Photoreduction of ^{99}Tc pertechnetate by nanometer-sized metal oxides: new strategies for formation and sequestration of low-valent technetium

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ABSTRACT

Technetium-99 (^{99}Tc) (β_{max} : 293.7 keV; $t_{1/2}$: 2.1×10^5 years) is a byproduct of uranium-235 fission and comprises a large component of radioactive waste. Under aerobic conditions and in a neutral- basic environment, the pertechnetate anion (TcO_4^-) is stable. TcO_4^- is very soluble, migrates easily through the environment and does not sorb well onto mineral surfaces, soils or sediments. This study moves

forward a new strategy for the reduction of TcO_4^- and chemical incorporation of the reduced Tc into a metal oxide material. This strategy employs a single material, a polyoxometalate (POM), $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$, that can be photoactivated in the presence of 2-propanol to transfer electrons to TcO_4^- , and incorporate the reduced Tc covalently into the $\alpha_2\text{-}$ framework to form the $\text{Tc}^{\text{V}}\text{O}$ species, $\text{Tc}^{\text{V}}\text{O}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})^{7-}$. This occurs via the formation of an intermediate species that slowly converts to $\text{Tc}^{\text{V}}\text{O}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})^{7-}$. EXAFS and XANES analysis and preliminary EPR analysis, suggests that the intermediate consists of a $\text{Tc(IV)} \alpha_2\text{-}$ species where the Tc is likely bound to only 2 of the 4 W-O oxygen atoms in the $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ defect. This intermediate then oxidizes and converts to the $\text{Tc}^{\text{V}}\text{O}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})^{7-}$ product. The reduction and incorporation of TcO_4^- was accomplished in a “one pot” reaction using both sunlight and UV irradiation, and monitored as a function of time using multinuclear NMR and radio TLC. The process was further probed by the “step-wise” generation of reduced $\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}^{12-}$ through bulk electrolysis followed by the addition of TcO_4^- . The reduction and incorporation of ReO_4^- , as a non-radioactive surrogate for ^{99}Tc , does not proceed through the intermediate species, and $\text{Re}^{\text{V}}\text{O}$ is incorporated quickly into the $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ defect. These observations are consistent with the periodic trends of Tc and Re. Specifically, Tc is more easily reduced compared to Re. In addition to serving as models for metal oxides, POMs may also provide a suitable platform to study the molecular level dynamics and mechanisms of the reduction and incorporation of Tc into a material.

INTRODUCTION

Technetium-99 (^{99}Tc) comprises a large component of radioactive waste found in waste tanks at Hanford and Savannah River as well as water and soil samples around national laboratory sites in the United States. The chemistry of Tc suggests that under aerobic conditions and in a basic environment, the stable heptavalent pertechnetate anion (TcO_4^-) predominantly exists. This oxyanion is the most thermodynamically stable form of technetium at high pH.¹ It is very soluble, migrates easily through the

environment and does not sorb well onto mineral surfaces, soils or sediments.¹⁻¹⁰ The long half-life of Tc (2.1×10^5 years) and the high environmental mobility of the pertechnetate anion create a particular concern when trying to develop waste remediation strategies.

One of the most commonly considered potential strategies for ^{99}Tc remediation is focused on pertechnetate reduction. The mobile pertechnetate ion can be removed from solution by reduction to insoluble, low-valent Tc^{IV} species (such as $^{99}\text{TcO}_2 \cdot n\text{H}_2\text{O}$), which can then be physically adsorbed to a solid surface, or mixed within glass, cement or ceramic. It has been shown that physical mixing of TcO_2 with these materials ultimately results in oxidation of the Tc^{IV} to $\text{Tc}^{\text{VII}}\text{O}_4^-$.¹¹

Bioimmobilization efforts have also been employed in the efforts to reduce and stabilize TcO_4^- in soil by natural organic matter.^{8,12} In these studies chemical reduction^{7,13} and microbial reduction^{5,14} led to the formation of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. However, the reduced $^{99}\text{Tc}^{\text{IV}}$ in the form of the amorphous oxides also reoxidizes back to the mobile $\text{Tc}^{\text{VII}}\text{O}_4^-$ anion.⁶

Taking a cue from radiopharmaceutical chemistry, that employs the tracer isotope of technetium, $^{99\text{m}}\text{Tc}$, may provide a new strategy for reduction of pertechnetate and covalent chemical incorporation of the reduced Tc into a material. In typical radiopharmaceutical “kits”, $^{99\text{m}}\text{Tc}$, as pertechnetate, $^{99\text{m}}\text{TcO}_4^-$, is reduced by stannous ion in the presence of coordinating ligands, and the low valent $^{99\text{m}}\text{Tc}$ covalently bonds to the ligands forming a $^{99\text{m}}\text{Tc}$ coordination complex.

In fact, this approach has been presented in a preliminary communication describing the reduction of $^{99}\text{TcO}_4^-$ and incorporation into a stannous phosphate material.¹⁵ A similar study employed amorphous FeS for reduction of TcO_4^- and binding of the reduced Tc to the Fe-S material as probed by XANES, EXAFS, FT-IR, and energy dispersive X-ray spectroscopy (EDS). The TcO_4^- -FeS reductive immobilization reaction product was found to be predominantly TcO_2 .⁴

Herein we move this approach forward taking advantage of the chemistry of the element. We identify a metal oxide system that can serve as both a reducing agent for the reduction of $^{99}\text{TcO}_4^-$ as well as a host that binds covalently to the reduced ^{99}Tc species. This new strategy employs a single material, a polyoxometalate (POM) both as the reducing agent and coordinating ligand. Moreover, we can

identify the final reduced ^{99}Tc product on the molecular level and we can begin to understand the mechanism of the process.

Polyoxometalates are polyanionic aggregates of early transition metals (Mo^{VI} and W^{VI}) and are strong, tunable electron donors to substrates.¹⁶⁻²² POMs undergo stepwise, multi-electron redox reactions while maintaining their structural integrity. They can be reversibly reduced through a variety of methods including photochemical reduction²²⁻³², reduction by γ radiolysis³³ in the presence of a sacrificial organic electron donor, electrochemical reduction and chemical reduction using appropriate reducing agents.³⁴

Due to their multi-electron redox properties, reduced POMs, especially Keggin ions, have been used for the reduction of metal ions such as Ag^+ , Pd^{2+} , Au^{III} , Pt^{IV} , Cu^{2+} in aqueous systems to lower oxidation states or to their metallic state.^{17-20,25,26,35-37} The tunable redox nature and facile electron transfer properties of POMs render them suitable materials for the synthesis of colloidal metal nanoparticles that are stabilized by the re-oxidized POMs.^{19,37-39}

While most of the published POM photocatalysis studies employ the “plenary” or parent polyoxometalates (Lindqvist, Keggin, Wells-Dawson), this study focuses on using the “lacunary” or defect Wells-Dawson isomer, $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$. **Figure 1** shows the parent Wells-Dawson ion, $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, and the $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ isomer that is formed by removal of a $\text{W}^{\text{VI}}=\text{O}$ from the “cap” region. This $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ species possesses a site wherein four oxygen atoms can bind to a metal ion such as a reduced Tc, depicted in **Figure 1**.

We hypothesize that the $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ can not only transfer electrons to TcO_4^- , but can also incorporate the reduced Tc covalently into the $\alpha_2\text{-}$ framework to form the $\text{Tc}^{\text{V}}\text{O}$ species, $\text{Tc}^{\text{V}}\text{O}(\alpha_2\text{-}\text{P}_2\text{W}_{17}\text{O}_{61})^{7-}$. We can then compare the $\text{Tc}^{\text{V}}\text{O}(\alpha_2\text{-}\text{P}_2\text{W}_{17}\text{O}_{61})^{7-}$ synthesized via this approach with the chemically synthesized complex that we recently reported.⁴⁰ A general mechanism for this procedure, shown in **Figure 2**, will be addressed in detail in the ensuing sections.

In this study, we also evaluate the reduction of ReO_4^- by photoactivation of $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$. Re is often considered a non-radioactive surrogate for ^{99}Tc . This practice should be used with caution

because the reduction potentials, kinetics and even coordination environments can be different between these 2nd and 3rd row congeners. Performing studies with both ⁹⁹Tc and Re, provides the opportunity to compare the chemistry, speciation and fundamental differences between these two elements⁴⁰⁻⁴² and also allows for a more detailed understanding of the polyoxometalate speciation.

