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Kinetic and Mechanistic Studies of Uncatalyzed Substitution of Coordinated Cyanide in Hexacyanoferrate(II) by 2,2'-Bipyridine

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Abstract

The kinetics of uncatalyzed reaction between hexacyanoferrate(II) and 2,2'-Bipyridine (further designated as Bipy) has been followed spectrophotometrically by monitoring the increase in absorbance at 400 nm, the λ_{max} *of cherry red complex,* $[Fe(CN)_4Bipy]^{2-}$ *as a function of pH, Ionic strength, temperature and concentration of reactants. In this reaction, the coordinated cyanide ion in hexacyanoferrate(II) get replaced by incoming ligand Bipy under the following specified reaction conditions. Temperature =* 30 ± 0.1^oC, *pH =* 3.8 ± 0.02 *and I = 0.10 M* (KNO_3).

The uncatalyzed reaction between $[Fe(CN)_6]^{4-}$ *and Bipy is very slow. The reaction follows first order dependence each in* $[Fe(CN)_6]^{4-}$ *and [Bipy]. It was found that the initial rate varies linearly with increasing concentration of hexacyanoferrate(II), keeping other variables fixed at an optimum value. The initial rate is also found to increase in the beginning with increasing concentration of [Bipy] up to [Bipy]* $\leq 1.5\times10^{-4}$ *M, passes through a maximum and then finally falls. The effect of pH, ionic strength on initial rate have also been studied and explained. The activation parameters for reaction have been evaluated. A most plausible mechanistic scheme has been proposed based on the experimental observations.*

Keywords: Hexacyanoferrate(II), Ligand substitution kinetics, Uncatalyzed ligand

1. Introduction

The kinetics and mechanism of ligand substitution reactions in pentacyano(ligand)ferrate(II) complexes have attracted the attention of many investigators[1-8.] The experimental studies have revealed that the rate of dissociation of an uncharged ligand from $[Fe(CN)_5L]^{3-}$ do not depend on solvent polarity and the mechanisms involved therein are dissociative in nature [1,3-5.] Numerous complexes of the type $[Fe(CN)_5L]^{(3-n)-}$ (n: charge on the ligand and L : N_3^-, PhNO, amines, pyrazine, N-methylpyrazinium cation (mpz^+), nitroso-R-salt *etc.*) have also synthesized by direct substitution in pentacyano(amino)ferrate(II) or by metal catalyzed substitution in $[Fe(CN)_6]^{4-}$ [5-15] Therefore, such kinetic and mechanistic investigation of monodentate ligand substitution in octahedral iron(II) complexes by another monodentate ligand have been of increasing importance in the view of synthesizing new class of substitutionally inert metal complexes as well as in analytical chemistry [16-21] , Such studies have further enhanced the interest of several investigations to continue with kinetic and mechanistic studies on ligand substitution reaction on low-spin iron(II) complexes, mainly centered around pentacyano(ligand) ferrate(II) $[Fe(CN)_5L]^{(3-n)-}$ complexes [1,2,3-8,22-31].

Apart from this, there is fewer number of studies on metal catalyzed substitution kinetics and mechanism on hexacyanoferrate(II) [9-14, 18, 32,] 33 because of its least labile character among cyano complexes of transition metal ions [2].Most of the substituted cyanocomplexes of Iron(II) are monosubstituted products, which have been obtained either through photochemical aquation [2] of hexacyanoferrate(II) or by metal assisted substitution [5-15] with the incoming ligand.

