

Kinetic and Mechanistic Study of Mercury(II) - Catalyzed Ligand Substitution Reaction between Hexacyanoferrate(II) and 2,2'-Bipyridine

Radhey Mohan Naik *, Jyoti Rai, Shalin Kumar, Richa Rastogi, Sheel Ratan

Abstract—The exchange of cyanide ion by a bidentate neutral organic ligand 2,2'-Bipyridine (Bipy) around the central Fe²⁺ ion of hexacyanoferrate(II) yields an intense cherry- red product [Fe(CN)₄Bipy]²⁻ that absorbs at 400 nm. The present study is concerned with the Hg(II) promoted abstraction of cyanide from hexacyanoferrate(II) by bipyridine spectrophotometrically forming a highly stable ternary complex [Fe(CN)₄Bipy]²⁻, as a function of pH, ionic strength, temperature, [Hg²⁺], [Bipy] and [Fe(CN)₆]⁴⁻. The kinetic observations suggest that the substitution reaction is governed by an interchange dissociation (I_d) mechanism, which is further supported by the thermal activation parameters viz. energy of activation (E_a), enthalpy of activation (ΔH[‡]) and entropy of activation (ΔS[‡]). The most probable mechanism consistent with the experimental findings has been proposed. The repetitive spectral scan is also provided as an evidence for the formation of a stable product during the course of reaction.

Index Term— Catalyzed Ligand Substitution reaction, Hexacyanoferrate(II), Kinetics, Thermal Activation Parameters, I_d mechanism, 2,2'-Bipyridine, Spectrophotometry.

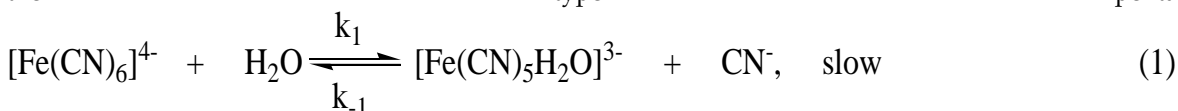


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1 INTRODUCTION

The kinetic and mechanistic studies involving the exchange of coordinated ligand in low-spin pentacyano(ligand)ferrate(II) complexes has been the subject of increasing interest until recently [1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11], [12], [13]. However, non-toxic [14], [15] highly stable [16] and least labile hexacyanoferrate(II) among cyano-complexes of transition metal is relatively least investigated with respect to ligand substitution reactions involving in it [17], [18], [19], [20], [21], [22], [23], [24], [25], [26], [27], [28], [29]. The literature survey has revealed that majority of such investigations have also been applied for specific analytical applications in trace determinations [26], [30], [31], [32], [33], [34]. It has also been observed that exchange of labeled cyanide in [Fe(CN)₆]⁴⁻ with free cyanide or aminopyridine is extremely slow process, but it engendered [Fe(CN)₅H₂O]³⁻ and CN⁻ reversibly in presence of UV radiation [35]. The substitution reaction at aquapentacyanoferrate(II) is slow, where strongly bonded cyanide ligand forces iron atom to adopt low spin t_{2g}⁶ electronic configuration, with maximum crystal field stabilization [36], [37], [38].

The majority of substituted cyano-complexes of Fe(II) and mono-substituted products are generated either through photochemical aquation or metal catalyzed dissociation of [Fe(CN)₆]⁴⁻ [21], [22], [23], [24], [25], [26]. The thermal and photochemical aquation of [Fe(CN)₆]⁴⁻ to [Fe(CN)₅H₂O]³⁻ is shown in equation (1). The [Fe(CN)₅H₂O]³⁻ so produced, found to react with few nitrogen heterocycles [21-26] or with few nitroso compounds [21,23], producing colored low-spin complexes of the type pentacyano(ligand)ferrate(II).



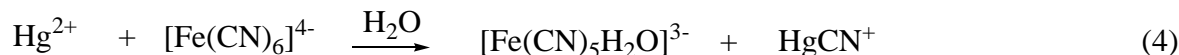
The equilibrium, in equation (1) in the dark, is shifted almost completely towards left but it is prevented due to the introduction of incoming ligand bipyridine in accordance with equation (2), where the species [Fe(CN)₅H₂O]³⁻ reacts with bipyridine, producing a cherry-red colored complex, [Fe(CN)₄Bipy]²⁻ irreversibly and rapidly.