EXPERIMENTAL SECTION

General. ⁹⁹Tc, a weak β^- emitter (⁹⁹Tc: β_{max} : 0.29 MeV; $t_{1/2}$: 2.1×10^5 years) was obtained from Oak Ridge National Laboratory (as NH₄TcO₄). ¹⁸⁸ReO₄⁻ (¹⁸⁸Re: β_{max} : 2.12 MeV; γ : 155 keV (8%); $t_{1/2}$: 16.9 hrs) was eluted from a ¹⁸⁸W-¹⁸⁸Re generator that was obtained from Oak Ridge National Laboratory. All reported ⁹⁹Tc and ¹⁸⁸Re manipulations were performed in an appropriately equipped laboratory approved for the use of low-level radioactivity. Suitable radioactive material handling procedures were employed throughout.

All materials were purchased as reagent grade and used without further purification. Pure water was used throughout, and was obtained using a Millipore Direct Q5 system (conductivity = 18 $\mu\Omega$). Solid ammonium pertechnetate (NH₄TcO₄) was treated with H₂O₂ to oxidize any reduced forms of Tc.⁴³ Standardization of prepared aqueous NH₄TcO₄ solutions were conducted according to an established UV-Vis procedure.^{43,44} Polyoxometalates, K₁₀(α_2 -P₂W₁₇O₆₁) (**α_2**),⁴⁵ K_{7-n}H_n[Tc^VO(α_2 -P₂W₁₇O₆₁)] (**Tc^VO- α_2**)⁴⁰ and K_{7-n}H_n[Re^VO(α_2 -P₂W₁₇O₆₁)] (**Re^VO- α_2**)⁴⁶ were synthesized using literature procedures. All UV-Vis data were collected on a Varian Cary 50 UV-Visible Spectrophotometer at 300 K.

Collection of NMR Data. NMR data were collected on a JEOL GX-400 spectrometer with 5 mm tubes fitted with Teflon inserts that were purchased from Wilmad Glass. The resonance frequency for ³¹P and ⁹⁹Tc are 161.8 and 90.0 MHz respectively on this spectrometer. Chemical shifts are given with respect to external 85% H₃PO₄ for ³¹P and 0.5 M NH₄TcO₄ for ⁹⁹Tc (the more negative chemical shifts denote upfield resonances). Typical acquisition parameters for ³¹P spectra included the following:

spectral width, 10 kHz; acquisition time, 0.8 s; pulse delay, 1 s; pulse width, 15 μ s (50° tip angle). For ^{99}Tc ; spectral width, 9 kHz; acquisition time, 0.9 s; pulse delay 0.5 s; pulse width, 10 μ s (50° tip angle). Typically, between 200 and 2000 scans were acquired for ^{99}Tc and ^{31}P respectively. For all spectra, the temperature was controlled to ± 0.2 deg.

Collection of Electrochemical Data. Electrochemical data were obtained using a BASi Voltammetric Analyzer System controlled by BASi CV-50W software (for PC). The one-compartment cell used for cyclic voltammetry (CV) contained a glassy-carbon working electrode (BASi MF-2012 standard disk electrode, 3 mm OD), a Pt wire auxiliary electrode (0.5 mm) and a Ag/AgCl reference electrode (BASi MF-2052). Prior to obtaining electrochemical data, solutions were de-aerated for at least 30 min with high purity Ar. A positive pressure of Ar was maintained during subsequent work. Preparation, including fine polishing of the glassy-carbon working electrode was adapted from the procedure of Keita and co-workers.⁴⁷ Unless indicated otherwise, scan rates were 10 mVs⁻¹, and all experiments were carried out at ambient temperature under an atmosphere of Ar. Electrochemical reduction was achieved using Bulk Electrolysis in a BASi Bulk Electrolysis cell. The working electrode was a reticulated vitreous carbon cage (BASi MF-2077), the auxiliary electrode was a platinum wire separated from the bulk electrolyte solution via a fritted compartment and the reference electrode was Ag/AgCl (BASi MF-2052).

Radio Thin Layer Chromatography (Radio TLC). Radio TLC was performed on a radio TLC Imaging Scanner Bioscan Ar-2000. Quantitation of peaks is automatically performed, providing the percent of total activity for each peak. Chromatography paper (Whatman, 3MM CHR) was cut into 1 cm x 10 cm strips. 3 μ L of sample was spotted onto each TLC strip and developed in a 0.9 % saline solvent system.⁴⁸ Radio TLC monitors the β emission of the ^{99}Tc and both the β and γ emissions of the ^{188}Re . This technique is thus species-specific for ^{99}Tc and ^{188}Re containing compounds. Control experiments were performed to determine that, when eluted with saline, both $^{99}\text{TcO}_4^-$ and $^{188}\text{ReO}_4^-$ move with the

solvent front (Supporting material) and chemically synthesized $\text{K-}^{99}\text{Tc}^{\text{V}}\text{O-}\alpha\mathbf{2}^{40}$ remains at the origin (**Figure S1**).

Stability of $\text{K}_{10}(\alpha\mathbf{2}\text{-P}_2\text{W}_{17}\text{O}_{61})$ ($\alpha\mathbf{2}$) at low pH as a function of concentration. The reduction of TcO_4^- to low-valent states is favored at low pH.^{49,50} While Keggin ions are known to be extremely stable at low pH²¹, the stability of $\alpha\mathbf{2}$ at low pH has not been fully investigated. ³¹P NMR data of the $\alpha\mathbf{2}$ POM dissolved in a 3:1 mixture of 0.5 M H_2SO_4 (pH 0.33): D_2O over time show that the POM stability is concentration dependent. (**Figure S2**) The more concentrated solutions (30 mM) resulted in large amounts of decomposition to the plenary $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ over the period of one week, while lower concentrations (4 mM, 8 mM and 16 mM) showed only minimal amounts of decomposition during this time frame. The latter were thus chosen for the photoreduction experiments. (For photoreduction of TcO_4^- by sunlight, a concentration of 32 mM $\alpha\mathbf{2}$ was also employed and, as expected, decomposition to $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ occurred). A 5 mM concentration of $\alpha\mathbf{2}$ was used for the bulk electrolysis experiments; in addition to minimized decomposition, the low concentration of POM is convenient for the operation of the electrolysis instrumentation.

Preparation of samples for reduction of $^{99}\text{TcO}_4^-$ and ReO_4^- : Three methods were employed to monitor the reduction of MO_4^- (where $\text{M} = ^{99}\text{Tc}$ or Re). For most of the reductions, a stock solution of 0.28 M MO_4^- was used in a 1.2 - 1.4 molar excess. For experiments involving the tracer isotope ^{188}Re ; 500 μL of “cold” stock (0.28 M) ReO_4^- solution was spiked with 1 μL of 9 $\mu\text{Ci}\mu\text{L}^{-1}$ of $^{188}\text{ReO}_4^-$. Reduction solutions were prepared by mixing 0.5 M H_2SO_4 :2-propanol: D_2O in a 2:1:1 volume ratio. Reduction solutions containing electrolyte were prepared by mixing 0.5 M H_2SO_4 (containing 0.5 M Na_2SO_4):2-propanol: D_2O in a 2:1:1 volume ratio.