The thermal decomposition of $[Fe(CN)_6]^{4-}$ without any interference of oxidation is a slow and reversible process[2]. The exchange of labeled cyanide between $[Fe(CN)_6]^{4-}$ and free cyanide is slow when reversible aquation takes place with the formation of $[Fe(CN)_5H_2O]^{3-}$ and CN^- [2, 34]. In a recent study from our laboratory [35] on substitution of phenylhydrazine by one of the coordinated cyanide in $[Fe(CN)_6]^{4-}$, it was observed that the aquapentacyanoferrate(II) *i.e.* $[Fe(CN)_5H_2O]^{3-}$ reacts with phenylhydrazine producing highly stable complex $[Fe(CN)_5Ph]^{3-}$.Very recently similar observation was made by Prasad et.al [36]. However, till date no kinetic and mechanistic study has been made on uncatalyzed substitution between $[Fe(CN)_6]^{4-}$ and bipyridine.

Therefore, in continuation of our recent works on kinetics of ligand substitution in $[Fe(CN)_6]^{4-}$, it is considered worthwhile to investigate the kinetics and mechanism of ligand substitution in $[Fe(CN)_6]^{4-}$ by another bidentate ligand 2,2'-Bipyridine in order to strengthen our earlier proposed mechanisms and also to gain better understanding on such type of reactions.

2. Materials and Methods

All chemicals applied were of analytical reagent grade. Double distilled water was used throughout the experiment. Stock solution of hexacyanoferrate(II) was prepared by direct weighing of $K_4[Fe(CN)_6].3H_2O$ (Merck) and dissolving in water. The solution was kept in a dark ambered-colored bottle to prevent photodecomposition. The appropriate dilutions were made from above solutions immediately before use. Bipy (Merck) solution was prepared by weighing its desired amount and dissolved in a small amount of absolute alcohol followed by the dilution with distilled water.

Potassium hydrogen phthalate-hydrochloric acid buffer of required pH was prepared according to the literature methods [37]. $NaClO_4$ was found to give 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 0.10 M.

Equipments or Apparatus

Shimadzu double beam spectrophotometer, model UV-1700 has been used for the recording single spectrum and repetitive spectral scans of the reaction mixture. The UV–visible spectrum of the product formed during the course of uncatalyzed reaction between $[Fe(CN)_6]^{4-}$ and bipyridine is shown in Fig. 1. The pH measurements were made on a digital pH meter model CL-46 (Toshniwal, India). The standard BDH buffers were used to standardize pH meter from time to time. The SISCO visible spectrophotometer model DIGI-110 equipped with circulatory arrangement of water for the monitoring the cell compartment was used to monitor the progress of reaction at λ = 400 n.

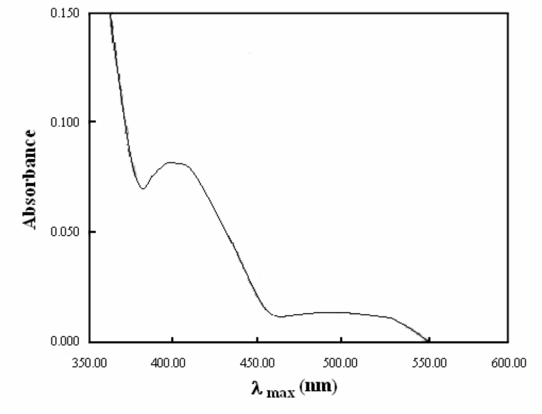


Fig. 1

Fig. 1UV-Visible spectrum of product, [Fe(CN)4bipy] 2- at [Fe(CN)64-] = 3.25 × 10-3 M; [Bipy] = 1.5 × 10-4M; pH = 3.8+0.02; Temperature = 30+0.1°C and I = 0.10 M (KNO3)

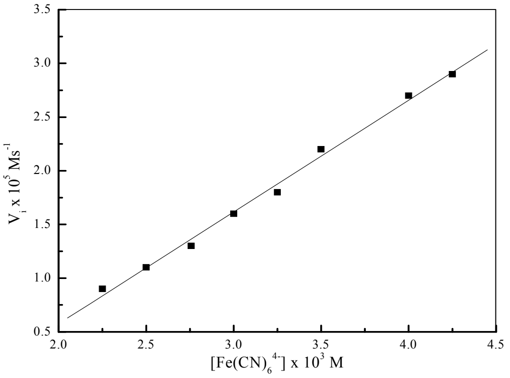


Fig. 2

Fig. 2: The effect of [Fe(CN)64-] on initial rate of uncatalyzed ligand exchange reaction between [Fe(CN)64-] and 2,2' Bipyridine at [Bipy] = 1.75 × 10-4 M; pH = 3.8+0.02; Temperature = 30+0.1°C and I = 0.10 M (KNO3).

