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Inner-sphere oxidation of a ternary dipicolinatochromium(III) complex involving a malonic acid co-ligand

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Abstract

The oxidation of a ternary complex of chromium(III), [Cr-III(DPA)(Mal)(H₂O)(2)](-), involving dipicolinic acid (DPA) as primary ligand and malonic acid (Mal) as co-ligand, was investigated in aqueous acidic medium. The periodate oxidation kinetics of [Cr-III(DPA)(Mal)(H₂O)(2)](-) to give Cr(VI) under pseudo-first-order conditions were studied at various pH, ionic strength and temperature values. The kinetic equation was found to be as follows: where k (6) (3.65 x 10⁻³ s⁻¹) represents the electron transfer reaction rate constant and K (4) (4.60 x 10⁻⁴ mol dm⁻³) represents the dissociation constant for the reaction and K (5) (1.87 mol⁻¹ dm³) and K (6) (22.83 mol⁻¹ dm³) represent the pre-equilibrium formation constants at 30 A degrees C and I = 0.2 mol dm⁻³. Hexadecyltrimethylammonium bromide (CTAB) was found to enhance the reaction rate, whereas sodium dodecyl sulfate (SDS) had no effect. The thermodynamic activation parameters were estimated, and the oxidation is proposed to proceed via an inner-sphere mechanism involving the coordination of IO₄⁻ to Cr(III).

Keywords

KeyWords Plus: PERIODATE-OXIDATION; KINETICS; MECHANISM; IMINODIACETATOCHROMIUM(III); CHROMIUM

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