Research Program to Investigate the Fundamental Chemistry of Technetium

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Research Objective

Technetium (^{99}Tc, half-life = 2.13×10^5 years, β-emitter) is one of the radionuclides of major concern for nuclear waste disposal. This concern is due to the long half-life of ^{99}Tc, the ease with which pertechnetate, TcO_4^-, migrates in the geosphere, and the corresponding regulatory considerations. The problem of mobility of pertechnetate in the environment is compounded by the fact that pertechnetate is the thermodynamically stable form of technetium in oxidizing environments. Because of this stability, pertechnetate was presumed to be the predominant chemical form of technetium in the aqueous phase of nuclear waste tanks. However, recent studies indicate that a significant fraction of the technetium is in a different chemical form.[1,2] These factors present challenges the disposition of technetium.

Research Progress and Implications

Radiation chemistry of technetium in alkaline solution. As of February, 2000, our efforts have principally focused on exploring the radiation chemistry of pertechnetate in alkaline solution with added organic compounds, nitrate, and/or nitrate. The most important results are 1) the chemistry and identity of the organic radicals control the rate of reduction of pertechnetate during radiolysis, and 2) organic radicals can reduce pertechnetate even if a large excess of nitrate or nitrite is present.

Radiolysis in water at high pH produces mainly e^- and O^- as the primary radiolysis products. At high pH, the radiation-chemical yields, G, of e^- and O^- are $G_e \cong G_0 = 0.32 \ \mu mol \ J^{-1}$. The hydrated electron, e^-, reacts quickly with TcO_4^- to give TcO_4^{2-}; e^- also reacts quickly with NO_3^- and NO_2^-. Because nitrate and nitrite react quickly with e^-, reduction of TcO_4^- by e^- is strongly suppressed in solutions with high $[NO_3^-]$ or $[NO_2^-]$. The oxide radical ion, O^-, reacts rapidly with organic molecules by H-abstraction to give organic radicals. Organic radicals can reduce TcO_4^- in the presence of a large excess of nitrate or nitrite since organic radicals react very slowly with NO_3^- and NO_2^- but react quickly with TcO_4^-.[3,4] Consequently, radiolysis can reduce TcO_4^- even in high concentrations of nitrate and nitrite. Figure 1 shows $G(-TcO_4^-)$ for radiolysis of solutions of 200μM TcO_4^-, 2M NaOH, 0.1M iminodiacetate (IDA), and varying concentrations of nitrate or nitrite. In addition, Figure 1 shows calculated $G(-TcO_4^-)$, which were determined using a rate law derived from the reaction scheme illustrated in Figure 2. The most important result shown in Figure 1 is the fact that $G(-TcO_4^-)$ approaches a limiting value as $[NO_3^-]$ increases. This limiting value, 0.006 μmol J^{-1}, is presumably the radiation-chemical yield for reduction of the TcO_4^- by the carboxy(carboxymethylamino)methyl radical generated by H-abstraction from IDA.
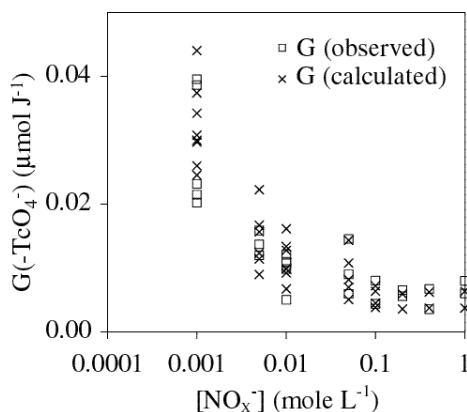

Figure 1: Observed and calculated radiation-chemical yields for the reduction of TcO_4^- in 0.1M (IDA) versus $[NO_3^-]$ and $[NO_2^-]$.
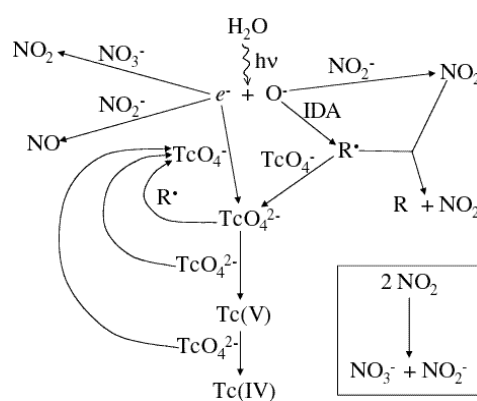
Figure 2: Reaction scheme for calculating the radiation-chemical yields for the reduction of TcO_4^- in solutions of IDA, nitrite, and nitrate.

