

E2-30: Kinetics of the oxidation of N-methylaniline by alkaline hexacyanoferrate(III)

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Metal ions/complexes of metal ions are considered very important in synthetic organic chemistry as they are capable of oxidizing a wide variety of organic compounds. In particular, oxidation of amines with mild one electron oxidants such as hexacyanoferrate(III)[HCF(III)] has been a subject of much interest as stimulated by the importance of biological oxidation of amine nitrogen atom. In a continuing effort to examine the products and rates of oxidation of different types of secondary amines, the reaction of N-methylaniline with hexacyanoferrate (III) in alkaline medium is reported.

Kinetic studies were carried out under pseudo-order conditions by reacting hexacyanoferrate(III) with excess N-methylaniline under alkaline conditions in aqueous ethanol. The progress of the reaction was monitored spectrophotometrically by measuring the variation of the absorbance of hexacyanoferrate(III) with time at different N-methylaniline concentrations at constant pH and vice versa.

The aforementioned kinetic experiments revealed that the reaction exhibits a rate law, $\text{rate} = k[\text{HCF(III)}][\text{amine}][\text{H}^+]^{-1}$ where k is the overall rate constant calculated as $1.058 \times 10^{-15} \text{s}^{-1}$ at 300K. The final product in the oxidation reaction was characterized as the N-aldehyde PhNHCHO. A mechanism involving a rapid simultaneous electron transfer together with proton abstraction to give a radical intermediate followed by slow electron transfer to form a cationic species (11) has been proposed, consistent with the rate law.

This reaction demonstrates the usefulness of hexacyanoferrate (III) as a reagent which can bring about the oxidation of secondary amines with N-alkyl side chains. This is in contrast to the formation of neutrinos with cyclic secondary amines.

