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The Mercury(II) Catalysed Ligand Substitution Reaction Between Hexacyanoruthenate(II) and Ligand 4, 4'bipyridine in Aqueous Medium

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Abstract

The Kinetic and mechanistic study of cyanide ion substitution in hexacyanoruthenate (II) by 4, 4'bipyridine (Bipy), catalyzed by mercury (II) has been studied spectrophotometrically at 390 nm in aqueous medium at pH = 4.0 ± 0.02, ionic strength, I = 0.01 M (maintained by KCl) and at temperature 25.0 ± 0.01^{0}C. Effect of the pH, ionic strength, temperature and [Bipy] and [Ru(CN) $^{4-}$] have been studied and analyzed for the reaction at hand. The catalytic activity of mercury (II) has also been studied as a function of its concentration. The kinetic and activation parameters for the titled reaction has been measured and calculated. The mechanism of ligand substitution has been proposed based on the experimental observations and the reaction was found to proceed through dissociative pathway.

Keywords: Ligand Substitution reaction, Kinetics and mechanism, Repetitive Spectral Scan, Activation Parameters.

Introduction

Transition metals have increasingly become an important weapon in chemist's arsenal [1-3]. These metals are important as they can coordinate to any functional group and thereby change its reactivity. They can be used both stoichiometrically as well as catalytically [4]. Ligand substitution is an important reaction pathway for η^6-transition metal complexes. The catalysed ligand substitution reactions play a very important role both for synthetic and analytical chemistry. Transition metals have a great ability to coordinate with arene system, most notably η^6-coordination system [5-7]. Ligand substitution reactions in octahedral complexes of trivalent cobalt [8], Cr [9] and Fe(II/III) [10-14] have been studied extensively in the last few years. The chemistry of ruthenium is currently receiving a lot of attention [15-16] because of its large electron transfer and substitution properties. The reactivity of ruthenium complexes depend on the stability and nature of the ligand bound.

The photochemical and electrochemical behaviour of ruthenium with phenanthroline and bipyridine are well known [17] but the kinetics and mechanism of these ruthenium complexes have gained a very little attention. Either a purely dissociative or an interchange dissociative mechanism has been proposed for the water replacement reactions of ruthenium(II) complexes [18-23]. Some deviations are also observed in the mechanism in which associative mechanism has been reported [24-26]. These mechanistic controversies led us to study the kinetics of substitution of $[Ru(CN)_6]^{4-}$ by 4, 4'Bipyridine in aqueous medium, leading to the formation of cherry red color complex, $[Ru(CN)_4(Bipy)]^{2-}$. It has been demonstrated that of all the heavy metals, mercury(II) easily forms bond with cyanide ion and slowly removes it from hexacyanoruthenate(II). Thus, it can strongly catalyze the substitution reaction of hexacyanoruthenate(II) or the decomposition of potassium hexacyanoruthenate(II) in a manner analogous to the action of U.V. light [27].

Experimental Work

Double distilled, de-ionized water was used throughout the present study. Chemicals used were of analytical grade and used without any further purification. The mercury(II)chloride and hexacyanoruthenate(II) solutions were diluted just before the use. Desired pH 4.0 ± 0.02 of the reaction mixture was maintained by adding KHP-NaOH buffer [28] to the solution and ionic strength of the reaction mixture was maintained to 0.01 M by adding appropriate amount of KCl.

Materials and Method

The absorption spectra were obtained by SYSTRONICS Double Beam Spectrophotometer model 2203 (Smart). pH-metric measurements were done by SYSTRONICS μ pH SYSTEM model 361.The pH meter was standardized using buffer solutions having values ,pH = 4 and 9.2 respectively.

Procedure

All the solutions were thermally equilibrated at 25 ± 0.01°C up to 30 min and 2.0 ml of each Bipy, phthalate buffer (pH 4.0) and mercury(II) chloride were mixed in a flask in the given sequence and left for 10 min to ensure complete reaction. Finally, 2.0 ml of $[Ru(CN)_6]^{4-}$ was added to this reaction mixture and the wavelength of maximum absorption (390 nm) was recorded. The repetitive spectral scan of the Hg(II)-catalyzed ligand substitution reaction between $[Ru(CN)_6]^{4-}$ and Bipy is shown in Figure1. This clearly reveals that a peak at 390 nm grows with time which is attributed to the formation of a cherry red color complex of $[Ru(CN)_4(Bipy)]^{2-}$ during the course of reaction.