2.1 Procedure

All the reactants used in the present study were equilibrated at 30$\pm$0.1^{o}C in a self-designed thermostat for at least half an hour. The reaction between $[Fe(CN)_6]^{4-}$ and 2,2'-Bipyridine was studied in buffered medium by mixing them in sequence, hexacyanoferrate(II), buffer and Bipy. The progress of reaction was monitored by registering an increase in absorbance as a function of time at 400 nm, leading to the formation of cherry red colored complex $[Fe(CN)_4Bipy]^{2-}$. Initial rates (V_i) were computed from the absorbance versus time plots for each of the dependence studied.

Initial rate (V_i), so evaluated was used to determine its dependence on pH, $[Fe(CN)_6^{4-}]$ and [Bipy], ionic strength and temperature.

3. Results and Discussion

3.1 The effect of $[Fe(CN)_6^{4-}]$ on the initial rate

The effect of $[Fe(CN)_6]^{4-}$ on the initial rate of the uncatalyzed reaction was studied with the optimum pH fixed at 3.8$\pm$0.02, temp = 30°C. I = 0.10 M (KNO_3), [bipy] =1.75 × 10^{-4}M. The $[Fe(CN)_6]^{4-}$ concentration was varied from 2.25 × 10^{-3} to 4.00 × 10^{-3} M. The reaction was found to be first order in $[Fe(CN)_6]^{4-}$ in the concentration studied. The plot of initial rate (V_i) versus $[Fe(CN)_6^{4-}]$ as given in Fig. 2

3.2 The effect of Bipy on initial rate

The influence of Bipy concentration on the reaction rate in the absence of Hg(II) was investigated by varying [Bipy] in the range of (2.50 – 17.5) × 10^{-5} M and shown in Fig. 3. It was found that the rate increases linearly with increasing the [Bipy] in the range of (2.5 – to 15) ×10^{-5} M and the line passes through a maximum, remains constant between (12.5 – 15) × 10^{-5} M and finally starts decreasing.

3.3 Effect of pH on initial rate

The rate of the reaction was studied as a function of pH in the pH range 1.2 – 3.8 and the results are shown in Fig. 4 at 30°C using the fixed time procedure where the absorbance measured at different times (A_t) was treated as closure measure of initial rate. It was found that the rate of reaction increases with increase of pH. These variation may be attributed either to the different reactivities of the many protonated and unprotonated forms of $[Fe(CN)_6]^{4-}$ having different reactivities [38]. The possibility of protonation of complexing agent Bipy is excluded in the pH range studied because of its low basicity.

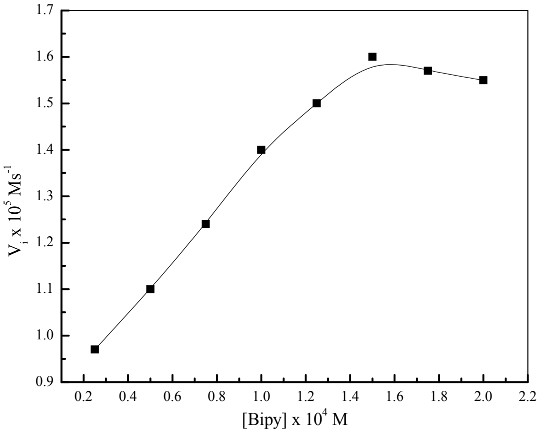


Fig. 3

Fig. 3: The effect of [Bipy] on initial rate of uncatalyzed ligand exchange reaction between $[Fe(CN)_6^{4-}]$ and 2,2' Bipyridine at $[Fe(CN)_6^{4-}]$ = 3.25 × 10^{-3} M; pH = 3.8±0.02; Temperature = 30±0.1°C and I = 0.10 M (KNO_3)