Now, the CN^- ions generated in equation (2) reacts with water, producing HCN and OH^- ions in accordance with equation (3)



Such reactions are found to be extremely slow and require few hours for their completion to some reasonable extent. Apart from this, the metal ions capable of quickly forming stable complexes with cyanide ions, viz. $\text{Hg}(\text{II})$, $\text{Ag}(\text{I})$, $\text{Pd}(\text{II})$ and $\text{Au}(\text{III})$ are also found to catalyze the exchange of CN^- or decomposition reactions of hexacyanoferrate(II)/ pentacyanoammineferrate(II), in a similar way as performed by action of UV light [18], [19], [20]. The complex, $[\text{Fe}(\text{CN})_4\text{Bipy}]^{2-}$ is very stable and obeys Lambert-Beer's law at $\lambda = 400 \text{ nm}$, and its stoichiometry has been established as 1:1 spectrophotometrically by using mole ratio and slope ratio methods. The catalyzed abstraction of coordinated cyanide in $[\text{Fe}(\text{CN})_6]^{4-}$ by bipyridine and regeneration of Hg^{2+} is believed to proceed according to equations (4-5).



In the alkaline medium, the catalyst Hg^{2+} is not required due to the lack of H^+ ions as shown in equation (5). Therefore, it is evident that Hg^{2+} promoted cyanide abstraction from hexacyanoferrate(II) is pH-dependent reaction.

In the present investigation, it was considered worthwhile to investigate the detailed kinetic and mechanistic studies on Hg^{2+} catalyzed reaction between hexacyanoferrate(II) and bipyridine in order to confirm the previous mechanistic scheme by other investigations on similar systems and also to enhance our understanding on ligand substitution reactions in highly stable hexacyanoferrate(II).

2 RESULT AND DISCUSSION

The effect of various reaction variables viz. pH, reactant concentration, temperature and ionic strength on initial rates were investigated by varying only one variable at a time, while all other variables were kept constant. The dependence of initial rate on different reaction variables has been reported in the following sections and discussed at length.

2.1 EFFECT OF pH ON INITIAL RATE

The rate of the reaction was studied at various pH values in the range of 1.7-5.0 at 25°C using the fixed time procedure by treating it as a closure measure of initial rate. The dependence of rate of reaction or absorbance on pH is given in **Figure 1**.

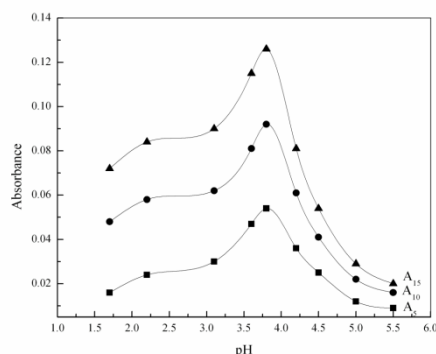


Figure 1: Effect of pH on Hg^{2+} catalyzed substitution of CN^- in hexacyanoferrate(II) by bipyridine at $[\text{Fe}(\text{CN})_6^{4-}] = 2.5 \times 10^{-3} \text{ M}$, $[\text{Bipy}] = 3.0 \times 10^{-4} \text{ M}$, $[\text{Hg}^{2+}] = 1 \times 10^{-5} \text{ M}$, temperature = $25 \pm 0.1^\circ\text{C}$ and $I = 0.1 \text{ M}$ (KNO_3). A5, A10 and A15 are the absorbances recorded at $\lambda = 400\text{nm}$ at $t = 5, 10$ and 15 minutes respectively.

The rate of formation of the cherry red reaction product was found to be highly dependent on the pH. The rate was found to be maximum when the value of pH of reaction mixture was adjusted in the pH range 3.8 - 4.0. Further increase in the pH resulted decrease in absorbance i.e. in rate of reaction. This decrease in rate at higher pH may be due to non-availability of H^+ ions needed to regenerate the catalytic species and or due to decrease in concentration of Hg^{2+} ions as a result of hydrolytic precipitation of its hydroxide.

The lower rate of reaction at low pH values is attributed due to formation of various protonated forms of $\text{K}_4[\text{Fe}(\text{CN})_6]$

having low reactivity, which consequently decreases the concentration of free $[\text{Fe}(\text{CN})_6]^{4-}$ [21], [22], [23], [24], [25], [26], [39] needed for the reaction.