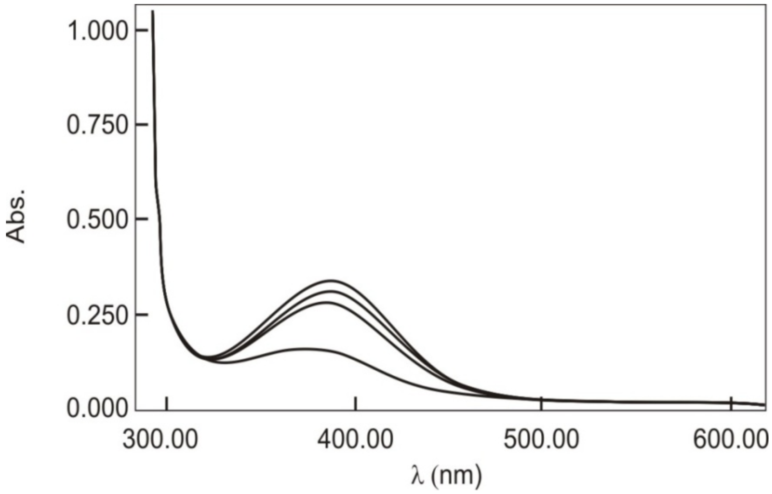


Figure 1: The repetitive spectral scan of ligand substitution reaction between $[Ru(CN)_6]^{4-}$ and 4,4'bipyridine in aqueous medium under the optimum reaction experimental condition**:** [Bipy] = 6.25×10^{-5} M, $[Ru(CN)_6^{4-}] = 2.25\times10^{-3}$ M, pH = 4.0 ± 0.02, I = 0.01 M (KCl) and $[Hg^{+2}] = 2.5\times10^{-4}$ M

At this wavelength, at various pH, first-order rate constants (k_{obs}) were determined by measuring the absorbance under pseudo first-order reaction condition with complex $[Ru(CN)_6]^{4-}$ in at least 10-fold excess over the ligand Bipy.

Reaction progress was monitored by measuring the change in the absorbance upon addition of $[Ru(CN)_6]^{4-}$ to a 5 ml cuvette, placed in a thermostated (25 ± 0.01°C) cell compartment, containing, KCl to maintain 0.01M ionic strength, necessary buffer to maintain pH (4.0 ± 0.02) and ligand Bipy. First-order rate constants (k_{obs}) were obtained by least-square fit to the data in Eq (1).

$$\ln (A_t - A_\infty) = k_{obs}.\ t \qquad (1)$$

Where A_t is the absorbance at time t and A_∞ is the final absorbance.

Result and Discussion

Effect of pH on Reaction Rate

The reaction has been carried out at various pH values between 2.5 to 10.0 at 30°C taking fix concentrations of all the reaction variables. It was found that the rate of reaction increases with increase of pH, attains a maximum rate at pH 4.0 ± 0.02 and then decrease with further increase of pH, shown in Figure 2. The decrease in rate at higher pH may be due to the lack of protons required to regenerate the catalytic species and/or to the decrease in concentration of Hg(II) as a result of its hydrolytic precipitation as the hydroxide. The rate is reduced at lower pH values due to the formation of various protonated forms of $[Ru(CN)_6]^{4-}$ like as in $[Fe(CN)_6]^{4-}$ [29, 30] which are less reactive species as compare to the $[Ru(CN)_6]^{4-}$.

