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The Kinetics and Mechanism of Ruthenium(III)-Catalyzed Oxidation of Tris(2-amino ethyl)amine by Hexacyanoferrate(III) in Aqueous Alkaline Medium

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Abstract: The kinetics of ruthenium(III)-catalyzed oxidation of TREN, i.e. tris(2-amino ethyl)amine(3-hydrochloride) by an outer sphere electron transfer oxidant, potassium hexacyanoferrate(III), was investigated spectrophotometrically in aqueous alkaline medium. The extent of the reaction was followed by registering a decrease in absorbance at 420 nm ($\bullet_{max}$ of $Fe(CN)_6^{3-}$) due to its consumption as a function of $[OH^-]$, ionic strength, $[Fe(CN)_6^{3-}]$, [TREN], and temperature by varying only one variable at a time and keeping all other variables constant. The rate data indicate that the reaction exhibited first order dependence in [oxidant] and at a lower concentrations of reductant. The overall reaction follows second order kinetics at constant $[OH^-]$ and proceeds via an associative Sn^2 reaction path. The reaction was found to be first order at lower alkali concentrations, tending towards zero at higher concentrations. The rate of reaction increased linearly with increased ionic strength of the medium. A most probable mechanistic scheme explaining all the observed results has been proposed. Activation parameters were computed using the Arrhenius and Eyring equations, which provided additional support to the proposed associative Sn^2 pathway.

Key Words: Ru(III) catalyzed oxidation, oxidation of TREN, hexacyanoferrate (III)oxidation of TREN

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