Method 1: *In situ* reduction by UV irradiation. Three different solutions were prepared by dissolving 50, 100 and 200 mg of $\alpha\mathbf{2}$ (0.01, 0.02 and 0.04 mmol respectively) in 2.5 mL of reduction

solution (with and without electrolyte) and mixed thoroughly. This resulted in 4, 8 and 16 mM POM solutions respectively. Each solution was placed in a quartz luminescence cuvette. Standardized MO_4^- (0.28 M) was added in a slight molar excess (50 μL for 50 mg of POM, 90 μL for 100 mg, 170 μL for 200 mg). The cuvettes were then sealed with a rubber septum and the solutions purged with N_2 for 30 min before irradiation with a UV lamp at 254 nm (power @ 5 cm from source = 17.9 @ 200 μW) for 16 hrs and up to 24 hrs. After the irradiation periods, the colorless solutions changed to either light or dark red-brown in the case of Tc, or to a light or dark purple color in the case of Re. Each experiment was conducted using $^{99}\text{TcO}_4^-$, non-radioactive (“cold”) ReO_4^- , and non-radioactive ReO_4^- spiked with (“hot”) $^{188}\text{ReO}_4^-$. The samples were characterized with ^{31}P NMR, ^{99}Tc NMR, in some cases, UV-Vis and radio TLC paper chromatography where applicable.⁴⁸

In these experiments 2-propanol was chosen as the sacrificial electron donor because it is known to be an effective photoreducing agent (through formation of a $(\text{CH}_3)_2\text{COH}$ hydroxyalkyl radical that can be easily oxidized to acetone)⁵¹ and has been used extensively to aid in the reduction of $(\text{PW}_{12}\text{O}_{40})^{3-}$, $(\text{SiW}_{12}\text{O}_{40})^{4-}$ and $(\text{P}_2\text{Mo}_{18}\text{O}_{62})^{6-}$.^{17-19,23,25,26}

To test a 1:1 $\alpha 2$: TcO_4^- stoichiometry, the $\alpha 2$ (57.9 mg, 11.6 μmol) was dissolved in 2.5 mL of reduction solution (with and without electrolyte) and mixed thoroughly. This resulted in a 4 mM POM solution. The solution was processed as described above and irradiated. After the irradiation, the colorless solutions changed to a light green/red after 19 hrs and a more intense red after 24 hrs. For the 19 hrs irradiation, ^{31}P NMR was taken immediately after irradiation was ceased and at timed intervals after irradiation was ceased. KCl (500 μL of a saturated solution) was added to the reaction solution directly through the septum via a syringe and the sample placed in the refrigerator overnight. The crystalline solid that formed (57 mg) was isolated by filtration. The solid was consequentially used for EPR studies, ^{31}P NMR and RadioTLC.

Method 2: Electrochemically reduced $\text{K}_{10}(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})$ ($\alpha 2$). 500 mg (0.1 mmol) of $\alpha 2$ was dissolved in a 0.5 M H_2SO_4 (containing 0.5 M Na_2SO_4): D_2O mixture (1:1 vol, 20 mL), resulting in a 5

mM **a2** solution. This solution was placed in an electrolysis cell and purged with argon for 30 min. A potential of -220 mV was applied via the working electrode to reduce the POM by 2 electrons. Upon applying the potential, the clear colorless solution immediately became deep blue. A slight excess of nitrogen-purged 0.28 M MO_4^- ($\text{M} = {}^{99}\text{Tc}$, Re) solution (500 μL , 1.4 eq) was quickly added to the solution of electrochemically reduced **a2** and a slow color change from dark blue to dark brown-red was observed in the case of Tc, and from dark blue to dark purple in the case of Re. Each experiment was conducted using Tc and “cold” Re. The reduction of MO_4^- was monitored via ${}^{31}\text{P}$ NMR and radio TLC in the case of Tc.

Method 3: *In situ* reduction by sunlight. Four different solutions were prepared by dissolving 50, 100, 200 and 400 mg of **a2** (0.01, 0.02, 0.04 and 0.08 mmol respectively) in a 2.5 mL mixture of reduction solution and mixed thoroughly. This resulted in 4, 8, 16 and 32 mM POM solutions respectively. Each solution was placed in a glass vial, whose top incorporated a rubber septum. Standardized TcO_4^- (0.28 M) was added in a slight molar excess (50 μL for 50 mg of POM, 90 μL for 100 mg, 170 μL for 200 mg, 340 μL for 400 mg). The vials were then sealed and the solutions purged with N_2 for 30 min before placing on a windowsill. These samples were exposed to sunlight over a period of 2 months. The solutions were monitored via ${}^{31}\text{P}$ NMR, UV-Vis spectroscopy and radio TLC. The 4 mM solution was also examined by X-ray Absorption Spectroscopy (EXAFS and XANES).

Preparation of UV-Visible Spectroscopy samples. UV-Vis data were collected on samples prepared by methods 1, 2, and 3 above. Samples of different starting concentrations (4 mM-32 mM) were diluted by transferring 10 μL , 5 μL , 2.5 μL and 1.25 μL of each solution, respectively to a quartz cuvette containing 1 mL of the appropriate reduction solution to yield same concentrations. Collected spectra were constricted between 400 - 800 nm to avoid saturation due to the large O-W LMCT band in the 200 – 400 nm region.

Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy: Two samples, a standard of chemically synthesized ${}^{99}\text{Tc}^{\text{V}}\text{O-a2}^{40}$ and a sample generated above by *in situ* reduction using sunlight (4

mM $\alpha 2$), were transferred to 2 mL screw capped, polypropylene centrifuge tubes, which were sealed inside two, nested polyethylene bags. Data were acquired at room temperature in transmission using Ar-filled ion chambers and in fluorescence using a 32 element Ge detector at SSRL beamlines 11-; data were collected using the locally written program XAScollect. Harmonic content of the beam was reduced by detuning the monochromator by 50%. Fluorescence data were corrected for detector deadtime, which was determined by adjusting the deadtime for each channel until the fluorescence XANES spectrum matched the transmission XANES spectrum. The data were processed using EXAFSPAK and Athena/ifeffit. {Newville, 2001 #90; Ravel, 2005 #91} Data were fit using Artemis/ifeffit and theoretical phases and amplitudes calculated using FEFF7. {Rehr, 1992 #92} The initial model used in the FEFF calculation was $(\text{NH}_4)_6(\text{P}_2\text{W}_{18}\text{O}_{62})$ with one W atom replaced by Tc. {D'Amour, 1976 #88} Additional scattering shells were added only if their inclusion lowered the value of reduced chi squared. XANES spectra were fit using the locally written code “fites.”

The F-test was used to analyze the significance of the fitting parameters including the significance of adding a scattering shell. {Bevington, 1992 #87} The null hypothesis is that the additional shell of atoms does not improve the fit. The result of the F-test is the probability, p , that this hypothesis is correct. If $p < 0.05$, the null hypothesis is rejected in favor of the alternative hypothesis that the additional shell significantly improves the fit. {Downward, 2007 #89}

RESULTS AND DISCUSSION

***In-situ* reduction of MO_4^- ($\text{M} = {}^{99}\text{Tc}$, Re) by $\text{K}_{10}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})$ ($\alpha 2$) via UV irradiation**

There is momentum in the scientific community to employ “green” strategies for photocatalytic reduction of organic materials and metal ions to metallic nanoparticles using plenary POMs. ^{17-19,23,25,26,30,35,37,52-59} These plenary POMs can be reduced by multiple electrons while maintaining their structural integrity and act as cathodes to efficiently transfer electrons to the organic material or metal. The re-oxidized plenary ion thus stabilizes the reduced organic material or metal nanoparticle by

electrostatic surface interactions.^{17-19,37-39,57,58} We have found that the plenary Keggin ions (PW₁₂O₄₀)³⁻, (SiW₁₂O₄₀)⁴⁻ and (AlW₁₂O₄₀)⁵⁻ photocatalytically reduce TcO₄⁻ to low valent Tc (Tc^V) and stabilize it.⁶⁰

Here we employ photoactivation of the lacunary **a2** for reduction of TcO₄⁻ and ReO₄⁻, and complexation of the reduced metal into the defect binding site. The **a2** accepts 2 electrons from a sacrificial electron donor and transfers these electrons to TcO₄⁻ for reduction to Tc^V quantitatively in a “one-pot” reaction. Moreover, the re-oxidized **a2** can quantitatively incorporate the generated Tc^V and Re^V covalently into the framework via bonding to the four basic oxygen atoms that comprise the **a2** defect site. This covalent bonding may be stronger compared to stabilization via electrostatic interactions as described for the plenary POMs. This study serves as a prototype to potential “green” strategies that may be used to reduce ⁹⁹TcO₄⁻ in the environment and sequester the reduced ⁹⁹Tc.

Reduction of ⁹⁹TcO₄⁻ and formation of Tc^VO(*a*₂-P₂W₁₇O₆₁)⁷⁻ (Tc^VO-**a2**)

“One-pot” irradiation reactions were examined at concentrations of 4 mM, 8 mM and 16 mM **a2** in the presence of 1.2 molar equivalents of TcO₄⁻ under acidic conditions with and without electrolyte. The slight excess of Tc was important to ensure that ³¹P NMR could monitor the process conveniently. The Tc speciation was monitored by radio TLC (monitoring the β⁻ of ⁹⁹Tc) and ⁹⁹Tc NMR gives an excellent handle for the ⁹⁹TcO₄⁻. The inclusion of 0.5 M Na₂SO₄ as an electrolyte in the UV irradiation experiments was found to expedite the kinetics of the reactions.