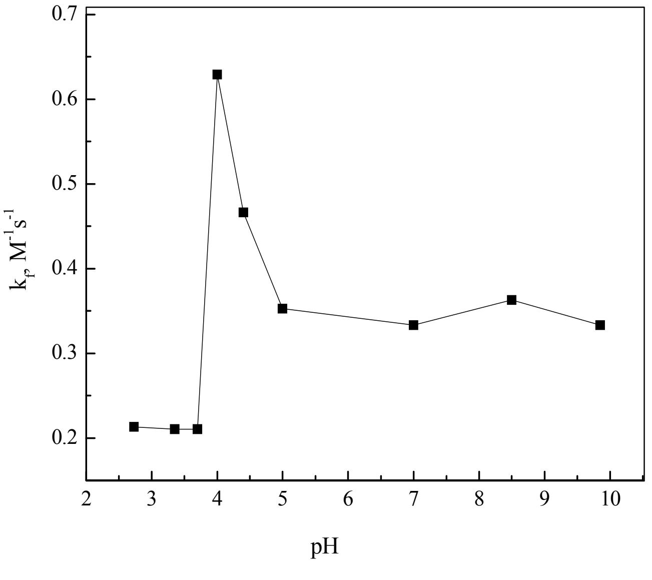


Figure 2: Effect of pH for the reaction of $[Ru(CN)_6]^{4-}$ with 4,4'bipyridine in aqueous medium under the optimum reaction experimental condition**:** [Bipy] = 2.0 × 10^{-5} M, $[Ru(CN)_6^{4-}]$ = 1.0 × 10^{-3} M, $[Hg^{+2}]$ = 1.5 × 10^{-4} M, Ionic strength = 0.01 M (KCl) and Temperature = 30.0 ± 0.01˚C

Effect of Ionic Strength on Reaction Rate

The influence of ionic strength was studied in the range of 0.01M to 0.25 M using KCl electrolyte at fixed concentration of all other reactants at 30°C. The higher ionic strength was not attempted due to limited solubility of KCl in water. The plot of k_f *versus* $I^{1/2} / (1 + I^{1/2})$ in Figure 3 shows that the k_f decreases linearly with increase in the ionic strength of the medium, depicting the negative salt effect in the reaction medium.

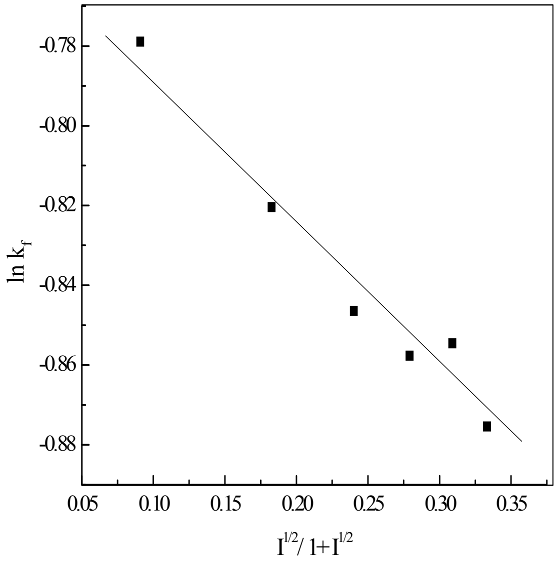


Figure 3: Effect of Ionic Strength for the reaction of $[Ru(CN)_6]^{4-}$ with 4,4'bipyridine in aqueous medium under the optimum reaction experimental condition**:** [Bipy] = 6.25×10^{-5} M, $[Ru(CN)_6{}^{4-}]$ = 2.25×10^{-3} M, pH = 8.6 ± 0.02, $[Hg^{+2}] = 1.5 \times 10^{-4}$ M and Temperature = 30.0 ± 0.01°C

Effect of [Bipy] on Reaction Rate

The effect of ligand concentration on the reaction rate was studied at fixed complex concentration 2.5×10^{-3} M at constant reaction conditions. The concentration of ligand was varied from 2.5×10^{-5} M to 2.5×10^{-4} M. It is observed that as ligand concentration increases, the rate constant increases in a linear fashion (Figure 4), which is characteristic of the ligand substitution reactions of octahedral complexes.