2.2 EFFECT OF [Bipy] ON INITIAL RATE

The initial rates were determined as a function of [Bipy] by varying its concentration from 2.5×10^{-5} M to 2.5×10^{-4} M keeping the other variables fixed at $[\text{Hg}^{2+}] = 1 \times 10^{-5}$ M, $[\text{Fe}(\text{CN})_6^{4-}] = 2.5 \times 10^{-3}$ M, $\text{pH} = 3.8 \pm 0.02$, $I = 0.1$ M (KNO_3) and the temperature = $25 \pm 0.1^\circ\text{C}$

At still lower [Bipy] the reactions was highly recognizable. The effect of variation of initial rate V_i with [Bipy] for the reaction at hand is given in **Figure 2**.

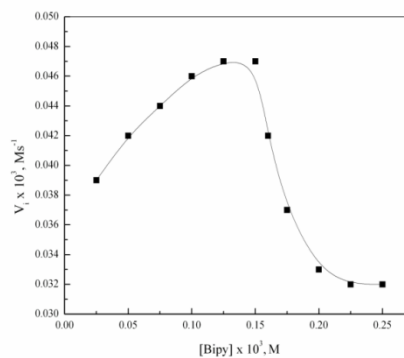


Figure 2: Effect of [Bipy] on initial rate at $[\text{Fe}(\text{CN})_6^{4-}] = 2.5 \times 10^{-3}$ M, $[\text{Hg}^{2+}] = 1 \times 10^{-5}$ M, $\text{pH} = 3.8 \pm 0.02$, temperature = $25 \pm 0.1^\circ\text{C}$ and $I = 0.1$ M (KNO_3)

This plot of initial rate (V_i) versus [Bipy] shows that the initial rate increases in the beginning up to the [Bipy] = 1.5×10^{-4} M, which then decreases sharply at still higher concentration and finally levels off to a constant value at still higher concentration. The decrease in the rate may be attributed to the inhibition of the catalytic activity of $\text{Hg}(\text{II})$.

2.3 EFFECT OF $[\text{Fe}(\text{CN})_6^{4-}]$ ON INITIAL RATE

The initial rates were evaluated as a function of $[\text{Fe}(\text{CN})_6^{4-}]$ by changing its concentration from 2.25×10^{-3} to 5.0×10^{-3} M, keeping all other experimental variables fixed at optimum values. The plot of log (initial rate) versus log $[\text{Fe}(\text{CN})_6^{4-}]$ is given in Figure 3. The rate data are compiled in the **Table 1**. The plot given in **Figure 3** suggests a variable order dependence in $[\text{Fe}(\text{CN})_6^{4-}]$ ranging from unity at its lower concentration up to 0.1 M to a fractional order at higher concentration but not tending towards zero- order.

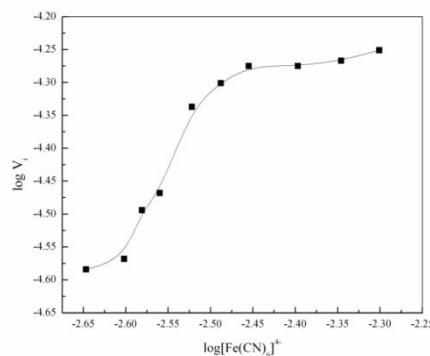


Figure 3: The effect of $[\text{Fe}(\text{CN})_6^{4-}]$ on initial rate of $[\text{Hg}^{2+}]$ catalyzed substitution reaction between $[\text{Fe}(\text{CN})_6^{4-}]$ and $[\text{Bipy}] = 2.25 \times 10^{-4}$ M, $[\text{Hg}^{2+}] = 1.0 \times 10^{-5}$ M, $\text{pH} = 3.8 \pm 0.02$, temperature = $25 \pm 0.1^\circ\text{C}$ and $I = 0.1\text{M}$ (KNO_3)

Table 1:

$[\text{Hg}^{2+}]$ variation at $[\text{Fe}(\text{CN})_6^{4-}]$ for Calculation of K under the conditions $[\text{Fe}(\text{CN})_6^{4-}] = 4.5 \times 10^{-4}$ M, $[\text{Bipy}] = 2.25 \times 10^{-4}$ M, $\text{pH} = 3.8 \pm 0.02$, $I = 0.1$ M (KNO_3), Temperature = $25 \pm 0.1^\circ\text{C}$.

