E2-28: Kinetics of oxidation of pyrollidone by hexacyanoferrate (III)

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Hexacyanoferrate (III)[HCF(III)] is well known for its oxidizing properties in aqueous solution. Continuing interest on the products and rates of oxidation of cyclic amines, the reaction of pyrollidine (Py,C_4H_9N) with HCF (III) in alkaline medium is reported.

Kinetic studies were carried out under pseudo order conditions by reacting HCF (III) with excess pyrollidine in aqueous sodium hydroxide. The progress of the reaction was monitored spectrophotometrically by measuring the absorbance of HCF (III) at 420 nm.

Variation of absorbance of HFC (III) with time at different pyrollidine concentrations at constant pH and vice versa, was measured. The results revealed that the reaction exhibits a rate law, rate = k $[HCF(III)][Py][H^+]^{-1}$. where k is the overall rate constant calculated as 4.12 x 10^{-14} s^{-1} at 300 K.

This value was about 10 orders of magnitude greater than that of piperidine ($C_5H_{11}N$, k=2.11 x 10^{-15} s^{-1} at 300 K) indicating that pyrollidine had enhanced nucleophilicity compared to that of the reaction with piperidine. In general, nucleophilicities take the same order as that of basicities for a particular element and hence the enhanced rate of pyrollidine was consistent with Pk_bvalues of these bases (Pyrollidine, Pk_b = 3.2 : Piperidine, Pk_6 = 3.5).

Oxidation appears to go *via* a series of steps culminating in the formation of pyrollidine-N-oxide (commonly referred to as nitrones). A mechanism consistent with the rate law has been proposed for this reaction.

SECTION E2