

Comparative Kinetic Study Between the Electron Transfer Reactions of Iron(III) and Iron(II) Complexes

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Summary: The kinetics of reduction of tris(1,10-orthophenanthroline)iron(III) ion by two different reductants hexacyanoferrate(II) ion and bis(π -cyclopentadienyl)iron(II) has been spectrophotometrically investigated in aqueous medium. Measurements were recorded under pseudo-first order conditions. The rate of electron transfer between tris(1,10-orthophenanthroline)iron(III) and each reductants was measured. The rate laws are suggested to be, rate = $k_1 [\text{Fe}(\text{CN})_6]^{4-} [\text{Fe}(\text{o-phen})_3]^{3+} / 1 + K[\text{H}^+]$ and rate = $k [\text{Fe}(\text{C}_5\text{H}_5)_2] [\text{Fe}(\text{o-phen})_3]^{3+}$ for the reduction of tris(1,10-orthophenanthroline)iron(III) ion with hexacyano-ferrate(II) ion and bis(π -cyclopentadienyl)iron(II) respectively, showing first order with respect to each of the reactants in the both cases. It was found that the rate of reaction with hexacyanoferrate(II) is faster than that of bis(π -cyclopentadienyl)iron(II) having the second order rate constant values of $8.33 \times 10^{-7} \text{ M}^{-1}\text{s}^{-1}$ and $5 \times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$ respectively.

Introduction

Kinetics of the redox reactions between ferrous-ferric and their complexes has been studied. These reactions have been found to follow both atom transfer and electron transfer mechanisms [1-5]. Radioactive tracers are usually employed to follow the course of the reaction. This technique was first introduced by Hevesy and Zechmeister [6] in 1920. Eichler and Wahl [7] used both radioactive tracer and optical activity methods in the study of the tris(1,10-orthophenanthroline)iron(II)-tris(1,10-orthophenanthroline)iron(III) electron transfer reaction. Oxidation of tris(1,10-orthophenanthroline)

iron(II) by periodate was studied by Ige and Soriyan [8]. The electron transfer reactions between iron(II) and iron(III) in aqueous media proceed by a mechanism of hydrogen atom transfer in the absence of catalysing ligands which would make the reactions occur by either inner-sphere or outer-sphere mechanism [9]. Thomson [10] studied the exchange reactions between iron(II)-Iron(III) and their complexes while Gordon [5] studied the oxidation of iron(II) by different coordinated complexes of Ag, Ru, Os and Ir. Structurally diverse π -cyclopentadienyl complexes of the main

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group elements were reported by Jutzi and Burford [11]. Farrukh and Naqvi [12] reported the dependence of the redox potentials of the ferri-ferrous and ferricyanide-ferrocyanide systems on the strength of different acidic mediums.

In this study the kinetics of the reduction of tris(1,10-orthophenanthroline)iron(III) ion with hexacyanoferrate(II) ion and bis(π -cyclopentadienyl)iron(II) was carried out. Second order rate constants values of the both reaction species were calculated and compared with each other. Results are concluded in view of Crystal Field and Molecular Orbital Theories.

Results and Discussion

Effect of $[\text{Fe(o-phen)}_3]^{3+}$ on Rate of Reaction.

The redox reaction was carried out under the pseudo first order condition with reductants $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ having excess concentration over $[\text{Fe(o-phen)}_3]^{3+}$. This was done in order to ascertain the influence of $[\text{Fe(o-phen)}_3]^{3+}$ concentration over the reaction rate, independent of $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ concentration. The data as shown in Table 1, was collected using initial rate method by plotting the initial rates versus initial concentrations of oxidant ($\text{Rate} = k_{\text{obs}}[\text{Fe(o-phen)}_3]^{3+}$). The plots of initial rate versus initial concentration of tris(1,10-orthophenanthroline)iron(III) at constant concentration of reductants [hexacyanoferrate(II) and bis(π -cyclopentadienyl)iron(II)] produced straight lines passing through the origin indicating that reaction is first order in tris(1,10-orthophenanthroline)iron(III) complex, as displayed in Figure 1. Pseudo first order rate constant ' k_{obs} ' values were calculated from slopes of the above plots.