$[\text{Hg}^{2+}] \times 10^5, \text{M}$	$V_i \times 10^5, \text{Ms}^{-1}$	$K \times 10^{-3}$	log K
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2.0	6.08	2.88	3.46
3.0	6.39	2.03	3.31
4.0	6.50	1.55	3.19
5.0	6.80	1.30	3.11
6.0	6.93	1.10	3.04
Kav = $1.77 \times 10^3 \pm 0.71$			log Kav = 3.22 ± 0.16

2.4 EFFECT OF TEMPERATURE ON INITIAL RATE

The rate of Hg^{2+} catalyzed ligand exchange between $[\text{Fe}(\text{CN})_6^{4-}]$ and bipyridine was studied as a function of temperature in the 25-50°C temperature range, keeping all other reaction variables fixed at an optimum value. The higher temperature was avoided due to the possibility of dissociation of the cherry red complex formed during the course of reaction. The Arrhenius Equation was used to determine the activation energy (E_a) for the catalyzed reaction.

The plot of $\log(V_i)$ versus $(1/T)$ yields a straight line ($r \geq 0.9967$ and $sd \leq 0.0167$) as shown in **Figure 4**. The activation energy has been determined from the slope of Figure 4. The other activation parameters, viz. enthalpy of activation (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) have also been evaluated using Eyring's equation (6)

$$\ln(\text{Initial rate}/T) = \ln(k_B / h \cdot e^{\Delta S^\ddagger/R}) - \Delta H^\ddagger/RT \quad (6)$$

The values of thermal parameters or activation parameters are:

$$E_a = 42.05 \pm 0.07 \text{ kJmol}^{-1}, \Delta H^\ddagger = 39.45 \pm 0.05 \text{ kJmol}^{-1}, \Delta S^\ddagger = -199.34 \pm 4.5 \text{ JK}^{-1}\text{mol}^{-1}$$

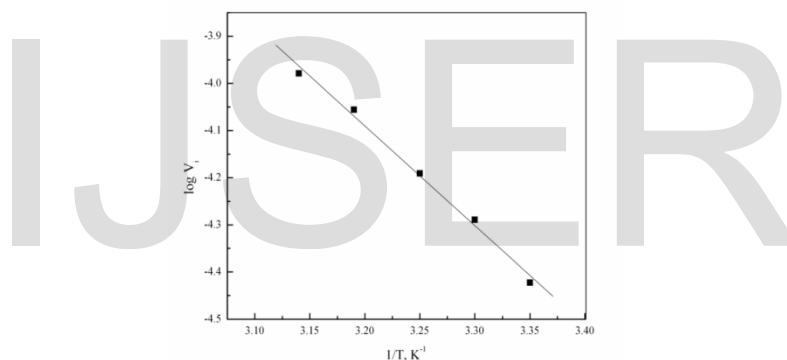


Figure 4: Determination of activation parameters for the $\text{Hg}(\text{II})$ catalyzed substitution of CN^- in hexacyanoferrate(II) by bipyridine $[\text{Fe}(\text{CN})_6^{4-}] = 3.0 \times 10^{-3} \text{ M}$, $[\text{Hg}^{2+}] = 1.5 \times 10^{-4} \text{ M}$, $\text{pH} = 3.8 \pm 0.02$, $I = 0.1 \text{ M}$ (KNO_3) and $[\text{Bipy}] = 2.25 \times 10^{-4} \text{ M}$

2.5 EFFECT OF IONIC STRENGTH ON INITIAL RATE

The influence of ionic strength was studied in the range of 0.01 - 0.30 M using KNO_3 . The still higher ionic strength was avoided due to the limited solubility of KNO_3 in water. The values of initial rates at different ionic strength are compiled in **Table 2**. It clearly indicates that the initial rate decreases with increase in ionic strength of the medium, confirming a negative salt effect on the reaction rate.