While the UV irradiation reactions discussed below were performed as “one pot” reactions for ³¹P NMR and radio TLC data, the reactions can be performed in stages provided that they are relatively air-tight. The step-wise reactions shown in **Figure 3** demonstrate the distinct color and UV-Visible spectral changes. Upon reduction, the **a2** turns blue in color (λ_{max} = ca. 700 nm) due to the mixed valent reduced species. Upon addition of clear, colorless TcO₄⁻ the solution takes on the red-brown (λ_{max} = ca. 540 nm) color of the ⁹⁹Tc^VO-**a2** complex.

The “one-pot” UV irradiation solutions, in the absence of electrolyte, showed a visible color change from clear and colorless to light orange-brown after 16 hrs of irradiation. This is consistent with the reduction of Tc^{VII} and incorporation of Tc^V into the **a2** framework. After 24 hrs, the more intensely

colored orange/brown solutions suggest an increased concentration of $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$. **Figure S3** shows the control experiment wherein TcO_4^- is irradiated in the identical reduction solution but without the POM, demonstrating no change in the UV-Visible spectrum.

The reaction mixtures at all concentrations, 4 mM, 8 mM and 16 mM, were monitored by ^{31}P NMR spectroscopy during irradiation at 16 and 24 hrs (**Figures 4** (4 mM) and **S4** (8 mM, 16 mM)). The irradiation was ceased at 24 hrs and the 8 mM and 16 mM solutions were monitored for a further 72 hrs after the irradiation was stopped (**Figure S4**). **Table 1** and **Table S1** identify the species and the relative integrations for 4 mM concentration and 8 mM and 16 mM concentrations, respectively. The species formed in this series of reactions as well as in those with electrolyte (*vide infra*) are (1) $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ (-11.84 ppm and -13.29 ppm), (2) an “intermediate” that subsequent studies suggest contains ^{99}Tc and phosphorus (-14.50 ppm), (3) unreacted $\alpha\mathbf{2}$ (-8.51 ppm, -12.58 ppm) and (4) the decomposition product, $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (-12.65 ppm). These chemical shifts (except for the Tc/P containing intermediate) have been assigned previously in independent studies where $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ has been chemically synthesized and characterized.⁴⁰

The ^{31}P NMR of the 4 mM $\alpha\mathbf{2}$ reaction (**Figure 4**) is straightforward and exemplifies the reaction speciation: after 16 hrs of irradiation the ^{31}P NMR shows significant amounts of “free” $\alpha\mathbf{2}$ ligand (60% integrated intensity of entire spectrum), modest amounts of $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ (9%), and an appreciable quantity of the Tc/P-containing intermediate (-14.50 ppm, 23%). While complexes of $\alpha\mathbf{2}$ generally require that the 2 inequivalent P atoms show 2 resonances, our subsequent studies on this particular complex suggest that the intermediate contains a paramagnetic center, since only one resonance is observed for the intermediate in this media. This would likely result in broadening of the resonance of the P atom close to the site of substitution of the paramagnetic ion. All ^{31}P NMR integration data reported here are based on 100% of the resonances observed. While comparisons of integration of the ^{31}P NMR spectra cannot give quantitative data, trends in the amounts of intermediate compared to $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ and $\alpha\mathbf{2}$ ligand with irradiation, concentration and time can be determined.

As the reaction progresses the resonances due to the **$\alpha 2$** ligand and the intermediate species decrease, while those for $^{99}\text{Tc}^{\text{V}}\text{O-}\alpha 2$ increase (> 90%) (**Figure 4**). After 24 hrs of irradiation $^{99}\text{Tc}^{\text{V}}\text{O-}\alpha 2$ (> 90%) is formed predominantly, accompanied by trace amounts of the decomposition product, $\alpha\text{-[P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (-12.65 ppm). No Tc/P-containing intermediate is observed after 24 hrs. This ^{31}P NMR speciation study suggests that, during the irradiation **$\alpha 2$** is reduced. The reduced **$\alpha 2$** in turn transfers electrons to TcO_4^- to form $^{99}\text{Tc}^{\text{V}}\text{O-}\alpha 2$ and/or the Tc/P-containing intermediate species which then converts to $^{99}\text{Tc}^{\text{V}}\text{O-}\alpha 2$.

Comparison of the ^{31}P NMR spectra for the 4 mM with 8 mM and 16 mM samples (**Figures 4 and S4, Table 1 and Table S1**) at 16 hrs of irradiation clearly shows the concentration dependence of the Tc/P-containing intermediate compared to the $^{99}\text{Tc}^{\text{V}}\text{O-}\alpha 2$. The intermediate decreases at high concentrations compared to the $^{99}\text{Tc}^{\text{V}}\text{O-}\alpha 2$; little or no intermediate is observed at 16 mM (**Figure S4**). In the 8 mM sample (**Figure S4**), the intermediate is converted to the $^{99}\text{Tc}^{\text{V}}\text{O-}\alpha 2$ during the 72 hrs period of no irradiation. The decomposition product, $\alpha\text{-[P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (-12.65 ppm), is observed in the 8 mM and is more prevalent in the 16 mM sample. These spectra show a very broad resonance at -8.51 ppm (assigned to the **$\alpha 2$** ligand) that is attributed to the $2e^-$ reduced $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ participating in electronic exchange with the oxidized **$\alpha 2$** . This phenomenon has been observed in systems containing high concentrations of $\alpha\text{-[P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ ⁶¹

Irradiation of the solutions, containing 0.5 M Na_2SO_4 , suggest that the electrolyte facilitates the electron transfer reactions (**Figure S5**). At all concentrations an increase in the Tc/P-containing intermediate, compared to solutions that do not contain electrolyte, was observed. Moreover, the intermediate persists in solution (**Figure S5 and Table S2**) and is concentration dependent. At 4 mM, with Na_2SO_4 electrolyte present, the intermediate consists of 3 peaks. This suggests that, in the media containing Na_2SO_4 electrolyte, at least two intermediate species exist. For all concentrations, the intermediate species converts to $^{99}\text{Tc}^{\text{V}}\text{O-}\alpha 2$ during the 72 hrs post irradiation. The decomposition product $\alpha\text{-[P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ is observed for 8 mM and 16 mM concentrations. The amount of $\alpha\text{-[P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ decomposition product formed at higher concentrations is expected from the stability studies described in the supporting material (**Figure S2**).

The combination of the radio TLC and the ^{31}P NMR data shows the progression of the reactions and provides evidence that the intermediate is composed of Tc as well as **$\alpha 2$** polyoxometalate. While the integrated intensities in the ^{31}P NMR are qualitative (in terms of absolute concentrations), the observed trends in the NMR track very well with the radioTLC data. For example, **Figure 5** shows the radio TLC data along with the ^{31}P NMR data for the 4 mM sample. In the TLC experiment, polyoxometalates, $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha 2$ and the Tc/P containing intermediate, remain at the origin and TcO_4^- moves with the solvent front. At 16 hrs, 63% of the activity remains at the origin and 37% of the activity moves with the solvent front. The integrated intensities of the ^{31}P NMR (**Table 1**) shows 81% Tc POM species (33% $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha 2$ + 48% Tc/P containing intermediate). Correcting for the excess TcO_4^- in the experiment, the calculated percentages are 67.5% activity as Tc POM species (that would remain at the origin) and 32.5% activity as TcO_4^- (that would move with the solvent front). In addition to radio TLC and ^{31}P NMR, ^{99}Tc NMR show that the excess Tc remains as TcO_4^- . See supporting material for details. This is further confirmed in the EXAFS/XANES experiments (*vide infra*).

Irradiation of 4mM **$\alpha 2$** in solutions comprised of 1:1 $\alpha 2$: TcO_4^- stoichiometry with 0.5 M Na_2SO_4 electrolyte for 19 hrs resulted exclusively in the intermediate species and **$\alpha 2$** (**Figure 6** and **Table 1**). The three resonances that comprise the intermediate species in the electrolyte solution are quite pronounced at this stoichiometry. The solution was monitored by ^{31}P NMR after irradiation was ceased. As observed for the cases above wherein a slight excess of TcO_4^- was maintained, the intermediate is seen to convert to $\alpha 2$ or $\alpha 2$ converted to product over time.

