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Manganese(II) catalyzed periodate oxidation of a ternary dipicolinatochromium(III) complex with iminodiacetate as co-ligand: mechanistic and kinetic study

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Abstract

The kinetics and mechanism of the oxidation of [Cr-III(DPA)(IDA)(H₂O)](-) (DPA = dipicolinate and IDA = iminodiacetate) by periodate in the presence of Mn(II) as a catalyst have been investigated. The rate of the reaction increases with increasing pH, due to the deprotonation equilibria of the complex. Addition of Mn(II) in the concentration range of (2.5-10) x 10⁻⁶ mol dm⁻³ enhanced the reaction rate; the reaction is first order with respect to both [IO₄⁻] and the Cr complex, and obeys the following rate law: Catalysis by Mn(II) is believed to be due to initial oxidation of Mn(II) to Mn(III), which acts as the oxidizing agent. It is proposed that electron transfer proceeds through an inner-sphere mechanism via coordination of IO₄⁻ to Cr(III). Thermodynamic activation parameters were calculated using the transition state theory equation.

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