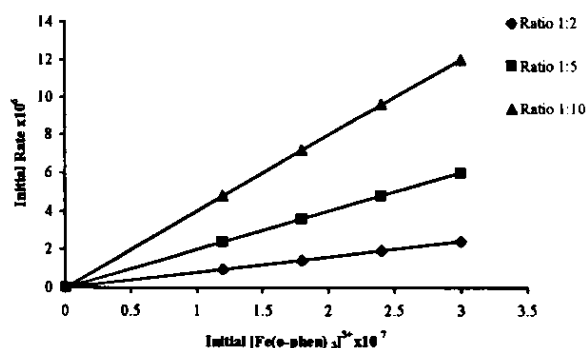


Fig.1. Plot of initial rates versus initial concentrations of tris(1,10-orthophenanthroline)iron(III)

Effect of Reductants [hexacyanoferrate(II) and bis(π -cyclopentadienyl)iron(II)] on Rate of Reaction.

At constant tris(1,10-orthophenanthroline)iron(III) concentration (1.8×10^{-6} M) and varying of reductants [hexacyanoferrate(II) and bis(π -cyclopentadienyl)iron(II)] concentration (1.8×10^{-5} M, 9.0×10^{-6} M, 3.6×10^{-6} M), different sets of experiments produced k_{obs} values which were found to alter with change in reductants [hexacyanoferrate(II) and bis(π -cyclopentadienyl)iron(II)] concentration at constant tris(1,10-orthophenanthroline)iron(III) concentration. The results were found to be dependent upon the ratio of the concentration of the two reactants, reductants and oxidant, tris(1,10-orthophenanthroline)iron(III). Thus there is no change in initial rate when initial concentration of reductants is varied in each set of experiments. However initial rate gets increased in these experiments as the ratios of concentrations of reductants and tris(1,10-orthophenanthroline)

Table 1 Kinetic rate data for pseudo first order reaction for the reduction of $[\text{Fe(o-phen)}_3]^{3+}$ with $[\text{Fe}(\text{CN})_6]^{4-}$ and $\text{Fe}(\text{C}_5\text{H}_5)_2$ $\lambda_{\text{max}} = 510\text{nm}$, $\text{pH} = 3.6$, 30°C , $\epsilon = 11000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

Set No.	Initial $[\text{Fe(o-phen)}_3]^{3+} \times 10^7 \text{M}$	Initial $[\text{Fe}(\text{CN})_6]^{4-}$ or $[\text{Fe}(\text{C}_5\text{H}_5)_2] \times 10^6 \text{M}$	Initial rate $\text{Ms}^{-1} \times 10^6$ with $[\text{Fe}(\text{CN})_6]^{4-}$	$k_{\text{obs}}^{-1} \text{Exp}$ with $[\text{Fe}(\text{CN})_6]^{4-}$	$k_{\text{obs}}^{-1} \text{Cal}$ with $[\text{Fe}(\text{CN})_6]^{4-}$	Initial Rate $\text{Ms}^{-1} \times 10^6$ with $[\text{Fe}(\text{C}_5\text{H}_5)_2]$	$k_{\text{obs}}^{-1} \text{Exp}$ with $[\text{Fe}(\text{C}_5\text{H}_5)_2]$	$k_{\text{obs}}^{-1} \text{Cal}$ with $[\text{Fe}(\text{C}_5\text{H}_5)_2]$
1	1.2	0.6	0.96	7.92	8.12	0.36	2.87	3.01
	1.8	0.6	1.4					
	2.4	0.6	1.9					
	3.0	0.6	2.4					
2	1.2	1.5	2.4	19.87	20.1	0.92	7.62	7.51
	1.8	1.5	3.6					
	2.4	1.5	4.8					
	3.0	1.5	6.0					
3	1.2	3.0	4.8	39.35	40.01	1.8	15.12	15.12
	1.8	3.0	7.2					
	2.4	3.0	9.6					
	3.0	3.0	12					