The plot of k_{obs} *versus* [Bipy] is found to be linear with almost zero intercept, which clearly indicates the minimum possibility of backward reaction in Eqs (2) and (3).

$$[Ru(CN)_6]^{4-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(CN)_5H_2O]^{3-} + CN^-, \quad \text{slow} \qquad (2)$$

$$[Ru(CN)_5H_2O]^{3-} + Bipy \longrightarrow [Ru(CN)_4Bipy]^{2-} + H_2O + CN- \qquad (3)$$

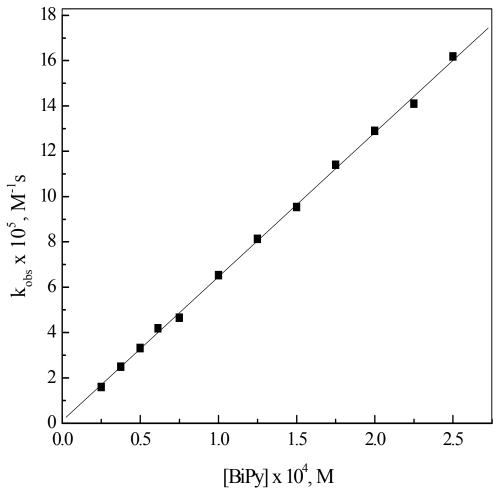


Figure 4: Effect of [Bipy] for the reaction of $[Ru(CN)_6]^{4-}$ with 4,4'bipyridine in aqueous medium under the optimum reaction experimental condition: $[Ru(CN)_6{}^{4-}] = 2.25 \times 10^{-3}$ M, $[Hg^{+2}] = 1.5 \times 10^{-4}$ M, pH = 8.6 ± 0.02, I = 0.01 M (KCl) and Temperature = 30.0 ± 0.01°C

Effect of $[Ru(CN)_6{}^{4-}]$ on the Reaction Rate

In the kinetic experiments, the $[Ru(CN)_6{}^{4-}]$ was varied from 1.5×10^{-3} M to 4.25×10^{-3} M at constant concentration of ligand 6.25×10^{-5} M, pH = 4.0, $[Hg^{2+}] = 5.0 \times 10^{-5}$ M at 30°C temperature in aqueous medium. Constant values of pseudo-first-order rate constant were obtained. That is the titled reaction is independent of complex concentration in the range of experimental condition.

Effect of $[Hg^{2+}]$ on Reaction Rate

The $[Hg^{2+}]$ was varied from 2×10^{-6} M to 1.25×10^{-3} M, keeping the concentration of other reaction variables fixed at an optimum value at 30°C (Table 1). The wide ranging variation in $[Hg^{2+}]$ was selected in order to test the linearity between reaction rate and $[Hg^{2+}]$ to make a comprehensive understanding of the changing role of mercury in mixture. From the data it is clear that rate initially increases linearly, reaching a maximum value at a concentration, $[Hg^{2+}] = 2.5 \times 10^{-4}$ M. The intercept computed from the initial linear portion of the curve provides the rate due to the uncatalyzed path. However, the decline in the rate of reaction at higher concentration is probably due to the formation of a binary adduct $[Ru(CN)_6{}^{4-} - HgCl_2]$, as also observed in $[Fe(CN)_6]^{4-}$ [31, 33].

Effect of Temperature

The temperature effect on the rate of catalyzed reaction has been investigated in the range 25- 50°C. The values of rate constants are cited in Table 2.

The reaction followed the Eyring and Arrhenius equations from which the activation parameters viz. enthalpy and entropy of activation and energy of activation were calculated (Table 3). On comparing the value of enthalpy with other ligands in the same reaction environment, it was found that $\Delta H\neq$ is almost constant in each case. This can be interpreted by assuming that $\Delta H^{\neq}$ is not sensitive to the nature of incoming ligand in the coordination sphere of $[Ru(CN)_6]^{4-}$.

Table 1 Effect of $[Hg^{2+}]$ under conditions [Bipy] = 6.25 × 10^{-5} M, $[Ru(CN)_6^{4-}]$ = 2.25 × 10^{-3} M, pH = 4.0 ± 0.02, I = 0.01 M (KCl) and Temperature = 30 ± 0.1°C

$[Hg^{2+}] \times 10^4$, M	k_f, $M^{-1}s^{-1}$
0.02	0.89
0.06	0.99
0.15	0.71
0.25	1.07
0.50	1.01
0.75	1.72
1.00	2.81
1.25	4.12
2.50	5.86
7.50	3.46
12.5	2.93

Table 2 Effect of Temperature under conditions [Bipy] = 6.25 × 10^{-5} M, $[Ru(CN)_6^{4-}]$ = 2.25 × 10^{-3}M, pH = 4.0 ± 0.02, I = 0.01 M (KCl) and $[Hg^{2+}]$ = 2.5 × 10^{-4} M

