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Kinetics and mechanism of periodate oxidation of two ternary nitrilotriacetate chromium (III) complexes involving histidine and aspartate co-ligands

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The oxidation of $[Cr^{III}(HNTA)(Hist) (H_2O)]$ - and $[Cr^{III}(HNTA)(Asp)(H_2O)]$ - (NTA=nitrilotriacetate, Hist=L-histidine and Asp=DL-aspartate) by periodate in aqueous medium has been studied spectrophotometrically between 15.0 and 35.0°C under pseudo-first-order conditions, $[IO_4]$ - [complex]. The rate increases over the pH range 3.40-4.45 in both cases, but the two complexes give different rate laws, in aqueous solutions, $[Cr^{III}(HNTA)(Hist)(H_2O)]$ - is oxidized by IO_4 - according to the following rate law: $d[CrV^I]/dt = (k_1K_2 + k_2K3K_1/[H+1))[IO_4-][Cr^{III}]T/{1+ (K_1/[H+1)) + (K_2 + K_1K3/[H+1))[IO_4-]}$. The other case is $[Cr^{III}(HNTA)(Asp)(H_2O)]$ - the derived rate law is given by equation: Rate= $k_1K_2[Cr^{III}]T/{1+ ([H+1]/K_1) + K_2[I^{VII}]T}$. Electron transfer, outer-sphere and inner-sphere mechanisms have been discussed. The nature, properties, chemical behavior and different species in aqueous solutions of periodate have been reported. A literature survey on the oxidation of organic and inorganic compound in aqueous solutions and in aqueous organic solvent was reported. The nature of α -amino acids and their metal complexes have been briefly discussed, it is clear that $[Cr^{III}(NTA)(Asp)(OH)]_2$ - may be the reactive species, an inner-sphere process may be still accommodating through replacement of coordinated H_2O in two species by IO4-. The rate of reaction increases with the increasing of complex concentration and ionic strength. The thermodynamic activation parameters were calculated, and we propose that electron transfer proceeds through an inner-sphere mechanism, via coordination of IO4-to chromium (III). A common mechanism for the oxidation of some to chromium(III) complexes by periodate is proposed by an excellent isokinetic relationship between and values for these reactions.

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