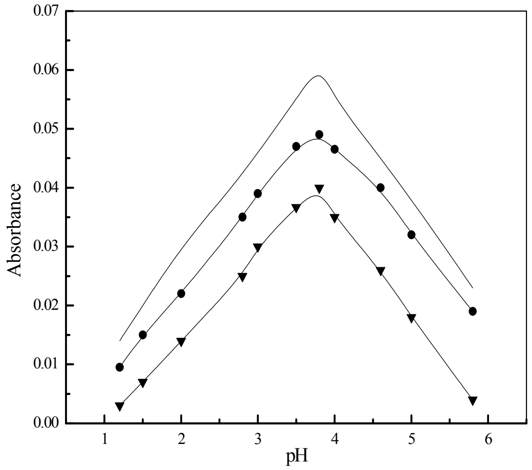


Fig. 4

Fig. 4: The effect of pH on initial rate of uncatalyzed ligand exchange reaction between $[Fe(CN)_6^{4-}]$ and Bipy at $[Fe(CN)_6^{4-}]$ and Bipy at $[Fe(CN)_6^{4-}]$ = 3.25 × 10^{-3}M; [Bipy] = 15 × 10^{-5}M; Temperature = 30±0.1°C and I = 0.10 M (KNO_3)

It can be seen from the species distribution of $[Fe(CN)_6]^{4-}$ [39] that in the pH range mentioned above, there exists mono, di, tri and tetraprotonated forms of $[Fe(CN)_6]^{4-}$ [39]. The later is ruled out as a reactive species because concentration of the same raises sharply between pH 1.2 to 3.8 as shown in Fig. 4. But if $[Fe(CN)_6^{4-}]$ was the sole species responsible for this observation, the rate would not have decreased beyond pH 3.80, where concentration of $[Fe (CN)_6]^{4-}$ is rising fast. It is therefore concluded that the decrease in rate between pH 4.0 to 5.8 is due to progressive decrease in the concentration of protonated form of Bipy. This is also because, the concentration of unprotonated Bipy and $[Fe(CN)_6]^{4-}$ or the intermediate $[Fe(CN)_5OH^{4-}]$ remains constant. This analysis leads to the conclusion that $[Fe(CN)_6]^{4-}$ on one hand and Bipy on the other are the active reacting species in the pH range of investigation.

3.4 Effect of temperature variation on initial rate of reaction

The effect of temperature on the uncatalyzed reaction rate was investigated and in order to evaluate the activation parameters, the reaction rate was studied in the temperature range 30-50°C. The plot of log (initial rate) versus (1/T) gave straight line (Fig. 5) and slope of this line gave the value of activation Energy (E_a). The entropy and enthalpy of activation were evaluated using Eyring's equation. The values of activation or thermal parameters are compiled in Table 1. The negative value of $\Delta S^{\neq}$ obtained in this work might be consistent with non-limiting S_N1 mechanism [12, 15].

Table 1: Activation parameter for the uncatalyzed replacement of (CN^-) in $[Fe(CN)_6]^{4-}$

Activation parameter	**Uncatalyzed**	**Catalyzed***
Ea (kJ mol^{-1})	49.54	42.05
$\Delta H^{\neq}$ (kJ mol^{-1})	46.56	39.45
$\Delta S^{\neq}$ (JK^{-1} mo^1)	–187.98	-199.34

$[Fe(CN_6)^{4-}] = 3.25 \times 10^{-3}$M; [Bipy] = 15×10^{-5}M; pH = 3.8±0.02; Temperature = 30±0.1°C