Table 2:

Effect of varying ionic strength on the $\text{Hg}(\text{II})$ -catalyzed substitution rate under the conditions $[\text{Fe}(\text{CN})_6^{4-}] = 2.5 \times 10^{-3} \text{ M}$, $[\text{Bipy}] = 2.5 \times 10^{-4} \text{ M}$, $[\text{Hg}^{2+}] = 1 \times 10^{-5} \text{ M}$, $\text{pH} = 3.8 \pm 0.02$, Temperature = $25 \pm 0.1^\circ\text{C}$.

I (KNO_3), M	$V_i \times 10^5, \text{Ms}^{-1}$
0.010	9.0
0.030	7.2
0.050	6.0
0.100	5.9
0.150	3.8
0.200	3.7
0.250	3.5
0.300	3.4

2.6 EFFECT OF $[\text{Hg}^{2+}]$ ON INITIAL RATE

The effect of $[\text{Hg}^{2+}]$ on initial rate was studied by varying $[\text{Hg}^{2+}]$ from 2×10^{-7} to 1×10^{-3} M, keeping the concentration $[\text{Fe}(\text{CN})_6^{4-}]$ and bipyridine fixed at an optimum value at $\text{pH} = 3.8 \pm 0.2$, $I = 0.1$ M (KNO_3) and temperature $25 \pm 0.1^\circ\text{C}$. This wide ranging variation in $[\text{Hg}^{2+}]$ was studied to check the linearity between the rate and range of $[\text{Hg}^{2+}]$ for its analytical application also to obtain an in depth understanding due to the changing role of mercury as a function of its concentration in the mixture.

The concentration of $[\text{Fe}(\text{CN})_6^{4-}]$ and bipyridine was kept constant at 3×10^{-3} M and 2.25×10^{-4} M respectively. The plot of the absorbance values, A_t ($t = 10, 15$ and 20 minutes) as a function of $[\text{Hg}^{2+}]$ is given in **Figure 5**. It is clear from this plot that absorbance increases linearly from 0.5×10^{-6} M to 2.5×10^{-6} M and then finally starts decreasing. The linearity between initial rate and mercury concentration in the range of $0 - 2.5 \times 10^{-6}$ M of $[\text{Hg}^{2+}]$ is shown in Figure 6 (vide supra).

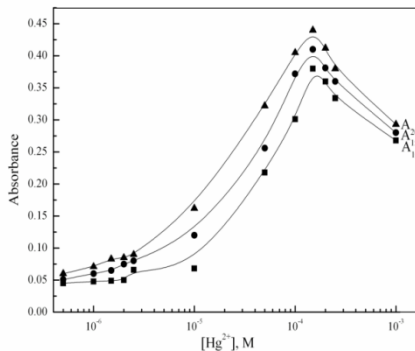


Figure 5: Dependence of the rate of substitution of CN^- in hexacyanoferrate(II) by bipyridine on $[\text{Hg}^{2+}]$ at temperature = $25 \pm 0.1^\circ\text{C}$, $[\text{Fe}(\text{CN})_6^{4-}] = 3 \times 10^{-3}$ M, $[\text{Bipy}] = 2.25 \times 10^{-4}$ M, $\text{pH} = 3.8 \pm 0.02$ and $I = 0.1$ M (KNO_3). A_{10} , A_{15} and A_{20} are the absorbances recorded at $\lambda = 400\text{nm}$ at $t = 5, 10$ and 15 minutes respectively.

It is interesting to note that the catalytic activity of mercuric chloride increases, though not linearly, till the concentration of $\text{Hg}(\text{II})$ ion is approximately equal to the concentration the $[\text{Fe}(\text{CN})_6^{4-}]$. The intercept can be obtained by extrapolation of the initial linear partition of the curve given in **Figure 6**. This gives rate due to uncatalyzed path. The observed decline in the rate at higher concentration of mercury may be due to formation of a binuclear adduct $[\text{Fe}(\text{CN})_6^{4-} \cdot \text{HgCl}_2]$, which would decrease the forward rate of reaction. It has also been observed that when $[\text{HgCl}_2]/[\text{Fe}(\text{CN})_6^{4-}]$ ratio is >3 , initially a thin yellow cloudiness appears, followed by a rapid formation of an intense pinkish-red color [27] as shown through equation (7). When, $[\text{Fe}(\text{CN})_6^{4-}]/[\text{HgCl}_2]$ ratio is >2 , initially a yellow color appears turning orange red with time and obeys equation (8). The spectrum of this complex is highly sensitive to the medium used.