T, K	$K_f \times 10^3$, $M^{-1}s^{-1}$
298	4.83
303	6.64
308	8.66
313	13.30
318	13.90
323	22.64

Table 3 Activation parameters of Hg^{2+}catalyzed reaction between $[Ru(CN)_6]^{4-}$ and [Bipy]

Reaction condition	E_a, KJM^{-1}	$\Delta H^{\neq}$, KJM^{-1}	$\Delta S^{\neq}$, $JK^{-1}M^{-1}$
$[Ru(CN)_6^{4-}]$ = 2.25×10^{-3} M, [Bipy] = 6.25×10^{-5} M, pH = 4.0 ± 0.02, I = 0.01 M (KCl), $[HgCl_2]$ = 2.5 ×10^{-4} M, Temperature. = 30.0 ± 0.01°C	47.38	45.10	-80.56

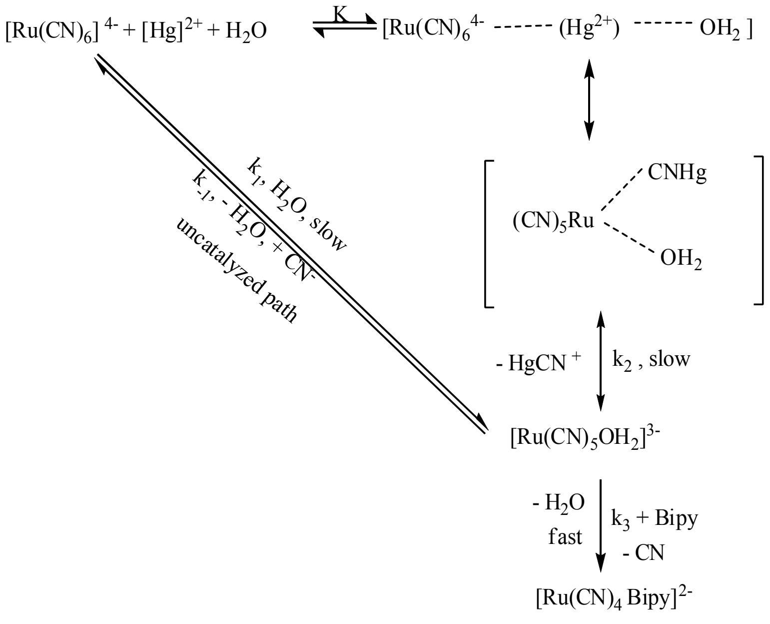
This observation is consistent with the view that the activation process is a bond – breaking one, so a dissociative mechanism applies to these reactions. In D- mechanism the ΔS≠ should be controlled by two factors:

(a) The activated complex being higher in energy, will have a loosen structure than the reactants and hence there will be a greater randomness of motion in the activated state. The formation of the latter will thus be accompanied by an increase in entropy.

(b) In D- mechanism, the size of the activated complex (pent coordinate) is smaller than that of reactant (octahedral). As such activated complex will attract more molecules of the polar solvent than reactant ions (electrostatic effect). Hence the randomness in the system is decreased in the transition state and a negative value of entropy of activation is expected to be observed.

The measured $\Delta S^{\neq}$ is, therefore really the resultant of these two opposing factors and a small negative value is observed. Taube and co-workers [24, 25] also obtained the similar negative values of $\Delta S^{\neq}$ for substitution reactions of $[Ru(NH_3)_5 H_2O]^{2+}$ complex with a wide variety of ligands and these reactions were classified as involving a dissociative mechanism. Equally convincing is Taube's correlation [34] which illustrates that dissociative pathways occurring by trigonal bipyramidal intermediates give positive value of $\Delta S^{\neq}$ while square pyramidal intermediates give negative values.