3.5 Effect of dielectric constant on the initial rate of reaction

The effect of dielectric constant of the reaction medium on the initial rate of reaction between $[Fe(CN)_6]^{4-}$ and bipyridine was studied by varying alcohol content from 10% to 35% in ethanol –water mixtures. Still higher content of ethanol was avoided due to limited solubility of $[Fe(CN)_6]^{4-}$ in the present binary aqueous solvent used. The value of initial rate (V_i) were calculated as a function of varying dielectric constant (D). A plot of log(V_i) *versus* 1/D yielded a straight line having a negative slope (Fig. 6, $r \geq 0.9991$, s.d. ≤ 0.00665), indicating a reaction taking place between two oppositely charged species. The increasing alcohol content or decreasing dielectric constant of medium resulted in the subsequent decrease in the initial rate of reaction as shown in Fig. 6. Such observation provides a justification that the intermediate complex formed during the course of reaction is relatively more polar than the reactants involved in the present reaction.

The results of the experimental observations and the study of the variation of initial rates for the substitution of coordinated cyanide from $[Fe(CN)_6]^{4-}$ by Bipy as a function of $[Fe(CN)_6]^{4-}$, [Bipy], pH, temperature and the study of the other effects point to the following mechanistic scheme

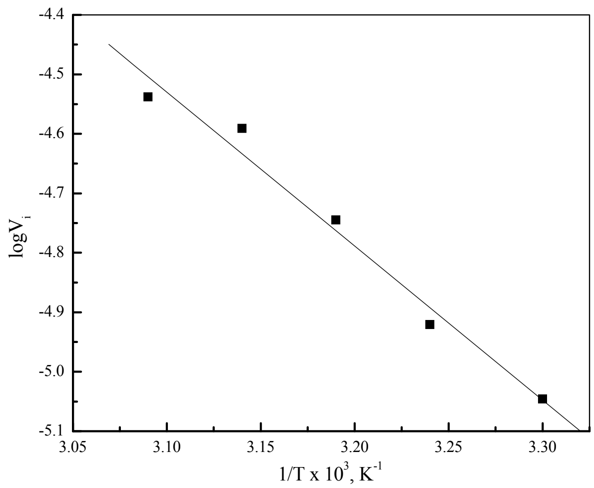


Fig. 5

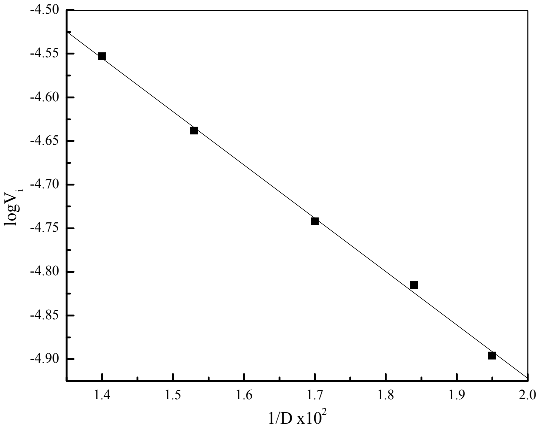
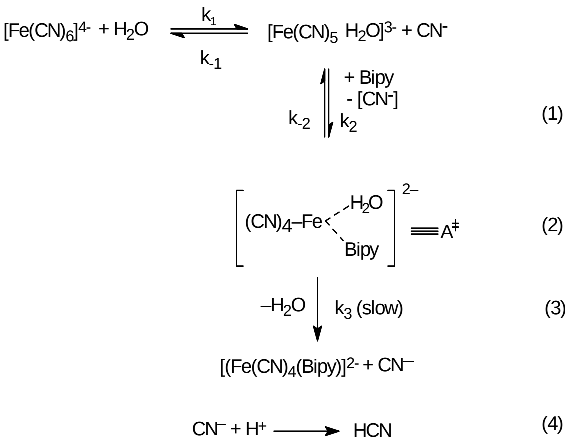