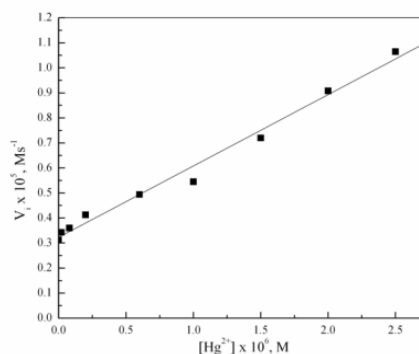
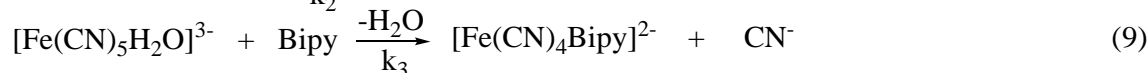
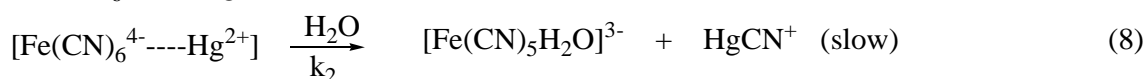
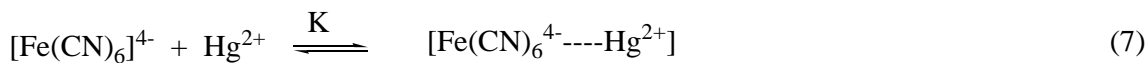


Figure 6: The effect of $[\text{Hg}^{2+}]$ on initial rate at high $[\text{Fe}(\text{CN})_6^{4-}]$ at temperature = $25 + 0.1^\circ\text{C}$, $[\text{Bipy}] = 2.25 \times 10^{-4}$ M, $[\text{Fe}(\text{CN})_6^{4-}] = 2.3 \times 10^{-2}$ M, $\text{pH} = 3.8 \pm 0.02$ and $I = 0.1$ M (KNO_3)

The interaction of Bipy with $[\text{Fe}(\text{CN})_6^{4-}]$ depends on the ratio $[\text{Hg}(\text{II})]/[\text{Fe}(\text{CN})_6^{4-}]$ in solution and gives complexes of the type $[\text{Fe}(\text{CN})_x\text{Ly}]$ ($x = 0, 2, 4$ and $y = 3, 2, 1$ respectively). In the present case, when $[\text{Hg}(\text{II})]/[\text{Fe}(\text{CN})_6^{4-}]$ ratio is 2, a cherry red colored complex having maximum absorption at $\lambda_{\text{max}} = 400$ nm of the formula $[\text{Fe}(\text{CN})_4(\text{Bipy})_2]^{2-}$ is produced. The stoichiometry of the complexes has been established by the mole ratio and slope ratio method [40].

2.7 MECHANISM

The study of influence of $[\text{Fe}(\text{CN})_6^{4-}]$, $[\text{Bipy}]$, $[\text{Hg}^{2+}]$ and other experimental observation reported above enabled us to propose the following scheme through equations. (7), (8), (9), (10).



The above suggested mechanistic scheme consists of four distinct steps. The first step is the formation of ion pair adduct $[\text{Fe}(\text{CN})_6^{4-} \cdots \text{Hg}^{2+}]$ which is followed by slow aquation to form $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$. Then ligand bipyridine displaces the CN^- and H_2O molecule from aquated product and form a substituted $[\text{Fe}(\text{CN})_4\text{Bipy}]^{2-}$ ion. Last step (equation 10) is the catalytic regeneration of Hg^{2+} with simultaneous release of HCN , which makes the slight acidic medium of reaction mixture.

