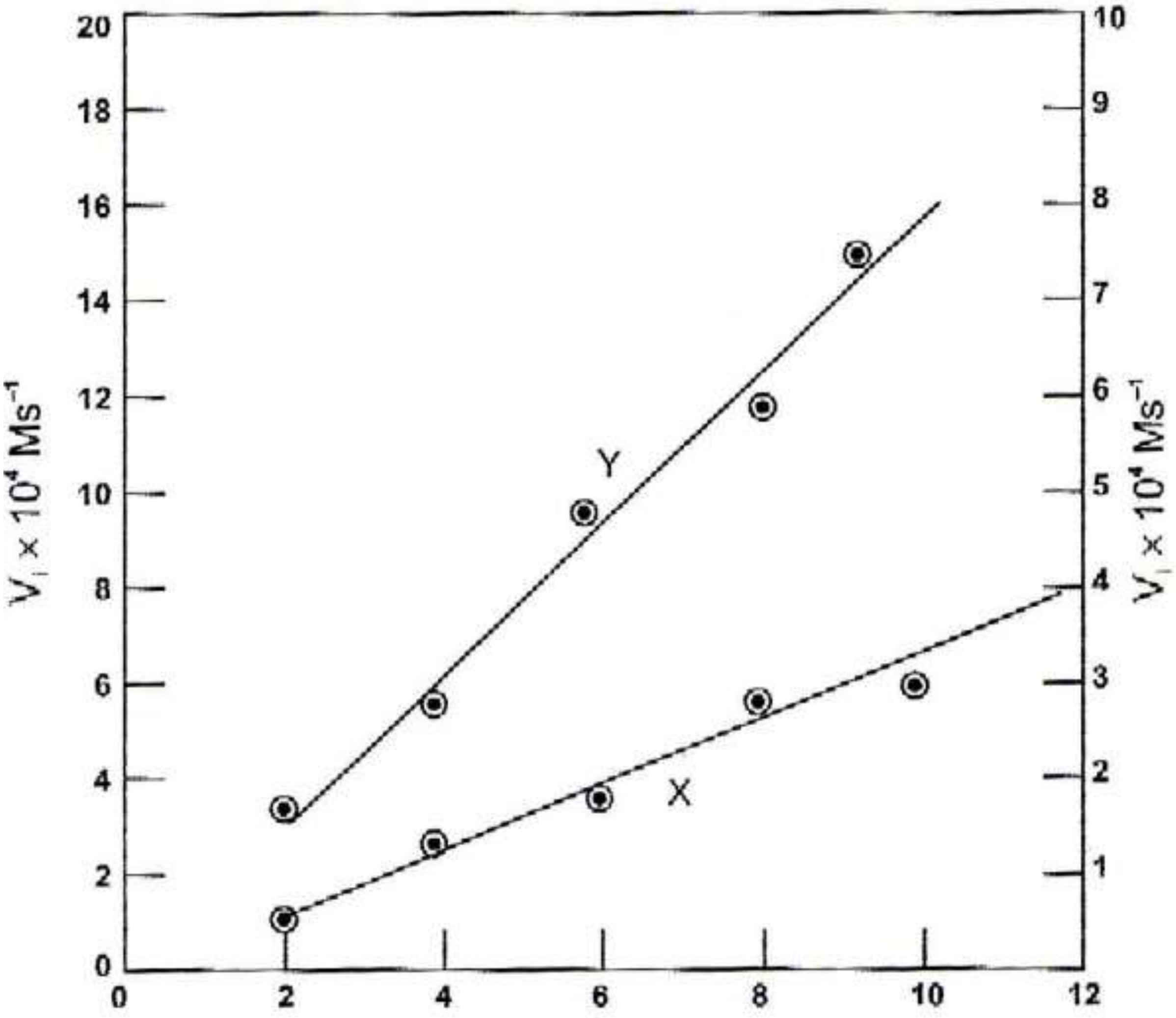
$$\text{Rate} = k'[Fe(CN)_6{}^{4-}]+k'_2K[Fe(CN)_6{}^{4-}][Ag^{+}] \qquad (14)$$

Eqn (14) gives the observed rate constant and $k_2' = k_2\ [H_2O]$.

At higher concentration of $[Fe(CN)_6]^{4-}K[Fe(CN)_6]^{4-} >> 1$ Eqn (13) takes the form of Eqn. (15).

$$\text{Rate} = k'[Fe(CN)_6{}^{4-}]+k'_2[Ag^{+}] \qquad (15)$$

Therefore, the rate constants k' and k'_2 were evaluated from the intercept and slope respectively of a plot of initial rate versus $[Ag]^{+}$ (Fig. 6) under conditions specified for Eqn (15) (Table 4). The rate constants at I = 0.2M, Temp. = 25^{0}C, pH = 2.5 are k' = (6.6 ± 0.15) x $10^{-3}s^{-1}$, $k_2 = 4.12 \pm 0.1s^{-1}$.