Table 2. Dependence of initial rate on $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{C}_5\text{H}_5)_2]$. pH = 3.6, 30°C

Set.No.	Initial $[\text{Fe}(\text{o-phen})_3]^{3+}$ $\times 10^7 \text{M}$	Initial $[\text{Fe}(\text{CN})_6]^{4-}$ $\times 10^6 \text{M}$	Initial rate $\text{M s}^{-1} \times 10^6$ with $[\text{Fe}(\text{CN})_6]^{4-}$	Initial rate $\text{M s}^{-1} \times 10^6$ with $[\text{Fe}(\text{C}_5\text{H}_5)_2]$	Stock $[\text{Fe}(\text{o-phen})_3]^{3+}$ $\text{M} \times 10^6$	Stock $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ or $[\text{Fe}(\text{CN})_6]^{4-}$ $\text{M} \times 10^5$
1	3.0	0.60	2.41	0.91	1.8	0.36
	3.0	0.36	2.39	0.87		
	3.0	0.84	2.4	0.92		
	3.0	1.2	2.43	0.93		
2	3.0	1.5	6.01	2.25	1.8	0.9
	3.0	0.9	6.02	2.22		
	3.0	2.1	6.01	2.27		
	3.0	2.7	6.03	2.26		
3	3.0	3.0	12	4.50	1.8	1.8
	3.0	1.8	12.1	4.49		
	3.0	4.2	12.1	4.51		
	3.0	5.4	12	4.52		

iron(III) were increased, as shown in Table 2, Figure 2. Plot of k_{obs} versus initial concentration of each reductants, $k_{\text{obs}} = k[\text{Reductants}]^n$, keeping all remaining conditions constant, was found to be straight line passing through the origin indicating first order kinetics with respect to each reductants. Data is given in Table 3 and displayed in Figure 3. An overall second order was found, having the rate constant (k) values of $8.33 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ respectively.

Table 3. Dependence of k_{obs} on reductants concentrations $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ pH = 3.0, 30°C

$[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{C}_5\text{H}_5)_2] \times 10^7 \text{ M}$	k_{obs} with $[\text{Fe}(\text{C}_5\text{H}_5)_2]$	k_{obs} with $[\text{Fe}(\text{CN})_6]^{4-}$
6	2.87	7.92
15	7.62	19.87
30	15.12	39.35

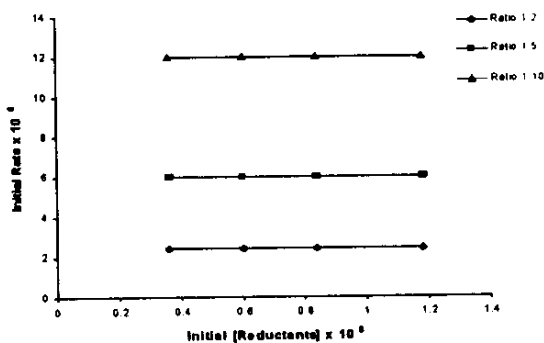
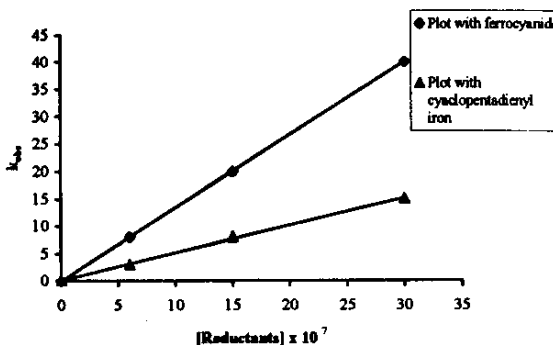


Fig.2. Plot of initial rate versus initial concentration of reductants, showing zero order reaction w.r.t. reductants due to isolation.