Under non-rate limiting $[\text{Bipy}]$ and after resorting some valid approximation, the rate expression for the formation of product, via catalyzed path can be given through equation (11).

$$\text{Rate} = \frac{d[\text{Fe}(\text{CN})_4\text{Bipy}^{2-}]}{dt} = k_3 [\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}] [\text{Bipy}] \quad (11)$$

There are two possible paths for the formation of the intermediate $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}]$, the catalyzed as well as uncatalyzed paths. Therefore, on inserting the steady state concentrations of the product, the rate of the reaction can be easily expressed through equation (12).

$$\text{Rate} = \frac{d[\text{Fe}(\text{CN})_4\text{Bipy}^{2-}]}{dt} = k' [\text{Fe}(\text{CN})_6^{4-}] + \frac{k_2' K [\text{Fe}(\text{CN})_6^{4-}] [\text{H}_2\text{O}] [\text{Hg}^{2+}]}{1 + K [\text{Fe}(\text{CN})_6^{4-}]} \quad (12)$$

Where, uncatalyzed rate = $k' [\text{Fe}(\text{CN})_6^{4-}]$

$$\text{Catalyzed rate} = \frac{k_2' K [\text{Fe}(\text{CN})_6^{4-}] [\text{H}_2\text{O}] [\text{Hg}^{2+}]}{1 + K [\text{Fe}(\text{CN})_6^{4-}]} \quad (13)$$

K is the equilibrium constant for association of electrophile $[\text{Hg}^{2+}]$ and water to $[\text{Fe}(\text{CN})_6^{4-}]$. Equilibrium is supposed to lie on right hand side of equation (12) and value of K to be >1 . When concentration of $[\text{Fe}(\text{CN})_6^{4-}]$ is smaller than $[\text{Fe}(\text{CN})_6^{4-}] \ll 1$ and as water concentration is in larger excess then equation (12) becomes equation (13).

$$\text{Rate} = k' [\text{Fe}(\text{CN})_6^{4-}] + [k_2' K [\text{Hg}^{2+}] [\text{Fe}(\text{CN})_6^{4-}]] \quad (14)$$

This gives the observed rate constant as:

$$k_{\text{obs}} = k' + k_2' [\text{Hg}^{2+}]$$

$$\text{Where } k_2' = k_2 [\text{H}_2\text{O}]$$

But for higher concentration of $[\text{Fe}(\text{CN})_6^{4-}]$: $K [\text{Fe}(\text{CN})_6^{4-}] \gg 1$

Then equation (12) becomes equation (15)

$$\text{Rate} = k' [\text{Fe}(\text{CN})_6^{4-}] + k_2' [\text{Hg}^{2+}] \quad (15)$$

Thus, the rate constants k' and k_2' can be evaluated from the intercept and slope (**Figure 6**) respectively of a plot of initial rate versus $[\text{Hg}^{2+}]$ ($r \geq 0.9809$ and $\text{sd} \leq 1.95 \times 10^{-5}$) in presence of higher concentration of $[\text{Fe}(\text{CN})_6^{4-}]$ using equation (15) at specified experimental conditions. The values of rate constants k' and k_2' are found to be $7.75 \times 10^{-3} \text{ s}^{-1}$, $3.98 \times 10^{-2} \text{ s}^{-1}$ respectively at $I = 0.1 \text{ M}$ (KNO_3), $\text{pH} = 3.8 \pm 0.02$, temperature $25 \pm 0.1^\circ\text{C}$. Now the values of k' and k_2' so obtained are substituted in equation (14) to calculate the values of equilibrium constant K at various $[\text{Hg}^{2+}]$ at low $[\text{Fe}(\text{CN})_6^{4-}]$. The evaluated values of K are compiled in Table 1 and the average value of K was found to be 1.77×10^3 or $\log K_{\text{av}} = 3.222 \pm 0.04$ which is in reasonably good agreement with the value reported by Beck [41] for $[\text{Fe}(\text{CN})_6^{4-}]$, $[\text{Hg}(\text{CN})_2]$ complex.

Lastly, the repetitive spectral scan were recorded in the range of 320-650 nm for the ligand substitution reaction between $K_4[\text{Fe}(\text{CN})_6]$ and bipyridine in aqueous medium are given in **Figure 7**. A sharp absorption band at 400 nm appeared,

corresponding to the formation of a metal to ligand charge transfer band. The Peak height at 400 nm grows with time and confirms the formation of $[\text{Fe}(\text{CN})_4(\text{Bipy})]^{2-}$ during the course of reaction