The substitution of one of the six cyanides coordinated to Ru(II) in $[Ru(CN)_6]^{4-}$ by Bipy is an extremely slow reaction. This reaction can be catalyzed by Hg^{2+} ions. Accordingly, the detailed kinetic investigations were made as a function of several reaction variables $[Ru(CN)_6^{4-}]$, [Bipy], pH, $[Hg^{2+}]$, ionic strength and temperature. These studies enabled us to propose the following plausible mechanistic scheme:



(4)

(5)

(6)

(7)

$$HgCN^{+} + H^{+} \longrightarrow Hg^{2+} + HCN \qquad (8)$$

The rate expression for the formation of the complex $[Ru(CN)_4(Bipy)]^{2-}$ can be given as follows through Eq (9).

$$d[Ru(CN)_4(Bipy)^{2-}] /dt = k_3[Ru(CN)_4(Bipy)^{2-}] [Bipy] \qquad (9)$$

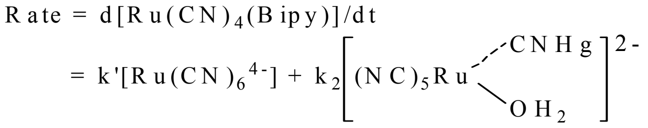
There are two possible paths for the formation of the intermediate $[Ru(CN)_4(Bipy)]^{2-}$, the catalyzed as well as the uncatalyzed paths.

The uncatalyzed reaction under the present experimental condition is too slow to be followed through an independent kinetic study. However, theoretically some uncatalyzed reaction may take place simultaneously much slower than the catalyzed reaction. The rate for uncatalyzed path can be given by Eq (10).

$$\text{Uncatalyzed rate} = k' [Ru(CN)_6]^{4-} \qquad (10)$$

Where, k' is a composite rate constant involving some concentration terms and rate constants.

If the slow decomposition of deactivated complex in the proposed mechanism (Eq 5) corresponds to the rate determining step, the overall rate of reaction due to both uncatalyzed as well as catalyzed reaction in non-rate limiting concentration can be given through the following rate Eq (11).



$$\begin{aligned} Rate &= d[Ru(CN)_4(Bipy)]/dt \\ &= k'[Ru(CN)_6{}^{4-}] + k_2\left[(NC)_5Ru\begin{array}{l}\diagup CNHg\\ \diagdown OH_2\end{array}\right]^{2-} \end{aligned} \qquad (11)$$

In Eq (11), the first and second terms correspond to rate due to uncatalyzed and catalyzed reactions respectively.

The total mercury ions in the reaction system can exist in the form of free and as mercury adduct.

$$[Hg^{2+}]_T = [Hg^{2+}]_{free} + \text{Mercury adduct} \qquad (12)$$

Now, Eq (12) can be easily transformed to Eq (13).

$$[Hg^{2+}]_T = [Hg^{2+}]_{free} + K[Ru(CN)_6{}^{4-}][Hg^{2+}]_{free}[H_2O]$$

Or

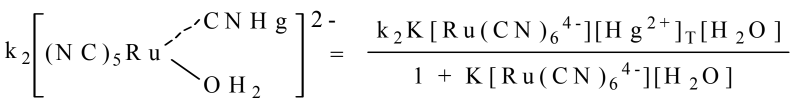
$$[Hg^{2+}]_{free} = [Hg^{2+}]_T \big/ 1 + K[Ru(CN)_6{}^{4-}][H_2O] \qquad (13)$$

In Eq (13), K refers to the association constant between catalyst, water and $[Ru(CN)_6]^{4-}$.

The second term in Eq (11) can be further expressed through Eq (14).

$$k_2\left[(NC)_5Ru\begin{array}{l}\diagup CNHg\\ \diagdown OH_2\end{array}\right]^{2-} = k_2K[Ru(CN)_6{}^{4-}][Hg^{2+}]_{free}[H_2O] \qquad (14)$$

Putting the value of $[Hg^{2+}]_{free}$ from Eq (13) into Eq (14), the value of second term or Eq (14) is transformed to Eq (15).



$$k_2\left[(NC)_5Ru\begin{matrix}CNHg\\ OH_2\end{matrix}\right]^{2-} = \frac{k_2K[Ru(CN)_6^{4-}][Hg^{2+}]_T[H_2O]}{1 + K[Ru(CN)_6^{4-}][H_2O]} \qquad (15)$$

Now the rate of the overall reaction, both uncatalyzed and catalyzed, in the presence of non-rate limiting amounts of bipyridine i.e. Eq (14) can be finally transformed to Eq (16).

$$\begin{aligned} Rate &= d[Ru(CN)_4(Bipy)^{2-}]/dt \\ &= k'[Ru(CN)_6^{4-}] + \frac{k_2K[Ru(CN)_6^{4-}][Hg^{2+}]_T[H_2O]}{1 + K[Ru(CN)_6^{4-}][H_2O]} \end{aligned} \qquad (16)$$

In Eq (16), the first term corresponds to the rate due to uncatalyzed reaction and second term corresponds to the rate due to the catalyzed reaction and demonstrates the tendency towards levelling off in the rate at higher concentration of $[Ru(CN)_6]^{4-}$ exhibiting a variable order dependence in $[Ru(CN)_6]^{4-}$ in the presence of small concentration of mercury.