The addition of KCl, followed by cooling of the solution resulted in a crystalline solid. EPR of that solid, **Figure S6**, shows a signal suggesting that the reduction solution contains a paramagnetic species. While the nature of the intermediate needs to be further evaluated, the X-ray Absorption Spectroscopy (XAS) studies, described below, suggest that the intermediate may be comprised of a partially coordinated Tc(IV) species.

Reduction of ReO_4^- and formation of $\text{Re}^{\text{V}}\text{O}(\alpha 2-\text{P}_2\text{W}_{17}\text{O}_{61})^{7-}$ ($\text{Re}^{\text{V}}\text{O}-\alpha 2$)

Irradiation (at 254 nm) of a solution consisting of **$\alpha 2$** in the reduction solution containing 0.5 M Na₂SO₄ and ReO₄⁻ results in the formation of **Re^VO- $\alpha 2$** . This parallels the previous experiments with ⁹⁹TcO₄⁻. The ³¹P NMR data is presented in **Figure 7** (4mM **$\alpha 2$**) and **Figure S7** (8 mM and 16mM **$\alpha 2$**) and summarized in **Table 1** and **Table S3**. All three concentrations of **$\alpha 2$** were irradiated under the same conditions for 16 hrs. For the lowest concentration, 4 mM, formation of > 99% of the **Re^VO- $\alpha 2$** product is complete after 16 hrs of irradiation. Significant amounts of free **$\alpha 2$** ligand are observed to remain in solution for the 8 and 16 mM samples. This is to be expected as all samples were exposed to the same intensity light source for an equal amount of time.

To monitor the radio TLC, a 4 mM reaction was “spiked” with ¹⁸⁸Re, a radioactive tracer. After irradiation for 16 hrs with 254 nm light, the ³¹P NMR (**Figure S8** supporting material) shows a predominance of the **Re^VO- $\alpha 2$** complex. The speciation, assessed by radio TLC developed in saline (**Figure S8**), shows that 75% of activity remains at the origin (¹⁸⁸Re^VO- **$\alpha 2$**). The 25% excess activity that migrates with the solvent front is due to the excess ¹⁸⁸ReO₄⁻ in the irradiation reaction. This behavior is consistent with the ³¹P NMR showing > 99% **Re^VO- $\alpha 2$** product formation.

The reduction of ReO₄⁻ and incorporation of the reduced Re into the **$\alpha 2$** framework at all concentrations is significantly faster than for the Tc analogs (NMR data for corresponding Tc reactions are shown in **Figures 5** and **S5** and **Table 1** and **Table S2**). Formation of the **Re^VO- $\alpha 2$** complex at 4 mM was complete in 16 hrs while the analogous Tc reaction showed 33% ⁹⁹Tc^VO- **$\alpha 2$** , approximately 48% of the Tc/P-containing intermediate and 19% **$\alpha 2$** ligand at 16 hrs. This observation appears inconsistent with Tc/Re periodic trends where the reduction of rhenium compared to technetium in acidic aqueous solution is consistently more difficult (by ~120 mV) and the kinetics are slower.^{41,42,62,63} However, we observe no formation of an intermediate species in any reactions with Re. It is likely that the mechanisms of the Tc and Re reactions differ.

Reduction of MO₄⁻ (M=⁹⁹Tc, Re) by $\alpha 2$ -[P₂W₁₇O₆₁]¹²⁻ generated by bulk electrolysis

To further probe the reduction and incorporation of $M^V O$ ($M = {}^{99}\text{Tc}, \text{Re}$) into the **$\alpha 2$** framework, we employed bulk electrolysis to completely reduce the **$\alpha 2$** ligand by 2 electrons prior to addition of MO_4^- .

${}^{99}\text{TcO}_4^-$

The reduced $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ was produced by bulk electrolysis by applying a voltage of -220 mV to a 5 mM solution of **$\alpha 2$** dissolved in 1:1 0.5 H_2SO_4 (containing 0.5 M Na_2SO_4): D_2O via the working electrode. The characteristic blue color of reduced POM appeared immediately. Under inert atmosphere, the rest potential of the reduced POM solution remained constant over a period of 30 min, thus ensuring that the $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ remained reduced once the applied potential was removed. Upon addition of degassed TcO_4^- (1.4 eq) to the blue solution, under gentle stirring, the rest potential began to increase to more positive potential and the solution slowly changed from a dark blue to a dark red/brown color.

The rest potential initially increased from -220 to -85 mV over the first 30 s (**Figure S9A**), indicating that the $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ oxidized to **$\alpha 2$** coupled to a reduction of TcO_4^- . The rate of the change slowed down between 30 s and 5 min then increased rapidly to reach another plateau after 21 min. From 21 min up to 48 hrs the rest potential very slowly increased to +393 mV. The sharp jump of +135 mV in the first 30 s and the consequent plateau after 5 min after addition of TcO_4^- supports the hypothesis that $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ is rapidly transferring electrons to TcO_4^- and, the slow rise in rest potential, suggests that a reduced form of Tc is slowly incorporating into the POM framework. ${}^{31}\text{P}$ NMR and radio TLC were used to monitor the course of the reaction.

${}^{31}\text{P}$ NMR data, collected 12 min, 1.5 hrs and 24 hrs post TcO_4^- addition (**Figure 8, Table S4**) show the same speciation as for the photoactivated reduction experiments: free **$\alpha 2$** , the ${}^{99}\text{Tc}^V\text{O-}\alpha 2$ complex, the Tc/P containing intermediate and the plenary $\alpha\text{-[P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ decomposition product. The speciation observed in the ${}^{31}\text{P}$ NMR data correlates with the observed rest potential changes as a function of time.

The combination of ${}^{31}\text{P}$ NMR spectroscopy and rest potential over the course of the reaction, suggests a mechanism wherein the reduction of TcO_4^- is rapid, and initially a Tc/P-containing intermediate is formed. This is indicated by the combination of the initial rise in rest potential (after 30

16

s) and plateau at 5 min and the ^{31}P NMR, after 12 min, showing the formation of the intermediate species. The conversion of that intermediate species to $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha 2$ is consistent with the second increase in the rest potential to a plateau after 21 min. This correlates to the ^{31}P NMR after 1.5 hrs showing a significant increase in the $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha 2$ and a decrease in the Tc-intermediate. The observation of the $\alpha 2$ lacunary in the ^{31}P NMR after 1.5 hrs, coupled with the $> 80\%$ $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha 2$ formation at 24 hrs attest to the slow incorporation of reduced Tc into the $\alpha 2$ lacunary site.

Radio TLC, performed on the reaction solution at the same time points as for the ^{31}P NMR (**Figure 8**) track the ^{31}P NMR data, further suggesting that the intermediate species contains ^{99}Tc and P and is likely a Tc- $\alpha 2$ containing species (see supporting material). The intermediate undergoes a slow conversion to $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha 2$ product.

Figure S10A shows the CV of $\alpha 2$ before and after bulk electrolysis and 48 hrs after the addition of TcO_4^- . It can be seen that after 48 hrs a new redox wave appears c.a. 800 mV. This is attributed to the $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha 2$ species where the Tc^{V} is incorporated into the polyoxometalate framework. The CV is identical to the chemically synthesized $\text{K}-\text{Tc}^{\text{V}}\text{O}-\alpha 2$ complex⁴⁰ (**Figure S10A**). The symmetrical peak at ca. 630 mV is a stripping wave of the TcO_4^- from the working GC electrode. This wave is visible only when scans are made to potentials lower than -550 mV and indicates, as expected, the presence of excess TcO_4^- .

ReO_4^-

The production of reduced $\alpha 2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ (by bulk electrolysis) and subsequent reduction of ReO_4^- was conducted under the same conditions at the Tc experiment. As described below, the two metals behave differently. Upon addition of the degassed ReO_4^- solution to the reduced $\alpha 2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ solution the rest potential increased (**Figure S9B**) and the solution quickly changed from a dark blue to a purple color. The rest potential increased from -220 to -104 mV after 30 s, which indicates that the $\alpha 2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ is being oxidized to $\alpha 2$ in conjunction with the reduction of ReO_4^- . The rate of the change in reduction potential then slows down and plateaus after 60 min at around 26 mV. There is only one

plateau in the rest potential change for the Re experiment compared to the Tc experiment where there were 2 plateaus.