Fig. 6

Fig. 5: Determination of activation parameters for the uncatalyzed substitution of CN^- in Hexacyanoferrate(II) by 2,2' Bipyridine at $[Fe(CN)_6^{4-}] = 3.25 \times 10^{-3}$ M; [Bipy] = 15×10^{-5}M; pH = 3.8±0.02; Temperature = 30±0.1°C and I = 0.10 M (KNO_3)

Fig. 6: Effect of dielectric constant on initial rate of uncatalyzed ligand exchange reaction between $[Fe(CN)_6]^{4-}$ and bipyridine at$[Fe(CN)_6^{4-}] = 3.25 \times 10^{-3}$ M; [Bipy] = 2.0×10^{-4}M; pH = 3.8±0.02; Temperature = 30±0.1°C and I = 0.10 M (KNO_3



Scheme I: A Plausible Mechanism

The rate law based on this scheme can be expressed by equation (5).

$$\frac{d[Fe(CN)_4\,Bipy^{2-}]}{dt} = k_3[A^{\neq}] \qquad (5)$$

If $k_{-2} >> k_3$, the formation of $[A^{\neq}]$ is due to fast equilibrium and for the condition where $[Fe(CN)_5H_2O]^{3-} <$ [Bipy] the equilibrium concentration of the activated complex (or Ion-pair) can be evaluated through the following algebraic manipulation and finally given through equation (6).

$$[A]^{\neq} = [Fe(CN)_5H_2O^{3-}] - [Fe(CN)_5H_2O^{3-}]_f$$

or

$$[A]^{\neq} = [Fe(CN)_5H_2O^{3-}] - \frac{[A]^{\neq}}{K_2[Bipy]}$$

or

$$[A]^{\neq}\left(1 + \frac{1}{K_2[Bipy]}\right) = [Fe(CN)_5H_2O^{3-}]$$

Or

$$[A]^{\neq} = \frac{K_2[Fe(CN)_5[H_2O]^{3-}[Bipy]}{1 + K_2[Bipy]} \qquad (6)$$

Where $K_2 = \dfrac{[A]^{\neq}}{[Fe(CN)_5H_2O^{3-}]_f[Bipy]}$

and ‘f’ refers to free concentration of $[Fe(CN)_5H_2O]^{3-}$.

Applying steady state treatment to the intermediate $[Fe(CN)_5H_2O]^{3-}$, one gets:

$$[Fe(CN)_5H_2O]^3 = \frac{k_1(1 + K_2[Bipy][Fe(CN)_6{}^{4-}][H_2O]}{k_{-1}[1 + K_2[Bipy][CN^-] + k_2K_2[Bipy]^2} \qquad (7)$$

Substituting equation (7) in equation (6), we get:

$$[A]^{\neq} = \frac{k_1K_2[Bipy][Fe(CN)_6{}^{4-}][H_2O]}{k_{-1}[CN][1 + K_2[Bipy][CN^-] + k_2K_2[Bipy]^2} \qquad (8)$$

Considering equation (7) and (8), the rate law is given by equation (5):

$$\frac{d[Fe(CN)_4Bipy^{2-}]}{dt} = \frac{k_3k_1K_2[Bipy][Fe(CN)_6{}^{4-}][H_2O]}{k_{-1}[CN^-] + K_2k_{-1}[Bipy][CN^-] + k_2K_2[Bipy]^2} \qquad (9)$$

If in this equation k2 and k–1 are comparable (both are fast) the following two conditions may exist.

(i) At low [Bipy], k-1[CN–] >> k2 [Bipy]. Therefore ,equation (9) can be rewritten as equation (10).

$$\frac{d[Fe(CN)_4Bipy^{2-}]}{dt} = \frac{k_3k_1K_2[Bipy][Fe(CN)_6^{4-}][H_2O]}{k_{-1}[CN^-]} \qquad (10)$$

The second term in the denominator of equation (9) is greater than the third term and the second term is multiple of small concentration terms. Thus, both can be neglected in comparison to $k_{-1}[CN^-]$. We should expect an increase in rate as [Bipy] increases.