Equilibrium is supposed to lie on right hand side of Eq (16) and value of K to be > 1. When concentration of $[Ru(CN)_6]^{4-}$ is smaller i.e. $[Ru(CN)_6]^{4-} << 1$ and as water concentration is in large excess then Eqn (16) reduces to Eq (17)

$$Rate = k'[Ru(CN)_6^{4-}] + k_2'K[Ru(CN)_6^{4-}][Hg^{2+}] \qquad (17)$$

This gives the observed rate constant as,

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

where, $k_2' = k_2 [H_2O]$

But at higher concentration of $[Ru(CN)_6^{4-}]$; $K[Ru(CN)_6^{4-}] >> 1$, Eq (17) can be written as,

$$Rate = k'[Ru(CN)_6^{4-}] + k_2'[Hg^{2+}] \qquad (18)$$

According to Eq (18), the plot of rate i.e. $(k'[Ru(CN)_6^{4-}])$ *versus* $[Hg^{2+}]$ should yield a straight line. The rate constant k' and k_2' can be evaluated from the intercept and slope, respectively of a plot of initial rate *versus* $[Hg^{2+}]$ in the presence of higher concentration of $[Ru(CN)_6^{4-}]$ {Eq (18) and Figure (5)}.

Although the value of k_2 was obtained at high $[Ru(CN)_6^{4-}]$, it can be shown to be valid at lower concentration as well. It is possible to obtain k_2 from a plot of rate *versus* $[Hg^{2+}]$ at any concentration of $[Ru(CN)_6^{4-}]$ by Eq (19).

$$Rate = k'[Ru(CN)_6^{4-}] + \frac{k_2K[Ru(CN)_6^{4-}][H_2O][Hg^{2+}]}{1 + K[Ru(CN)_6^{4-}]} \qquad (19)$$

k_2 can be calculated from the slope of this plot using values of K and $[Ru(CN)_6]^{4-}$.

The rapid increase in rate at $[Hg^{2+}] > 5.0 \times 10^{-5}$ M may be explained by taking into consideration 28% ionic character of Hg-Cl bond in Hg_2Cl_2 [35] along with the following equilibria:

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

$$HgCl^+ + Cl^- \overset{K_2}{\rightleftharpoons} HgCl_2$$

The values of K_1 and K_2 are not available for the condition under which these experiments were carried out.

Like with $[Fe(CN)_6]^{4-}$, it may not be unreasonable to assume that $HgCl^+$ can also form an ion pair with $[Ru(CN)_6]^{4-}$ (log K_{HgCNCl} = 10.52 and log $K_{HgCN}{}^+$ = 17.0) [36] but this adduct formed is a looser one in comparison to the adduct formed with Hg^{2+}.