The ^{31}P spectrum of the solution (**Figure 8**), taken 1.5 hrs after the addition of ReO_4^- , shows exclusively $\text{Re}^{\text{V}}\text{O}-\alpha\mathbf{2}$ product; the spectrum is identical to that of chemically synthesized $\text{Re}^{\text{V}}\text{O}-\alpha\mathbf{2}$.⁴⁶ An intermediate species is never observed in the ^{31}P NMR for any of the Re experiments. At the same time point (1.5 hrs), the Tc analog showed 42% $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ product, 11% intermediate and 47% $\alpha\mathbf{2}$. Reduction of ReO_4^- and incorporation of reduced rhenium into the $\alpha\mathbf{2}$ framework is faster than that of Tc and, as no intermediate is observed in the Re reactions, it is likely that the Re reactions occur by a different mechanism than that of Tc. This set of experiments demonstrates a significant difference between technetium and rhenium.

Figure S10B shows the CV of $\alpha\mathbf{2}$ before and after bulk electrolysis and 99 min after the addition of ReO_4^- . It can be seen that after 99 min a new redox wave appears c.a. 260 mV which is due to an incorporated Re species into the polyoxometalate framework. The CV is identical to the chemically synthesized $\text{K-Re}^{\text{V}}\text{O}-\alpha\mathbf{2}$ complex⁴⁰

This experiment supports a rapid reduction of both rhenium (VII) and technetium (VII) as evidenced by the rapid rise in the rest potential upon addition of MO_4^- to the reduced $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{12-}$. After this initial rapid rise in rest potential, Tc and Re differ. The Tc undergoes a slow rise in rest potential to form a plateau after 21 min and then another plateau after approximately 48 hrs. This timing tracks with the observation of the Tc/P intermediate in the NMR and TLC, and the slow conversion of the intermediate into the $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ product. Alternatively, the Re reaches a single final plateau after 60 min tracking with the NMR data that shows complete conversion to the $\text{Re}^{\text{V}}\text{O}-\alpha\mathbf{2}$ product in 1.5 hrs.

Comparison of the two approaches

The interaction of TcO_4^- and ReO_4^- with reduced $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{12-}$, formed by photoactivation/reduction of $\alpha\mathbf{2}$ in the presence of 2-propanol, and with reduced $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{12-}$, that is generated by bulk electrolysis, show identical products according to ^{31}P NMR and consistent kinetic

profiles. For Tc, these products include $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ and the Tc/P-containing intermediate. For Re, the $\text{Re}^{\text{V}}\text{O}-\alpha\mathbf{2}$ product was observed with no intermediate. The kinetic trends are also the same: the Tc reactions were always slower than the Re reactions. This may be due to a rapid reduction of both TcO_4^- and ReO_4^- with a slow incorporation of the Tc/P-containing intermediate to the $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ product and a relatively concerted mechanism for the formation of $\text{Re}^{\text{V}}\text{O}-\alpha\mathbf{2}$. The possibility of ReO_4^- for expansion of the coordination sphere to produce a $\text{ReO}_4^- : \alpha\mathbf{2}$ “complex” may facilitate a concerted incorporation/reduction step in the case of Re.^{62,64,65} Potential mechanisms for both Tc and Re are put forward in **Scheme 1** (detailed discussion later).

The mechanism of the electron transport process from reduced $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ to TcO_4^- likely differs in the two strategies. In the UV irradiation procedure, the $\alpha\mathbf{2}$ ligand is continuously reduced upon irradiation in the presence of 2-propanol and in turn the reduced $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ continuously transfers electrons to TcO_4^- to form the Tc/P containing intermediate or into the $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ product. In contrast, the bulk electrolysis method generates reduced $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ all at once and will reduce a certain amount of TcO_4^- before being consumed.

The UV-Visible spectra for the $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ products formed by the two types of reactions along with the chemically synthesized $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ are compared in **Figure S11**. The d-d band in the spectrum of the chemically synthesized product is identical to that produced by generating $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{12-}$ via electrolysis (500 nm). The spectrum of the $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ product formed by the UV irradiation procedure shows an absorbance at 540 nm. While the ^{31}P NMR data are identical for the $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ products generated by the 3 methods, the UV-irradiated samples consistently show a red shifted absorbance in the visible spectra.

The continued irradiation in an acidic mixture, containing 2-propanol, results in continuous reduction of the $\alpha\mathbf{2}$ and concomitant oxidation of the 2-propanol. This process may result in a subtle but more complex ^{99}Tc speciation pattern than that for the procedure involving bulk electrolysis and that may underlie the UV–Visible spectroscopic differences. EPR and XAS data suggest that the intermediate consists of a Tc(IV) species. (The +4 oxidation state is observed in the electrochemistry of the

chemically synthesized $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ product in a reversible 5/4 couple across a pH range of 0.33 to 7.^{40,66}) Small amounts of paramagnetic $\text{Tc}^{\text{IV}}\text{O}-\alpha\mathbf{2}$ species would contribute to the sensitive visible spectra. Moreover, the degradation products of the 2-propanol or sulfate from the electrolyte may be ligating to the $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ product, also impacting the visible spectra but not necessarily the ^{31}P NMR or radio TLC. We plan to investigate this further in future studies.

Reduction of TcO_4^- using photolytically reduced $\text{K}_{10}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}) (\alpha\mathbf{2})$ in sunlight

The most abundant source of light is sunlight and the photoactivation of $\alpha\mathbf{2}$ for reduction of TcO_4^- and incorporation of the reduced Tc does indeed occur with the sun as the source of irradiation. Although sunlight encompasses a continuum of wavelengths, not all wavelengths are efficient in photoexciting the POM. Moreover, the reduction samples were prepared in glass vials, which absorb much of the high energy irradiation that would otherwise facilitate the reduction of $\alpha\mathbf{2}$. Not surprisingly, the reactions take longer than with a constant, controlled irradiation source.

Solutions of $\alpha\mathbf{2}$ dissolved in the reduction solution and a 1.2 molar excess of TcO_4^- were photolytically reduced using sunlight over a period of 2 months. The concentrations of POM in this experiment ranged from 4 mM to 32 mM. The formation of the dark orange color provided evidence of TcO_4^- reduction. The resulting solutions were monitored by UV-Vis spectroscopy and ^{31}P NMR spectroscopy (**Figure 9**).

The ^{31}P NMR experiment reveals that, as observed for the UV photoactivated experiments, the Tc/P containing intermediate is more abundant at the lower concentrations. As expected, more $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ decomposition product (-12.66 ppm) is formed at the higher concentrations. In addition, the intermediate species appears more prevalent and longer lived when using sunlight for the photoactivation of the POM. Both the 4 mM and 8 mM concentration samples show a λ_{max} at 470 nm with a broad tail at the low energy side. This can be explained by considering the ^{31}P NMR, where the $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ product and the intermediate are both observed. The highest concentration, 32 mM, shows a λ_{max} at 540 nm, identical to the absorbance observed for all of the photoactivated irradiations (**Figure 20**

S11); at this concentration no Tc/P intermediate is observed in the ^{31}P NMR. The concentration of 16 mM shows a broad peak encompassing the two limiting wavelengths.

Clearly, sunlight may not be the most efficient light source for photocatalytic reduction of TcO_4^- mediated by the **$\alpha 2$** POM. However, the above experiments provide proof of principal that this strategy works. Altering the POM to one that absorbs in the visible region⁶⁷, sensitization of the POM using a transition metal⁶⁸ or employing a palette of POMs with a variety of absorbances may lead to a more efficient reduction of TcO_4^- and incorporation of the reduced Tc into the POM framework.

X-ray Absorption Fine Structure Spectroscopy provides information of Tc/P containing intermediate

A solution of 4 mM **$\alpha 2$** dissolved in the reduction solution and a 1.2 molar excess of TcO_4^- that was photolytically reduced using sunlight over a period of 2 months was subjected to EXAFS and XANES spectroscopy at the Tc K-edge. The XANES spectrum of this sample is shown in **Figure S12** along with the XANES spectrum of $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha 2$.⁴⁰ The half height of the absorption edge of intermediate spectrum is ~ 0.7 eV lower in energy than that of $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha 2$, which is surprising in light of the fact that excess TcO_4^- is present in this sample. Therefore, the spectrum of this sample was fit using the spectra of TcO_4^- , $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha 2$ ⁴⁰, and Tc(IV) gluconate (Tc(IV) gluconate is monomeric and has six oxygen neighbors at 2 Å) (see **Figure S13** and **Table S5**).¹ The XANES fit indicates that the sample consists of approximately 25% Tc(VII), 55% Tc(V), and 20% Tc(IV). While the presence of Tc(VII) in the sample is not unexpected (excess TcO_4^- was present and the reaction may not have proceeded to completion), the presence of Tc(IV) is surprising and suggests that either the intermediate is a Tc(IV) species or that multiple intermediates (Tc(IV), Tc(V)) exist. The presence of Tc(IV) also explains the ^{31}P NMR spectrum in that the resonance of the P proximal to Tc(IV) will be significantly shifted due to the local moment of the paramagnetic Tc(IV) center and will also be strongly broadened by fast relaxation of the ^{31}P spin. The preliminary EPR data also are consistent with a Tc(IV) species.

