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Use of Nitrogen Containing Heterocyclic ligand; Phenanthroline to study the kinetics of uncatalysed ligand substitution reaction of hexacyanoferrate (II)

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ABSTRACT-The kinetics and mechanism of uncatalysed substitution of co-ordinated cyanide in hexacyanoferrate (II) by a nitrogen donar heterocyclic ligand, phenanthroline at 528nm (λmax of a dark coloured compound [Fe (CN)5Phen]3- as a function of $[Fe (CN)_6]^{4-}$ and [Phen] under the conditions, pH= 3.0±0.02, temperature = 25.0± 0.10oC , Ionic strength (I) = 0.03 M(KNO_3).The reaction is a first order each in [Fe (CN)6]4- and [Phen] at low [Phen] concentration. The rate of the reaction in determined from the slopes of absorbances versus time plots. As [Phen] increases the rate of the reaction increases, passes through a maximum and them falls, suggesting that the course of the reaction is different at low [Phen] and high [Phen]. The effect of temperature and pH on the initial rate have also been explained and studied. The repetitive spectral scans is also provided as an evidence for exchange of cyanide ions by [Phen] in [Fe(CN)6]4-. Activation parameters have also been evaluated and provided in support of the proposed mechanistic scheme. The compositon of the complex was established as 1:1 by the mole ratio method.

Keywords: Nitrogen heterocycle, Phenathroline, hexacyanoferrate (II), ligand substitution, kinetics.

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1 INTRODUCTION

Phenanthroline (Scheme 1) is a heterocyclic organic compound. As a bidentate ligand in co-ordination chemistry, it forms strong complexes with most metal ions. It is used in transition metal chemistry for determination of metals, as an indicator for alkyl lithium reagents. It is used in metallocene industry and co-ordination of organometallic complexes. Complexes of the type $[Fe (CN)_5 INH_3$-] [1] and $[Fe (CN)_5 PhNHNH_2]3$- [2] have been obtained either through photo-chemical aquation of $[Fe (CN)_6]_4$- or by Hg+2 assisted complexes of the type $Fe (CN)_5 L$ (L= N_3^- , Ph NO, amines) have been prepared by substitution in pentacyano amino ferrate (II) or mercury catalysed substitution in hexacyanoferrate (II) molecular complexes of Pyrazine (Pz) and [Ru (CN)6]4- having molecular formula [Ru (CN)5 Pz]3- [7] and N-methyl Pyrazine and [Fe (CN)6]4- [8] have been reported.The thermal decomposition of hexacyanoferrate (II) ion is a slow reversible process according to equation 1. The pentacyanoaquo complex produced has been reported [9] to react with aromatic nitroso compounds giving intensely coloured products. There in limited information on the kinetics and mechanism concerning substitution in hexacyanoferrate (II) [10-13]. Exchange of labelled cyanide between [Fe (CN)6]4- and free cyanide is extremely slow, but under U.V. light reversible aquation takes place [14].

Most of the substituted cyano complexes of Iron (II) are metal assisted dissociation of hexacyanoferrate (II) [11, 15] followed by reaction with the incoming ligand. Many complexes of the pentacyano (ligand.) ferrate (II) type have been prepared by substitution in pentacyano (amino) ferrate (II) or by metal catalysed substitution in hexacyanoferrate (II) [2,8,11,12,16-21]. In accordance with our earlier investigation of the reaction of phenyl hydrazine [1] and pyrazine [7] with hexacyanoferrate (II), phenonthroline has also been shown to react with [Fe (CN)6]4- according to Equations [1-3].

$$[Fe(CN)_6]^{4-} + H_2O \underset{k_1}{\overset{k_2}{\rightleftharpoons}} [Fe(CN)_5 H_2O]^{3-} + CN^- \quad \text{Slow} \quad (1)$$

$$[Fe(CN)_5 H_2O]^{3-} + [Phen] \longrightarrow [Fe(CN)_5 Phen]^{3-} + H_2O \quad (2)$$

$$CN^- + H_2O \rightleftharpoons HCN + OH^- \quad (3)$$

The uncatalysed reaction takes about 24 hours to attain maximum absorbance. The stoichiometry of the complex has been established as 1:1 by the mole ratio [22] and slope method [23].

2 RESULTS AND DISCUSSION

Effect of $[Fe (CN)_6]^{4-}$

Effect of $[Fe (CN)_6]^{4-}$ on the initial rate of unanalyzed reaction between$[Fe (CN)_6^{4-}]$ and Phenanthroline was studied taking $[Fe (CN)_6^{4-}]$ = (1.0-8.0) x 10^{-3}M. The reaction was found to exhibit first order behavior in $[Fe (CN)_6^{4-}]$ in the concentration range studied. The plot of initial rate (Vi) versus $[Fe (CN)_6^{4-}]$ in a straight line as shown in Figure 1 ($r^2 \le 0.995, sd \le 0.223$).

Effect of [Phen]

The effect of [Phen] on the initial rate for uncatalysed ligand

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