

RESEARCH PAPER

Kinetics and mechanism of mercury catalysed ligand exchange reaction between hexacyanoferrate(II) and phenanthroline in aqueous medium

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ABSTRACT

Kinetic and mechanistic studies of Hg(II)-catalysed exchange of co-ordinated cyanide in hexacyanoferrate(II) by phenanthroline (Phen) were performed by following the appearance of the coloured complex $[\text{Fe}(\text{CN})_4\text{Phen}]^{3-}$ at 528 nm, temperature = $25 \pm 0.10^\circ\text{C}$, pH = 3.0 ± 0.02 . The effects of pH, $[\text{Fe}(\text{CN})_6]^{4-}$ and [Phen] concentrations on the reaction rate have been studied and explained. The rate shows variable order dependence on $[\text{Fe}(\text{CN})_6]^{4-}$. The effects of dielectric constant, water content, temperature and ionic strength of the medium on the reaction rates have been used to visualise the formation of a polar activated complex and suggest an interchange dissociative mechanism for the catalysed reaction. The varying catalytic activity of Hg(II) as a function of concentration has also been studied and explained in detail. Activation parameters of both catalysed and uncatalysed reactions have been derived and supported the proposed mechanistic scheme.

KEYWORDS: kinetics and mechanism, UV spectroscopy, ligand substitution, phenanthroline, hexacyanoferrate(II)

1. INTRODUCTION

Potassium hexacyanoferrate(II) has been known to be among the least labile cyano complexes of transition metal ions. A large number of sparingly soluble salts of formula $\text{K}_3\text{M}^{\text{II}}\text{Fe}(\text{CN})_6$ 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 $\text{Fe}(\text{CN})_6^{4-}$.