The EXAFS spectrum of the sample is shown in **Figure 10b** along with the EXAFS spectrum of a chemically synthesized, isolated and purified $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}^{40}$, which is shown in **Figure 10a** for comparison. The ^{31}P NMR (**Figure 9a**) shows a significant resonance at -14.3 ppm, assigned to the Tc/P containing intermediate, which persists in solution. Thus, the sample provides a reasonable model for employing EXAFS and XANES to understand the coordination and oxidation state of the intermediate. The fitting parameters are given in **Table 2**.

The EXAFS data reveals that the sample contains both short and long Tc-O bonds as well as an interaction between Tc and W atoms at 3.35 Å. Two Debye-Waller parameters are used for the model; the σ^2 of Tc=O is fixed at 0.002 Å², which is a typical value for a Tc terminal oxo ligand; the rest of the model uses a single Debye-Waller parameter for all shells. The fit of the model to the data is good though not perfect. As shown in **Figure 10b**, the Fourier transform contains two large peaks, which are well fit by the model; however, there are two small peaks between the main peaks that were not modeled (the large peak in the Fourier transform below 1 Å, is an experimental artifact, which is not in the region being modeled and does not affect the fit). Attempts to fit these small peaks using O, S, P, Tc, or W neighbors did not improve the fit.

As is obvious from the Fourier transform in **Figure 10**, the local environment of Tc in the photolytically reduced sample is reminiscent of the chemically synthesized $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$; however significant differences exist between the spectra. First, the amplitude of the EXAFS spectrum of the photolytically reduced sample is significantly smaller than that of chemically synthesized $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$, which is largely due to greater disorder as expected for a sample that consists of a mixture of species. As a result of this disorder, the coordination numbers given in **Table 2**, have low precision. Second, the only W neighbors observed in the EXAFS spectrum of the intermediate are those at 3.35 Å, which is significantly shorter than the shorter Tc-W distance in $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$, 3.42 Å. In addition, the W neighbors at 3.57 Å in $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$ are not observed in the intermediate spectrum. These differences strongly suggest that the Tc-W distance in the intermediate is not due solely to the presence of $^{99}\text{Tc}^{\text{V}}\text{O}-\alpha\mathbf{2}$. In other words, Tc is coordinated by the P_2W_{17} ligand in the intermediate as well as in the product. Unlike

the coordination numbers, the Tc-W distances are precise, even in a mixture of species, and can be used to address the interaction between Tc and P_2W_{17} in the intermediate. The distance, 3.35 Å, between the Tc and W atoms in the intermediate is not consistent with mono-dentate coordination of Tc to a single W atom, which would have a longer bond distance, ~ 4 Å, as well as significant enhancement of the EXAFS signal due to multiple scattering, neither of which is observed. Likewise, this distance is not consistent with Tc coordinated by 4 W atoms of ***α2***, which would produce a spectrum identical to $^{99}\text{Tc}^{\text{V}}\text{O}-\mathbf{\alpha 2}$. The only plausible interaction between ***α2*** and Tc that would result in a 3.35 Å Tc-W distance is a bidentate coordination of Tc by two of the W-O sites of ***α2***. The identities of the other ligands coordinated to Tc cannot be determined except that the atom coordinated to Tc must be O; coordination by either water or sulfate is consistent with the EXAFS spectrum

Discussion of intermediate and mechanism of Tc and Re incorporation

Reduction of TcO_4^- in these experiments to Tc(IV) is consistent with the experimental data, specifically, the EPR data and XAS experiments. First, electrochemical studies of the $^{99}\text{Tc}^{\text{V}}\text{O}-\mathbf{\alpha 2}$ show that the Tc(IV) oxidation state is accessible and reversible.⁴⁰ Second, reduction of TcO_4^- in the presence of poorly complexing ligands results in the $\text{Tc}^{\text{IV}}\text{O}_2 \cdot \text{H}_2\text{O}$ that precipitates out as a black solid. In this situation, however, ***α2*** and the potential ligands in the media likely sequester the Tc(IV) as an ***α2*** complex, wherein two of the W-O of the lacunary site coordinate to the Tc with the remainder of the coordination sphere taken up by other coordinating ligands that stabilize the intermediate complex. The amount of the intermediate complex increases when a stoichiometry of 1:1 ***α2*** : TcO_4^- is employed in irradiation experiments, leading to a method for attempted isolation of the intermediate complex(es) and further study.

The well known periodic comparisons of Tc and Re provide an understanding of the differences in the reduction of MO_4^- ($\text{M} = ^{99}\text{Tc}$ and Re) and complexation of the low valent metal into the ***α2*** framework. The reduction of Tc is more facile than that of Re; therefore, it is not surprising that the TcO_4^- can be reduced to a Tc(IV) intermediate while ReO_4^- is reduced to Re(V) with no intermediate formation. Moreover, the ability of ReO_4^- to expand the Re coordination from 4 to 6 may be operative

in this case.^{62,64,65} Kinetic studies, monitoring polarographic limiting current, conclude that the 1:1 ReO_4^- : citrate complex facilitates reduction to Re(V) .⁶⁵ A close association (or complex) of ReO_4^- with the **$\alpha 2$** in the reduction media may facilitate reduction to Re(V) and fast incorporation into the **$\alpha 2$** vacancy. Such an association of anions may occur via solvent-separated or solvent –shared anion-anion interactins.

CONCLUSION

The contaminant, TcO_4^- , is a mobile oxyanion that is found in the ground water and soils near national laboratory facility sites. Reduction of the Tc(VII) and incorporation into materials to form stable reduced Tc materials would facilitate remediation strategies. Presently, most efforts that have been tested for deployment in the field result in oxidation of the reduced Tc (mostly Tc(IV) in the form of TcO_2) back to TcO_4^- . Herein we introduce one material (the **$\alpha 2$** Wells-Dawson POM) to both reduce the TcO_4^- and incorporate the reduced Tc covalently into the bonds of the material. An advantage of our study is that we can identify the product on the molecular level and thereby address the process of metal reduction and incorporation.

The lacunary **$\alpha 2$** Wells-Dawson polyoxometalate is photoactivated by light and reduced by two electrons donated by a sacrificial electron donor (2-propanol). The reduced $\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}^{12-}$ efficiently transfers electrons to TcO_4^- (and ReO_4^-) and the reduced Tc^{V} (Re^{V}) is incorporated into the re-oxidized **$\alpha 2$** as $^{99}\text{Tc}^{\text{V}}\text{O-}\alpha 2$ (and $\text{Re}^{\text{V}}\text{O-}\alpha 2$). Addition of MO_4^- ($\text{M}=\text{Tc,Re}$) to reduced $\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}^{12-}$, probed by ^{31}P , TLC and observation of rest potential, all as a function of time, show that the reduction of MO_4^- is rapid in both cases, but in the case of Tc, a Tc/P-containing intermediate is formed. This intermediate then slowly converts to the $^{99}\text{Tc}^{\text{V}}\text{O-}\alpha 2$ product. EXAFS and XANES analysis and preliminary EPR analysis, suggest that the intermediate consists of a Tc(IV) oxo species bound to 2 oxygen atoms of the 4 W-O in the **$\alpha 2$** defect. The other coordination sites may be taken up by water or other entities, such as sulfate and/or the decomposition products of the 2-propanol.

The Re does not go through an intermediate and possesses faster kinetics to produce the **Re^VO-*a2*** product. This may be ascribed to the potential of ReO_4^- for expansion of coordination sphere to form a ReO_4^- complex, presumably with the ***a2***. As seen in early studies, such a ReO_4^- complex may facilitate electron transfer to form the **Re^VO-*a2*** complex. This study illustrates the sometimes-significant differences between the chemistry of technetium and rhenium, 2nd and 3rd row congeners.