Another approach to determine the order of reaction of the reductants is a \ln - \ln plot of $\ln k_{\text{obs}} =$

Fig. 3. Plot of k_{obs} versus reductants concentration, an indirect determination of order of reaction of the isolated species (reductants)

$\ln k + n \ln[\text{Reductants}]$. The slope of the plot of $\ln k_{\text{obs}}$ versus $\ln [\text{Reductant}]$ should equal to n 'order of reaction'. The value of slope determined by this method is equal to '1' so this is again an indication of first order reaction with respect to each of the reductants and over all order of reaction is second order. The intercept ($\ln k$) gives the value of second order rate constant.

Effect of $[\text{H}^+]$ on k_{obs} for the Reaction Between $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{o-phen})_3]^{3+}$.

To study the effect of $[\text{H}^+]$ on rate, kinetic runs were carried out at different pH values. The remaining conditions were kept unaltered. It was observed that rate decreased with increase in hydrogen ion concentration at the pH values 3.6, 3.8, 4.0, 4.2 (Table 4). This increase in the rate as the hydrogen ion concentration decreased suggests an inverse fractional order kinetics. Plot of k_{obs} versus $[\text{H}^+]$ was found to be curved (Figure 4) while a plot of $1/k_{\text{obs}}$ versus $[\text{H}^+]$ was found to be

Table 4. Dependence on $[H^+]$ for the reaction between $[Fe(CN)_6]^{4-}$ and $[Fe(o-phen)_3]^{3+}$.
 $[Fe(CN)_6]^{4-} = 1.8 \times 10^{-5} M$, $[Fe(o-phen)_3]^{3+} = 1.8 \times 10^{-6} M$, $30^\circ C$

$k_{obs} s^{-1}$	$[H^+] \times 10^4 M$	$1/k_{obs} s$
39.35	2.51	0.025
57.55	1.58	0.0174
80.12	1.0	0.0125
106.91	0.6	0.0092

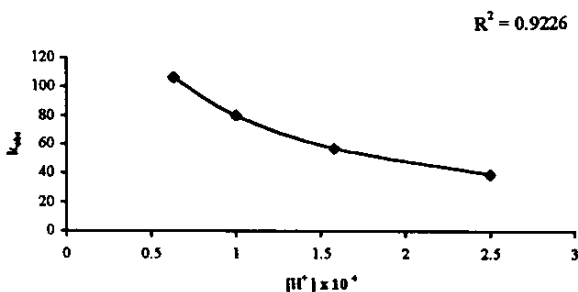


Fig.4. Plot of k_{obs} versus $[H^+]$, influencing electron transfer reaction through change in acidity.

straight line with positive slope (Eq. 7, Figure 5). R^2 values for the both plots are 0.9226 and 0.9998 respectively.

Effect of Temperature on Pseudo First Order Rate Constant (k_{obs}).

A kinetic run was carried out at $pH = 3.6$, tris(1,10-orthophenanthroline)iron(III) concentration of $1.8 \times 10^{-6} M$, reductants [hexacyanoferrate(II) and bis(π -cyclopentadienyl) iron(II)] concentration of $1.8 \times 10^{-5} M$ and the temperature was varied. The temperature dependence of k_{obs} was studied in the range of $30^\circ C$ to $45^\circ C$.

a) Reduction by $[Fe(CN)_6]^{4-}$

The results are given in Table 5 and plotted as $\ln k_{obs}$ versus $1/T$ by using Arrhenius equation of $\ln k = \ln A - E_a / RT$ (Figure 6). The graph is linear with a slope of $-1185K$ and intercept 9.01 . From slope and intercept values of E_a and A were

Table 5. Dependence of k_{obs} on temperature
 $[Fe(CN)_6]^{4-}$ and $[Fe(C_5H_5)_2] = 1.8 \times 10^{-5} M$, $[Fe(o-phen)_3]^{3+} = 1.8 \times 10^{-6} M$, $pH=3.6$