[Ag^+] × 10^7 M

Fig. 6 Effect of variation of Ag+ on initial reaction rate

Under condition : X=$[Fe(CN)_6]^{4-}$ = 3.0×10^{-2} M, [dpq]= 6.0×10^{-4} M,I= 0.2M(KNO_3)
Y =$[Fe(CN)_6]^{4-}$ = 8.0×10^{-3} M, [dpq]= 8.0×10^{-4} M,I= 0.2M(KNO_3),Temp. 25.0±0.1^{0}C, pH = 2.5±02

Table 4 Effect of variation of Ag^{1+} at high $[Fe(CN)_6]^{4-}$ on initial rate

Ag1+ x 10^7 M	Vi x 10^4 M sec^{-1}
2	3.8
4	4.9
6	7.9
8	10.2
10	14.7

Under Conditions: $[Fe(CN)_6]^{4-} = 2.0 \times 10^{-2}$ M , [Dpq] = 5.0×10^{-4}M, pH = 2.5 ± 0.02, temp. = 25.0 ± 0.1^0C, I = 0.05 M (KNO_3)

The rate constants k' and k_2 obtained above were kept in Eqn (14) to obtain corresponding value of equilibrium constant K, at various concentration of Ag^{1+} at low $[Fe(CN)_6]^{4-}$. The Calculated values of K are listed in Table 5 and the average value of log K was found to be 2.79$\pm$0.08 which is in good agreement with the value determined by Beck [35] for the $[Fe(CN)_6]^{4-}.[Hg(CN)_2]$ complex (Log K = 2.38) although the values of k_2 have been evaluated for high $[Fe(CN)_6{}^{4}]$, it was found to be valid for lower concentrations of $[Fe(CN)_6]^{4-}$, by transforming Eqn (14) to Eqn (16)

$$k_2 = \frac{rate - k\,[Fe(CN)_6]^{4-}}{K[Fe(CN)_6]^{4-}[Ag^+][H_2O]} \qquad (16)$$

Table 5. Calculation of K $[Ag^{1+}]$ variation at low $(Fe(CN)_6]^{4-}$

$10^7[Hg^{+2}]$(M)	10^4Vi(Ms^{-1})	K[Calculated using Eq. (14)]
2	2.1	350.13
4	2.7	349.47
6	3.9	351.85
8	5.1	354.09
10	6.6	363.01
		Av. 353.71+8.01

Under Conditions: $[Fe(CN)_6]^{4-}$ =7x10^{-3}M, [Dpq] = 7x10^{-5}M, pH =3.0$\pm$0.02, Temp. = 25+0.1°C and I =0.1 M(KNO_3).

Using the values of rate, concentration terms and K from table 5, k_2 was calculated to be 4.42+0.1s^{-1}, this is in excellent agreement with the experimentally observed value 4.01+0.1s^{-1}. The rapid enhancement in rate at $[Ag^{+2}]$> 2.8x10^{-5} M may be explained by taking into consideration a 29% ionic character for the Hg-Cl [50-53].Hence, the supposition about the catalytic role of Ag in the proposed mechanistic scheme appears to be quite reasonable. After initial association between $[Fe(CN)_6]^{4-}$ and Ag^{1+} the ion pair quickly isomerizes to .$[Fe(CN)_5 \ldots\ldots AgCN \ldots\ldots H_2O]^{2-}$ which forms the final product $[Fe(CN)_5\, dpq]^{3-}$ easily [54-56].

Conclusion

This study presents a detailed kinetic and mechanistic investigation of the Ag(I)-catalyzed substitution of cyanide ligands in hexacyanoferrate(II) by dipyridoquinoxaline (dpq). The uncatalyzed reaction is extremely slow, but the introduction of Ag^+ ions significantly enhances the reaction rate. The substitution process was monitored spectrophotometrically at 547 nm under controlled temperature and pH conditions. The optimum pH for maximum catalytic efficiency was found to be 2.5, consistent with the stability of the silver ion and the reactive intermediates in acidic media.

The kinetic data reveal a complex dependence on $[Fe(CN)_6]^{4-}$ and dpq concentrations, indicating the involvement of pre-equilibrium steps and a rate-determining substitution. The derived activation parameters, including negative entropy of activation, support an interchange dissociative (I_d) mechanism. Additionally, a negative salt effect was observed, implying that electrostatic interactions play a role in the transition state stabilization or destabilization.

The proposed mechanism involves the formation of a transient Ag^+-coordinated intermediate, followed by aquation and subsequent rapid substitution by dpq. This provides a clearer understanding of the ligand exchange process in low-spin iron(II) systems and offers a framework for exploring similar reactions in transition metal chemistry.In summary, this work contributes to the field of coordination chemistry by elucidating a greener, efficient catalytic route for cyanide ligand substitution, and paves the way for future applications in analytical sensing, catalyst development, and sustainable chemical transformations.

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