

Redox and complexation chemistry of the CrVI/Cr V/CrIV-d-glucuronic acid system

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When excess uronic acid over CrVI is used, the oxidation of d-glucuronic acid (Glucur) by CrVI yields D-glucaric acid (Glucar) and CrIII as final products. The redox reaction involves the formation of intermediate CrIV and CrV species, with CrVI and CrV reacting with Glucur at comparable rates. The rate of disappearance of CrVI, and CrV increases with $[H^+]$ and $[substrate]$. The experimental results indicated that Cr IV is a very reactive intermediate since its disappearance rate is much faster than CrVI/CrV and decreases when $[H^+]$ rises. Even at high $[H^+]$ CrIV intermediate was involved in fast steps and does not accumulate in the reaction. Kinetic studies show that the redox reaction between Glucur and CrVI proceeds through a mechanism combining one- and two-electron pathways for the reduction of intermediate Cr(iv) by the organic substrate: CrVI? Cr IV? CrII and CrVI? Cr IV? CrIII. The mechanism is supported by the observation of free radicals, CrO_2^{2+} (superoxoCr III ion) and CrV as