T/K	$1/T \times 10^3 K^{-1}$	$k_{obs} s^{-1}$ with $[Fe(CN)_6]^{4-}$	$\ln k_{obs}$ with $[Fe(CN)_6]^{4-}$	$\ln (k_{obs}/T)$ with $[Fe(CN)_6]^{4-}$	$k_{obs} s^{-1}$ with $[Fe(C_5H_5)_2]$	$\ln k_{obs}$ with $[Fe(C_5H_5)_2]$	$\ln (k_{obs}/T)$ with $[Fe(C_5H_5)_2]$
303	3.30	39.35	3.67	-2.04	15.12	2.72	-2.99
308	3.25	42.10	3.74	-1.99	15.87	2.76	-2.97
313	3.19	45.05	3.81	-1.94	16.63	2.81	-2.93
318	3.14	47.89	3.86	-1.89	17.39	2.85	-2.91

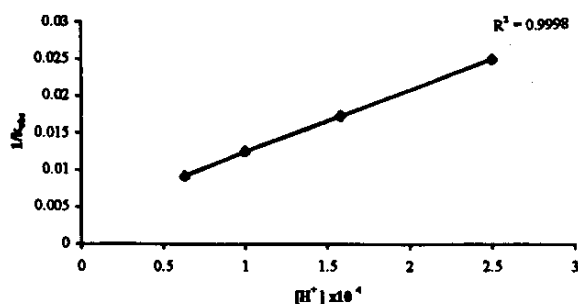


Fig. 5. Plot of $1/k_{obs}$ versus $[H^+]$, for the determination of order of reaction w.r.t. H^+ concentration.

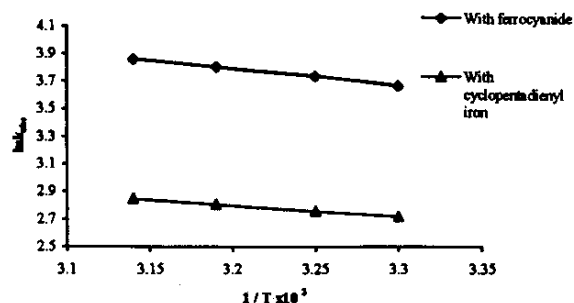


Fig. 6. Plot $\ln k_{obs}$ versus $1/T$, for the calculation of energy of activation.

calculated as $9.85 kJ mol^{-1}$ and $8.1 \times 10^3 S^{-1}$. Another graph between $\ln (k_{obs} / T)$ versus $1/T$ was plotted by using Transition State Theory [2] of $\ln(k/T) = \ln(\kappa/h) + \Delta S^\ddagger / R - \Delta H^\ddagger / RT$ (Figure 7). This graph is also linear with a slope of $-925K$ and intercept 1.0124 . From slope and intercept activation parameters ΔH^\ddagger and ΔS^\ddagger were calculated and found to be $7.69 kJmol^{-1}$ and $-189 JK^{-1}mol^{-1}$.

b) Reduction by $[Fe(C_5H_5)_2]$

Same graphs were plotted for reaction between tris(1,10-orthophenanthroline) iron (III) and bis(π -cyclopentadienyl) iron(II), and activation parameters were found to be $E_a = 6.78 kJmol^{-1}$, $\Delta H^\ddagger = 4.32 kJmol^{-1}$, $\Delta S^\ddagger = -208 JK^{-1}mol^{-1}$. Results

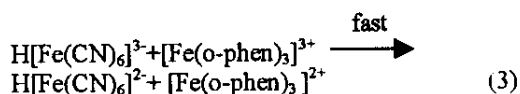
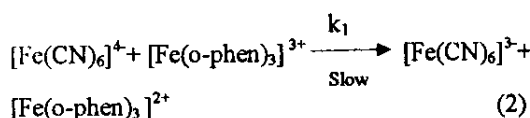
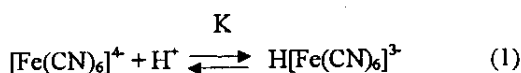
are given in Table 5 and displayed in Figures 6 and 7.