(ii) At high [Bipy], k_2[Bipy] >> k_{-1} $[CN^-]$ the third term in the denominator of equation (9) is greater than first and second term and thus rate law can be rewritten as:

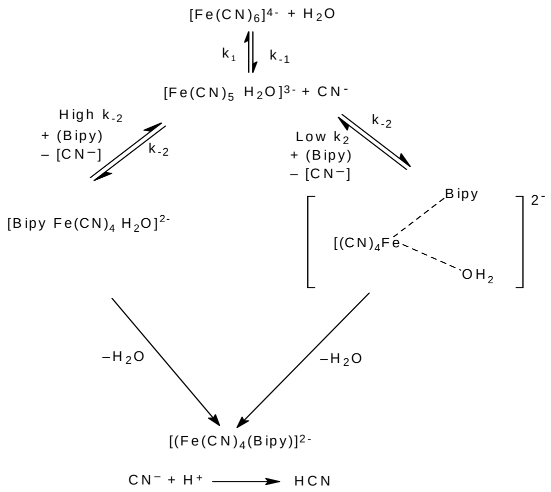
$$\frac{d[Fe(CN)_4Bipy^{2-}]}{dt} = \frac{k_3k_1[Fe(CN)_6^{4-}][H_2O]}{k_2[Bipy]} \qquad (11)$$

The above expression indicates that a decrease in rate of formation of product with an increase in concentration of Bipy is to be expected. This has been observed experimentally and shown in Fig. 1.

In order to understand the nature of the intermediate, the reaction between bipyridine and an aqueous solution of pentacyanoaquoferrate(II) was scanned (not shown). It was found that Bipy behaves in a similar manner with $[Fe(CN)_5NH_3]^{3-}$ and consequently $[Fe(CN)_5H_2O]^{3-}$ as with $[Fe(CN)_6{}^{4-}]$ at similar experimental conditions except that the concentration of $[Fe(CN)_5NH_3]^{3-}$ was taken not greater than 10^5 M to present dimerisation [40]. Similar observation was found in a previous investigation on the substitution of coordinated cyanide from $[Fe(CN)_6]^{4-}$ by paranitrosodipheylamine (p-NDA) [41]. It was observed that the nature of the intermediate complex seems to be similar in reaction of $[Fe(CN)_6{}^{4-}]$ and Bipy as for the reaction between $[Fe(CN)_5NH_3]^{3-}$ and Bipy. This adds to the justification of the proposed mechanism.

The value of Ea (49.54 kJ mol^{-1}) indicated the rupture of a metal-ligand bond and thus lends further support to the suggested mechanism. This value of E_a is comparable with an earlier reported value (53.85 kJ mol^{-1}) for the substitution of cyanide by phenylhydrazine [35]. The decrease in entropy of activation gives further evidence in favor of an I_d mechanism. The lower negative value of entropy of activation ($\Delta S^{\neq}$) is associated with a relatively lower degree of free rotation of the incoming ligand which favors and Id over the pure D-mechanism.

Hence, on the basis of all the experimental observations, a most plausible general mechanistic scheme-II has been for the reaction between $[Fe(CN)_6]^{4-}$ and 2,2'-Bipyridine in confirmation with our earlier proposed mechanism [36]



Scheme II: A general plausible mechanistic scheme for uncatalyzed reaction between $[Fe(CN)_6]^{4-}$ and 2,2'-Bipyridine.

4. Conclusions

The present study reveals that a strong monodentate coordinated ligand to most stable hexacyanoferrate(II) can be replaced by the incoming bidentate ligand 2,2'-Bipyridine under the specified reaction conditions,forming a stable cubstituted complex ,$[Fe(CN)_4Bipy]^{2-}$.

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