Identity of Radiolysis Products.[5] Radiolysis of alkaline solutions of TcO_4^- in the presence of ethanol, ethylenediaminetetraacetate (EDTA), nitrilotriacetate (NTA), IDA, or citrate produces an insoluble precipitate. This material has a characteristic electron paramagnetic resonance (EPR) spectrum, which is shown in Figure 3. Figure 3 also shows the EPR spectrum of $TcO_2 \bullet xH_2O$ produced by hydrolysis of $TcCl_6^{2-}$. The EXAFS spectra and Fourier transforms of the insoluble radiolysis product and $TcO_2 \bullet xH_2O$ are shown in Figure 4. Because the EPR and EXAFS spectra of the insoluble radiolysis product and $TcO_2 \bullet xH_2O$ are the same, we conclude that the insoluble radiolysis product is simply $TcO_2 \bullet xH_2O$. This result shows that the Tc(IV) complexes of EDTA, NTA, IDA, or citrate are not stable in highly alkaline solutions.

Radiolysis of TcO_4^- in 2M NaOH in the presence of glyoxylate ($^-O_2CCHO$), formaldehyde, or ethylene glycol produces pink solutions with no precipitate. These solutions all have weak absorption peaks at 500 nm in their UV/Vis spectra, similar to $(EDTA)_2Tc_2(\mu\text{-}O)_2$.[6] The EXAFS spectrum of one of these solutions is shown in Figure 3d. The EXAFS spectrum of $(EDTA)_2Tc_2(\mu\text{-}O)_2$ is shown for comparison in Figure 3c. In comparison to $(EDTA)_2Tc_2(\mu\text{-}O)_2$, the soluble radiolysis product has a longer Tc-Tc distance of 2.58 Å. The spectra of the soluble radiolysis product are consistent with a molecule having the same $Tc_2(\mu\text{-}O)_2$ core as $(EDTA)_2Tc_2(\mu\text{-}O)_2$, but having different ligands. Since Tc(V) complexes with diolate ligands are stable in strongly alkaline solution,[7] it is possible that the soluble radiolysis products are $(diol)_4Tc_2(\mu\text{-}O)_2$, where diol is $^-OCH_2CH_2O^-$ (ethylene glycol), $(^-O)_2CHCO_2^-$ (glyoxylate), or $(^-O)_2CH_2$ (formaldehyde).

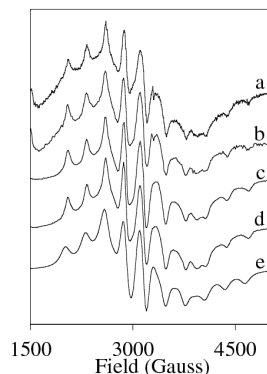**Figure 3.** EPR spectra of a) $TcO_2 \cdot xH_2O$, b-d) Insoluble products of radiolysis in citrate, ethanol, and EDTA, respectively, d) simulated spectrum.
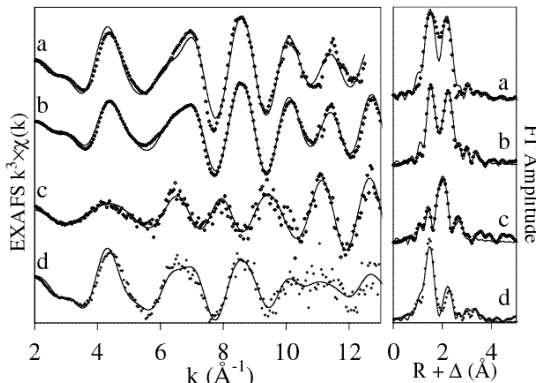
Figure 4. EXAFS spectra (left) and Fourier transforms (right) of a) Insoluble product of radiolysis of TcO_4^- in 2M NaOH and 0.3M EDTA, b) $TcO_2 \cdot xH_2O$, c) $(EDTA)_2Tc_2(\mu\text{-}O)_2$, c) soluble product of radiolysis of TcO_4^- in 2M NaOH and 0.1M glyoxylate.

Immobilization of technetium. Initial studies with technetium have focused on the use of hydrophobic supports, particularly commercially available functionalized polystyrene. Adapting literature chemistry, both amine ($-NH_2$) and isocyanato ($-NCO$) functionalized resins were generated. These resins were found to bind and remove heptavalent technetium complexes ($MeTcO_3$ and Me_3SiTcO_3) readily from nonaqueous media. EXAFS and IR spectral data suggest that while comparable rhenium complexes can undergo reduction upon contacting with the support, technetium is bound as Tc(VII). Leaching experiments were performed in both acidic and basic media (with coadditives to promote swelling of the polymers to minimize phase effects). Minimal leaching into aqueous solution was noted; somewhat higher levels of leaching were observed using organic solvents.

Future Work

Solutions containing the soluble radiolysis product will be examined using EXAFS and Raman techniques. Furthermore, we will attempt to crystallographically characterize either the Tc(IV) or Re(IV) complexes. Radiolysis of TcO_4^- in 2M NaOH with added ethanol, nitrate and nitrite will be investigated, and the rate law for radiolysis of TcO_4^- in 2M NaOH with added organics, nitrate and nitrite will be refined. Further studies on technetium immobilization will examine the use of functionalized, water-soluble polymers for binding pertechnetate in aqueous media.

References

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