Proposed Mechanism

Scheme 1

Rate law for the reaction between tris(1,10-orthophenanthroline)iron(III) and hexacyanoferrate (II).

The mechanism is suggested to involve reactions, numbered 1-3



The rate of reaction is given by

$$\text{Rate} = k_1 [\text{Fe}(\text{CN})_6]_F^{4-} [\text{Fe}(\text{o-phen})_3]^{3+} \quad (4)$$

and over all rate law is expressed as

$$\text{Rate} = \frac{k_1 [\text{Fe}(\text{CN})_6]_T^{4-} [\text{Fe}(\text{o-phen})_3]^{3+}}{1 + K[\text{H}^+]} \quad (5)$$

Where

$$[\text{Fe}(\text{CN})_6]_T^{4-} = [\text{Fe}(\text{CN})_6]_F^{4-} + \text{H}[\text{Fe}(\text{CN})_6]^{3-}$$

$[\text{Fe}(\text{CN})_6]_F^{4-}$ is Free concentration of ferrocyanide

$[\text{Fe}(\text{CN})_6]_T^{4-}$ is Total concentration of ferrocyanide

As pseudo first order conditions prevail, first order rate constant is taken as

$$k_{\text{obs}} = \frac{k_1 [\text{Fe}(\text{CN})_6]_T^{4-}}{1 + K[\text{H}^+]} \quad (6)$$

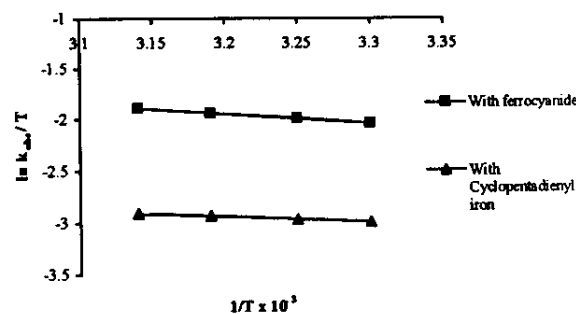


Fig. 7. Plot of $\ln(k_{\text{obs}}/T)$ versus $1/T$, for the calculation of enthalpy of activation and entropy of activation.

taking reciprocals on both sides equation 6 becomes

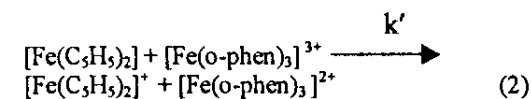
$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1 [\text{Fe}(\text{CN})_6]_T^{4-}} + \frac{K[\text{H}^+]}{k_1 [\text{Fe}(\text{CN})_6]_T^{4-}} \quad (7)$$

Plot of $1/k_{\text{obs}}$ versus $[\text{H}^+]$ is linear if all other factors were kept constant. The equilibrium constants K and second order rate constant k_1 were calculated from slope and intercept and were found to be $2.1 \times 10^4 \text{ M}^{-1}$ and $8.33 \times 10^7 \text{ M}^{-1} \text{ S}^{-1}$ respectively. A good agreement was found between the recalculated pseudo first order rate constants from equation 6 and experimental rate constants (k_{obs}). This confirms the proposed mechanism. Further to that K ($2.1 \times 10^4 \text{ M}^{-1}$) calculated from the slope of this plot agrees with the K value represented in the literature ($2 \times 10^4 \text{ M}^{-1}$) [14]

Scheme 2

Rate law for the reaction between tris(1,10-orthophenanthroline)iron(III) and bis(π -cyclopentadienyl)iron(II).

