



The Kinetic Study of Ligand Substitution Reaction Using Lead as Catalyst

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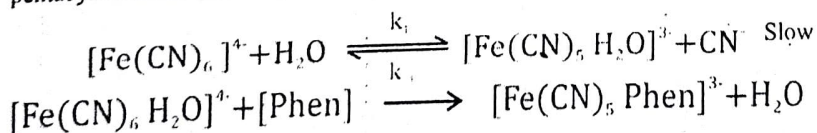
ABSTRACT

The Kinetic study of Pb (II) catalyzed exchange reaction between hexacyanoferrate (II) and phenanthroline (Phen) were studied as ligand substitution reaction which followed a dark coloured complex $[\text{Fe}(\text{CN})_5\text{Phen}]^{3-}$ at 528 nm. $\text{pH}=3.0\pm 0.02$. temperature $=25\pm 0.5^\circ\text{C}$. The effect of various parameters like Concentration of [Phen] and $[\text{Fe}(\text{CN})_6]^{4-}$ on the rate of reaction rate were also seen and explained in detail. The reaction rate showed variable order dependence in $[\text{Fe}(\text{CN})_6]^{4-}$. The effect of water , dielectric constant, ionic strength, temperature were also considered to arrive at a possible interchange dissociative mechanism for the catalysed reaction. Activation parameters of the reaction under study was calculated with the help of Eyring and Arrhenius equation and given in support of proposed mechanism.

INTRODUCTION

Out of the complex compound of transition metal series the Potassium hexacyanoferrate (II) is known to be the least labile cyano complex. A large number of sparingly soluble salts of formula $\text{K}_2\text{M}^{\text{II}}\text{Fe}(\text{CN})_6$ or $\text{KM}^{\text{III}}\text{Fe}(\text{CN})_6$ are obtained due to fixation of alkali, alkaline earth or transition metal ions in the outer sphere of $\text{Fe}(\text{CN})_6^{4-}$ [1-3]. The adducts of $\text{K}_4\text{Fe}(\text{CN} \text{BX}_3)_6$ (B = Boron, X = F,Cl) type are formed very slowly [4,5] and are suggested to contain cyano bridges recognised by shift in CN stretching band by about 100cm^{-1} towards higher frequency side [4].

A number of researches have been carried out for kinetic study of the ligand exchange reactions of low spin iron (II) complex compounds, however most of these reactions involved pentacyanoferrate (II) complex compounds [6-16].



The uncatalysed reaction takes several hours to complete but metals like lead [28, 29], silver [30] catalyse the reaction and bring down the required time of the reaction. Lead is used as catalyst in the reaction between hexacyanoferrate (II) and phenanthroline was under our investigation (31). We are trying to develop a method using lead as catalyst for the reaction between hexacyanoferrate (II) and 1,10 phenanthroline. The

To further augment our knowledge about the mechanism of these reactions a number of researches have been done in micellar [13,14] media or in concentrated aqueous solution of electrolyte [12]. Many research groups have also studied the kinetics of oxidation reactions of the hexacyano ferrate (II) complex compounds by many reagents, in different kinds of medium like neutral or acidic [17-19] but the information about the kinetics and mechanistic study of the substitution [20-24] is very less. Moreover many of these findings have already been taken up to solve different types of problems relating to analysis [20-23], instead of making a comprehensive study of the various aspects of the mechanism of these replacement reactions of hexacyanoferrate (II) [24]. Therefore there are several unsolved mysteries of the mechanistic and kinetic study of these replacement reactions of hexacyanoferrate (II) that are still left to be answered.

The hexacyanoferrate (II) undergoes aquation under the influence of near ultraviolet light in acidic medium synthesising $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ and CN^- [25]. A great amount of research of complexes substituted with P-, O-, N- and P- donor ligands have been formed from labile $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ ion [26, 27]. The thermal decomposition of hexacyano ferrate (II) ion is an extremely slow process that is reversible in nature in accordance to Eqn(1). The penta aqua cyanoferrate(II) complex produced has been reported to react with nitroso R-salt [28] and N-Methyl pyrazinium [29] ion. Thus the reaction of hexacyanoferrate (II) with phenanthroline is also believed to proceed through following Equations in conformity with the above investigated systems.