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

By: Ewais, HA (Ewais, Hassan A.)[1]; Al-Orabi, RO (Al-Orabi, Randa O.)[1]; Obaid, AY (Obaid, Abdulla Y.)[1]

View ResearcherID and ORCID

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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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Author Information

Reprint Address: Ewais, HA; Al-Orabi, RO (reprint author)

– King Abdulaziz Univ, Fac Sci, Dept Chem, POB 80203, Jeddah 21589, Saudi Arabia.
Organization-Enhanced Name(s)
King Abdulaziz University

Addresses:

– [1] King Abdulaziz Univ, Fac Sci, Dept Chem, POB 80203, Jeddah 21589, Saudi Arabia
Organization-Enhanced Name(s)
King Abdulaziz University

E-mail Addresses: hshalby2002@yahoo.com; randaorabi@yahoo.com

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