The mechanism is suggested as follows



Rate law is presented as

$$\text{Rate} = k' [\text{Fe}(\text{C}_5\text{H}_5)_2] [\text{Fe}(\text{o-phen})_3]^{3+}$$

Experimental

AnalaR grade, BDH chemicals were used and all the solutions were prepared in distilled and

deionize water. Tris(1,10-orthophenanthroline) iron(III) complex was prepared, its stability and ligand to metal ratio was determined as previously described [1,12]. The pH of the reaction mixture was brought to the values of 3.6, 3.8, 4.0, and 4.2 by using buffer mixtures of acetic acid-sodium acetate according to the details given in the literature [13].

Kinetic Measurements

The kinetic study of reduction of $[\text{Fe}(\text{o-phen})_3]^{3+}$ by $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ was carried out under the pseudo first order conditions in which concentration of reductants [hexacyanoferrate(II) and bis(π -cyclopentadienyl)iron(II)] was taken two, five and ten times greater than the corresponding iron(III) complex of orthophenanthroline. Different combinations of both tris(1,10-orthophenanthroline)iron(III) and reductants [hexacyanoferrate(II) and bis(π -cyclopentadienyl)iron(II)] were prepared by taking constant concentration of tris(1,10-orthophenanthroline)iron(III) (1.8×10^{-6} M) and varying the concentration of the reductants (1.8×10^{-5} M, 9.0×10^{-6} M, 3.6×10^{-6} M). Acetic acid-sodium acetate buffer was used to maintain the pH of 3.6. Various ratios of tris(1,10-orthophenanthroline)iron(III) and reductants solutions were mixed in a 1-cm quartz cells to a total volume of 3ml. The concentrations of components of the reaction mixture were predetermined and they were kept at 30°C in thermostat. The optical density was monitored spectrophotometrically as a function of time of each set of reaction mixture at wavelength of 510 nm. Initial rate was calculated from the slope by taking the tangent on absorbance-time curve in the kinetic mode of spectrophotometer. Pseudo first order plots of $\ln(A_\infty - A_t)$ versus time were also plotted, where A_t is the absorbance at any time and A_∞ is the absorbance at infinite time.

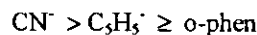
Instrumentation

Kinetic measurements were carried out on photometric and kinetic mode of Shimadzu UV-160, UV-visible spectrophotometer, using quartz cells. pH measurements were carried out on digital HANNA pH meter (HI-8314 model). Temperature controlled runs were carried on Thermostat (HAAKE KT 33).

Conclusions

Nature of ligands greatly affects the course of a reaction. Depending upon their ability to make

bonds with metal ions having no π -orbitals, filled π -orbitals, empty π -orbitals, and filled-empty π -orbitals, the electron exchange capabilities are influenced. The nature of bonding with these orbitals greatly affects the splitting energy (Δ_o), which depends on the ligand's strength, as order of increasing ligand strength is shown below



The splitting energy of ligands having filled π -orbitals is less than d-orbitals of the metal ions, which are involved in L \rightarrow M bonding. In this way an excess of negative charge is brought on metal from ligand which destabilizes the metal and decreases the Δ_o and hence stability of the complex. Accordingly an increase in the rate of reaction is observed. The energy of ligands having empty π -orbitals is more than d-orbitals of the metal ions, which makes bonding from M \rightarrow L i.e forms back bonding, and having reverse behavior than filled π -orbitals. It can be concluded that as the strength of the ligands in the electrochemical series increases (having greater splitting energy), electrode potential of the metal ions binding to these ligands decreases and hence rate of reduction decreases. Oxidation potential increases which increases the rate of oxidation. The reduction of tris(1,10-orthophenanthroline)iron(III) increases as the oxidation potential of reducing agent increases from hexacyanoferrate(II) (-0.358V) to bis(π -cyclopentadienyl)iron(II) (-0.40V) respectively. Due to these reasons second order rate constant value of tris(1,10-orthophenanthroline)iron(III) with hexacyanoferrate(II) is more than bis(π -cyclopentadienyl)iron(II).

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