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Pertechnetate-Induced Addition of Sulfide in Small Olefinic Acids: Formation of $[TcO(dimercaptosuccinate)_2]^{5-}$ and $[TcO(mercaptosuccinate)_2]^{3-}$ Analogues

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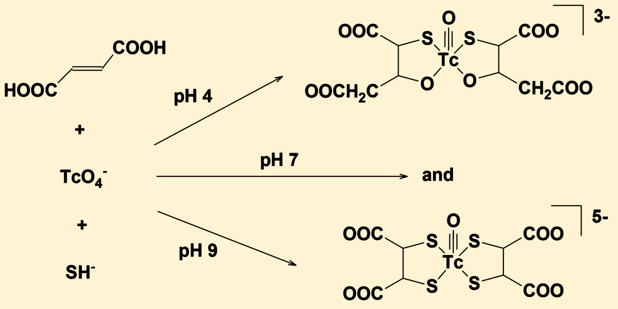
Supporting Information

ABSTRACT: Technetium-99 (^{99}Tc) is important to the nuclear fuel cycle as a long-lived radionuclide produced in ~6% fission yield from ^{235}U or ^{239}Pu. In its most common chemical form, namely, pertechnetate ($^{99}TcO_4^-$), it is environmentally mobile. In situ hydrogen sulfide reduction of pertechnetate has been proposed as a potential method to immobilize environmental $^{99}TcO_4^-$ that has entered the environment. Reactions of $^{99}TcO_4^-$ with sulfide in solution result in the precipitation of Tc_2S_7 except when olefinic acids, specifically fumaric or maleic acid, are present; a water-soluble ^{99}Tc species forms. NMR (^1H, ^{13}C, and 2D methods) and X-ray absorption spectroscopy [XAS; near-edge (XANES) and extended fine structure (EXAFS)] studies indicate that sulfide adds across the olefinic bond to generate mercaptosuccinic acid (H_3MSA) and/or dimercaptosuccinic acid (H_4DMSA), which then chelate(s) the ^{99}Tc to form $[^{99}TcO(MSA)_2]^{3-}$, $[^{99}TcO(DMSA)_2]^{5-}$, or potentially $[^{99}TcO(MSA)(DMSA)]^{4-}$. 2D NMR methods allowed identification of the products by comparison to ^{99}Tc and nonradioactive rhenium standards. The rhenium standards allowed further identification by electrospray ionization mass spectrometry. $^{99}TcO_4^-$ is essential to the reaction because no sulfide addition occurs in its absence, as determined by NMR. Computational studies were performed to investigate the structures and stabilities of the potential products. Because olefinic acid is a component of the naturally occurring humic and fulvic acids found in soils and groundwater, the viability of in situ hydrogen sulfide reduction of environmental $^{99}TcO_4^-$ as an immobilization method is evaluated.



INTRODUCTION

Technetium is a group 7 element situated below manganese and above rhenium and has no stable isotopes. Its redox chemistry is complex, with known oxidation states ranging from 1− to 7+. The most well-known radioisotope of technetium is ^{99m}Tc from its long-time use in diagnostic nuclear medicine, with compounds for myocardial stress/rest tests and bone scans among the approved radiopharmaceuticals. A second technetium radioisotope is of importance environmentally, namely, ^{99}Tc, because of its long half-life ($t_{1/2} = 2.1 \times 10^5$ years) and ~6% yield from the thermal neutron fission of ^{235}U and ^{239}Pu. Technetium exists predominantly as one of two species in the environment, either pertechnetate (TcO_4^-) or technetium(IV) oxide (TcO_2).

^{99}Tc has entered the environment from the nuclear era, and the pertechnetate anion, the most common chemical form under oxic conditions, is mobile. Hanford, WA, was one of the larger sites used for nuclear weapons development for the Manhattan Project, with several tons of nuclear fuel reprocessed to isolate ^{239}Pu. Underground storage tanks were used to contain the 54 million gallons of radioactive waste generated during reprocessing, and some of the tanks have leaked, with more than 1 million gallons of radioactive waste seeping into the vadose zone (soil above the water table).[1] Because of the close proximity of the Hanford Site to the Columbia River, ^{99}Tc is of significant environmental concern. Several studies aimed at remediating pertechnetate in the vadose zone through in situ stabilization have been reported,[2−7] with immobilization of environmental pertechnetate by reduction to an insoluble technetium(IV) species as a common theme.

In situ immobilization of technetium species requires either direct or indirect reduction of technetium(VII), the latter by reduction of surface iron(III) in minerals common in soils (e.g., goethite, hematite), which would then reduce the technetium. One potential method to immobilize metal ions involves in situ gaseous hydrogen sulfide reduction, which can act both directly and indirectly on technetium(VII).[8] Sulfides, such as sodium sulfide and hydrogen sulfide, react with pertechnetate in solution and precipitate technetium(IV) oxide or insoluble technetium

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