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**The Reduction of Chromium(VI) With Hydrogen sulfide and Thiols: Mechanistic Studies**

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**Introduction and Approach:** The oxidized hexavalent species present in complex anions, such as chromate ( $\text{CrO}_4^{2-}$ ), bichromate ( $\text{HCrO}_4^-$ ), and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ), is highly toxic, and likely a carcinogen and mutagen. However, the reduced Cr(III) that readily forms insoluble oxides and hydroxides,  $[\text{Cr}(\text{OH})_3]$ , is regarded as less toxic or non-toxic to organisms. Because the Cr(III) species is not poisonous, the reduction of Cr(VI) to Cr(III) may constitute a potentially valuable mechanism for remediating Cr(VI) toxicity. Both abiotic and biotic processes can reduce environmental Cr(VI) to Cr(III). The redox potential (Eh) of the immediate environment, its pH, and the presence of reductive molecules are some important factors controlling the rates of abiotic reduction. Reactive sulfur species, such as hydrogen sulfide and thiols, probably play a crucial role in reducing Cr(VI) under reducing conditions. While the reduction of Cr(VI) by sulfur nucleophiles is well recognized, the mechanisms and oxidation products of sulfur are not well understood. In this study, we used sulfur K-edge XANES spectroscopy to directly reveal the identity of the reaction products.

**Results:** We conducted mechanistic studies of the reaction of Cr(VI) with several sulfur nucleophiles including hydrogen sulfide, 3-mercaptopropionic acid, cysteine, and glutathione, at a pH range of 4-9 at ambient temperature. Experiments were also conducted with various initial ratios of Cr(VI) to sulfur nucleophiles. Our results show that the type of products formed is greatly affected by pH. With thiols, the main products formed at low pH was disulfides. However, with increasing pH in the basic range the oxidation proceeded to the level of sulfonates with intermediate stages, including sulfinates. Hydrogen sulfide was oxidized to thiosulfate and sulfate.

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