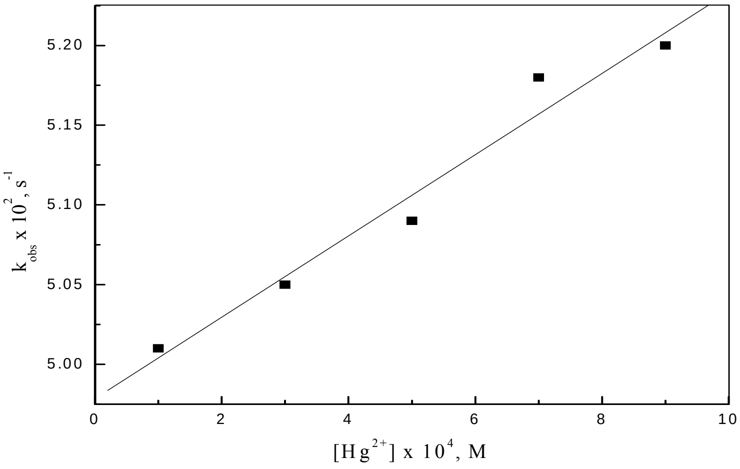
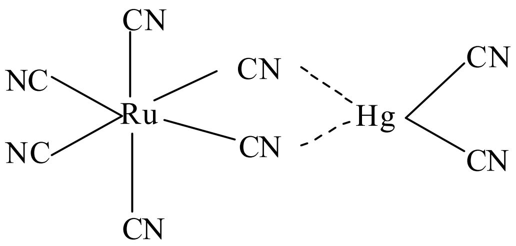
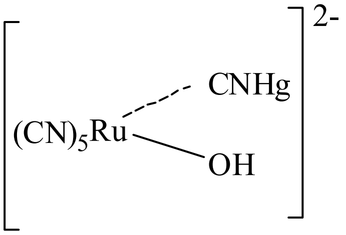


Figure 5: Effect of $[Hg^{2+}]$ at high concentration of $K_4[Ru(CN)_6]$ for the reaction of $[Ru(CN)_6]^{4-}$ with 4,4'bipyridine in aqueous medium under the optimum reaction experimental condition**:** [Bipy] = 6.25 × 10^{-5} M, $[Ru(CN)_6{}^{4-}]$ = 8.0 × 10^{-3} M, pH = 8.6 ± 0.02, I = 0.01 M (KCl) and Temperature = 30.0 ± 0.01°C

This adduct decomposes faster than that with Hg^{2+} and hence the rate is enhanced. With $[Hg^{2+}] = 1.5 \times 10^{-4}$ M (at $[Ru(CN)_6{}^{4-}] = 2.5 \times 10^{-3}$ M), the rate falls rapidly. It probably happens due to the formation of 1:1 complex or higher complexes between $[Ru(CN)_6{}^{4-}]$ and $HgCl_2$. This complexation removes the catalytic species viz. Hg^{2+} and $HgCl^+$ from the field and causes sharp decline in rate. This supposition is in line with an earlier work of Beck [33] who demonstrated the formation of 1:1 complexes in reactions of $Hg(CN)_2$ with some inert cyano complexes like $[Ru(CN)_6{}^{4-}Hg(CN)_2]$, $[Ru(CN)_6{}^{3-}Hg(CN)_2]$, and $[Ru(CN)_6{}^{2-}Hg(CN)_2]$ etc. However, another compound $Hg_2[Ru(CN)_2]$ is formed when $Hg(NO_3)_2$ is added to $[Ru(CN)_6]^{4-}$ solution [37]. According to Beck [33] the first complex may be represented as given below-



Thus our assumption regarding the catalytic role of Hg^{2+} in the proposed mechanistic scheme has been further reinforced. The ion pair formed as a result of the initial association of Hg^{2+} with $[Ru(CN)_6{}^{4-}]$ is followed by the rapid isomerisation to the following form:



This, then decomposes relatively slowly leading to the formation of $[Ru(CN)_5OH_2]^{3-}$ and $HgCN^+$. In the presence of 4, 4'bipyridine, the water molecules of aquapentacyanoruthenate (II) are quickly replaced leading to the formation of product $[Ru(CN)_4(Bipy)]^{2-}$.

The negative activation entropy ($\Delta S^{\neq}$) value for the present reaction $[Ru(CN)_6]^{4-}$–Bipy is supported by a similar ($\Delta S^{\neq}$) value for $[Ru(CN)_6]^{4-}$–L (L = pyrazine and nitroso-R-salt) though this result is in contrast with the positive values for some $[Ru(CN)_5L]^{(3-n)-}$ complex [23, 37]. This decrease in entropy of activation is the indication of a departure from purely D mechanism towards I_d mechanism in the order of activation energy evaluated for the system is supported to metal-ligand cleavage between Ru^{2+} and CN^-.

Conclusion

An attempt has been successfully made to comprehend the substitution of one of the six coordinated cyanide in hexacyanoruthenate (II) by Bipy in the presence of Hg^{2+} catalyst. Effect of various reaction parameters on reaction rate has been discussed and the most appropriate mechanistic scheme has been proposed to incorporate all the experimental observations.

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