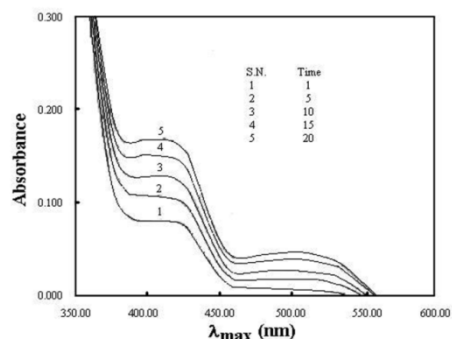


Figure 7: The repetitive spectral scan of Hg^{2+} catalyzed reaction between $[\text{Fe}(\text{CN})_6]^{4-} = 3.0 \times 10^{-3} \text{ M}$, $[\text{Bipy}] = 2.25 \times 10^{-4} \text{ M}$, $\text{Hg}^{2+} = 1.5 \times 10^{-4} \text{ M}$, $\text{pH} = 3.8 \pm 0.02$, $I = 0.1 \text{ M}$ (KNO_3) and temperature = $25 \pm 0.1^\circ\text{C}$.

3 EXPERIMENTAL

3.1 REAGENTS USED

Double distilled water was used throughout the study to prepare all solutions. All chemicals used in the present study were of analytical reagent grade HgCl_2 (Galaxo Laboratories), $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ (Merck) and 2,2'-Bipyridine (Merck) were used as received. 2,2'-Bipyridine solution was prepared by weighing its desired amount and dissolved in a small amount of absolute alcohol followed by the dilution with distilled water.

The solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ was prepared by weighing its desired amount and kept in dark amber colored bottles to prevent photodecomposition. The appropriate dilutions were made from above solutions immediately before use. Dilute solutions of HgCl_2 were also prepared daily to prevent loss due to its adsorption on glass surfaces. Bipyridine solution was prepared in 10% alcohol and was used throughout the present study. Potassium Hydrogen Phthalate-Hydrochloric acid buffer of required pH was prepared according to the literature methods [42]. The use of NaClO_4 was avoided as it gives some turbidity in the reaction mixture due to the formation of insoluble KClO_4 . Thus KNO_3 (Merck) was used to maintain the ionic strength at 0.1 M.

3.2 EQUIPMENTS OR APPARATUS

A Shimadzu UV-1700 double beam spectrophotometer was used for recording the absorption spectra of reactants and products as well as repetitive spectral scan of the reaction mixture. The temperature of reacting species was maintained at a desired value with an accuracy of $\pm 0.1^\circ\text{C}$ by using a self designed thermostat. The pH measurements were made on a digital Toshniwal pH meter model CL-46. The standard BDH buffers were used for standardization of pH meter from time to time. The SISCO visible spectrophotometer model DIGI-110 equipped with thermostated cell compartment was used to monitor the progress of reaction at 400 nm.

3.3 PROCEDURE

All reactant solutions were placed in the thermostatic bath for 30 minutes in order to attain a temperature of $25 \pm 0.1^\circ\text{C}$. The appropriate quantities of reactants were mixed in a 50 ml amber colored Borosil measuring flask in the sequence bipyridine, buffer and $\text{Hg}(\text{II})$. The reaction was started by injecting $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution into the mixture. The reaction mixture was properly shaken and immediately transferred to a cleaned 10 mm matched cuvette of spectrophotometer. The reaction was monitored by following the increase in absorbance at 400 nm, the λ_{max} of cherry red complex, $[\text{Fe}(\text{CN})_4(\text{Bipy})]^{2-}$ formed during the course of reaction. No absorbance correction was applied at the above wavelength because only this complex absorbs strongly and the other reactants viz. HgCl_2 , $\text{K}_4[\text{Fe}(\text{CN})_6]$ and bipyridine have negligible absorptions. The composition of the final reaction product, $[\text{Fe}(\text{CN})_4\text{Bipy}]^{2-}$ formed during the course of $\text{Hg}(\text{II})$ -catalyzed reaction between $[\text{Fe}(\text{CN})_6]^{4-}$ and bipyridine was found to be 1:1 by mole ratio method. The initial rates were calculated using linear least square method from the slopes of initial linear portion of absorbance versus time plots recorded at 400 nm during fifteen minutes of reaction. These initial rate measurements were used to find out order dependences in $[\text{Bipy}]$, $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Hg}^{2+}]$.

The fixed time procedure being a closure measure of reaction rate was used throughout the present study to find the dependence on $[\text{Hg}^{2+}]$ and pH. The effect of pH on the present reaction was made by using potassium hydrogen phthalate and hydrochloric acid buffer only in order to avoid any complication in the reaction system.

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