Reduction of TcO_4^- mediated by photoactivated ***a2*** to form **⁹⁹Tc^VO-*a2*** can also be accomplished in sunlight. While the sunlight reactions are not as efficient as employing a continuous irradiation source, the fact that this process works to form exclusively product is encouraging. Other POMs or other materials with absorbances in the visible region may be more appropriate when using sunlight as a photoactivation source.

This study opens the door for the use of metal oxide materials for reduction of TcO_4^- and incorporation of the reduced Tc covalently into the material. Moreover, polyoxometalates may provide a suitable platform to study the molecular level dynamics and mechanisms of the reduction of TcO_4^- and incorporation of the reduced Tc into a material.

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Figure captions

Figure 1. Polyhedral (top) and ball and stick (bottom) structural representations of the parent plenary Wells-Dawson ion; α -[P₂W₁₈O₆₂]⁶⁻ (left), monovacant lacunary α_2 -[P₂W₁₇O₆₁]¹⁰⁻ (center) and the complex Tc^V/Re^VO(α_2 -P₂W₁₇O₆₁)⁷⁻ (right). Phosphorus atoms are represented in yellow, tungsten atoms are shown in white, oxygen atoms shown in red and technetium is represented in green. Upon removal of (W=O)³⁺ unit from the “cap” region a defect site is formed in the monovacant α_2 -[P₂W₁₇O₆₁]¹⁰⁻ isomer. The four O atoms of the vacancy can bind to Tc and Re ions.

Figure 2. General strategy for photolytic reduction of TcO₄⁻ by α_2 -[P₂W₁₇O₆₁]¹⁰⁻. The α_2 -[P₂W₁₇O₆₁]¹⁰⁻ POM (white polyhedra) is promoted to an excited state by irradiation whereupon the excited POM is reduced by a sacrificial electron donor to the “reduced” α_2 -[P₂W₁₇O₆₁]¹²⁻ (blue polyhedra). The reduced α_2 -[P₂W₁₇O₆₁]¹²⁻ transfers electrons to TcO₄⁻ resulting in reduction to low valent Tc that will be incorporated into the lacunary POM as the Tc^V=O species.

Figure 3. The color changes and UV-Vis absorbances obtained during the photolytic reduction of TcO₄⁻ using α_2 -[P₂W₁₇O₆₁]¹⁰⁻. Upon expose to sunlight in the presence of 2-propanol the clear colorless α_2 -[P₂W₁₇O₆₁]¹⁰⁻ (A, yellow trace) becomes reduced and exhibits the characteristic blue solution (B, blue trace). Upon addition of a clear colorless solution of TcO₄⁻ (C, orange trace) the solution changes color from blue to dark orange (D, red trace). The inset is a 10x magnification of the 400 – 800 nm region.

Figure 4. ³¹P NMR for irradiation of ⁹⁹TcO₄⁻ in the presence of α_2 -[P₂W₁₇O₆₁]¹⁰⁻ and 2-propanol, D₂O and 0.5 M H₂SO₄ (1:1:2 vol.). Concentrations of α_2 -[P₂W₁₇O₆₁]¹⁰⁻ are 4 mM (Table 1 shows chemical shift and integration data).

Figure 5. Radio TLC chromatogram (monitoring β - emission of ⁹⁹Tc) for UV irradiation of ⁹⁹TcO₄⁻ in the presence of α_2 -[P₂W₁₇O₆₁]¹⁰⁻. Tc^VO(α_2 -P₂W₁₇O₆₁)⁷⁻ and Tc/P containing intermediate remain at the origin; ⁹⁹TcO₄⁻ moves with the solvent front. The reduction solvent was a mixture of 2-propanol, D₂O

and 0.5 M H₂SO₄ (containing 0.5 M Na₂SO₄) (1:1:2 vol.). The concentration of α_2 -[P₂W₁₇O₆₁]¹⁰⁻ is 4 mM. Irradiation times are 16 and 24 hrs. Also shown is the time point at 72 hrs after cessation of irradiation. The numbers above the TLC peaks are the relative integrations of the radioactivity. Shown on the left side of figure are the ³¹P NMR spectra for the same samples.

Figure 6. ³¹P NMR for irradiation of ⁹⁹TcO₄⁻ in the presence of α_2 -[P₂W₁₇O₆₁]¹⁰⁻ with 1:1 POM:⁹⁹TcO₄⁻ stoichiometry. The reduction solvent is a mixture of 2-propanol, D₂O and 0.5 M H₂SO₄ containing 0.5 M Na₂SO₄ supporting electrolyte (1:1:2 vol.). The concentration of α_2 -[P₂W₁₇O₆₁]¹⁰⁻ is 4 mM. Irradiation is stopped after 19 hrs (a) and the ³¹P NMR is observed 5hrs (b) 19hrs (c) and 24 hrs (d) after cessation of irradiation.

Figure 7. ³¹P NMR for irradiation of ReO₄⁻ in the presence of 4mM α_2 -[P₂W₁₇O₆₁]¹⁰⁻ at 16 hrs. The solvent was a mixture of 2-propanol, D₂O and 0.5 M H₂SO₄ (containing 0.5 M Na₂SO₄) (1:1:2 vol.). The concentrations 8 mM and 16 mM are shown in **Figure S7**, supporting information.

Figure 8. Comparison of reductions of ⁹⁹TcO₄⁻ and ReO₄⁻ by reduced α_2 -[P₂W₁₇O₆₁]¹²⁻ (produced by bulk electrolysis): The solutions for both experiments consist of 5 mM α_2 -[P₂W₁₇O₆₁]¹⁰⁻ in a 0.5 M H₂SO₄ (containing 0.5 M Na₂SO₄):D₂O mixture (1:1 vol, 20 mL). ³¹P NMR spectra (left, 25⁰C, D₂O) and radio TLC (center) for ⁹⁹Tc at 12 min, 1.5 hrs and 24 hrs after addition of TcO₄⁻ to reduced α_2 -[P₂W₁₇O₆₁]¹²⁻. ³¹P NMR spectrum for Re (right) at 99 min after addition of ReO₄⁻ to reduced α_2 -[P₂W₁₇O₆₁]¹²⁻. Two resonances at -12.20 ppm and -13.20 ppm represent product Re^VO(α_2 -P₂W₁₇O₆₁)⁷⁻ and match the chemically synthesized Re^VO(α_2 -P₂W₁₇O₆₁)⁷⁻. Note at the same time point (1.5 hrs), the Tc sample shows 42% product as well as α_2 -[P₂W₁₇O₆₁]¹⁰⁻ and the Tc/P containing intermediate.

Figure 9. ³¹P NMR (left) and normalized UV-Vis spectra (right) of TcO₄⁻ and α_2 -[P₂W₁₇O₆₁]¹⁰⁻ in 0.5 M H₂SO₄, D₂O and 2-propanol (2:1:1 vol.) following exposure to sunlight for 2 months as a function of concentration. (a) 4 mM (black traces); (b) 8 mM (blue traces); (c) 16 mM (orange traces); (d) 32 mM

(red traces). The minor absorbances between 650 and 800 nm are due to trace amounts of reduced α - $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$.

Figure 10. EXAFS spectrum (left) and Fourier transform (right) of (a) chemically synthesized and purified $\text{Tc}^{\text{V}}\text{O}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})^{7-}$ and (b) a 4 mM sample of $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ containing TcO_4^- , in 0.5 M H_2SO_4 , D_2O and 2-propanol (2:1:1 vol.) following exposure to sunlight for 2 months.

Figures

Figure 1.

Figure 2.

Figure 3.

Figure 4

Figure 5

Figure 6 .

Figure 7

Figure 8

Figure 9

Figure 10

Tables

Table 1. Multinuclear ^{31}P NMR data for irradiation of TcO_4^- and ReO_4^- in the presence of $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ and 2-propanol at concentration of 4 mM $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ at 25°C as a function of time. These samples possess stoichiometry of 1:1.2 $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{10-}$: TcO_4^- or ReO_4^- and 1:1 $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{10-}$: TcO_4^- as indicated on the table. All cases except one, as indicated, contain 0.5M Na_2SO_4 . The ^{31}P NMR spectra corresponding to these samples are shown in **Figures 4, 5 and 6** for Tc and **Figure 7**, for Re. The integrations are reported as % of the entire spectrum.

Time of irradiation at 254 nm	^{31}P NMR (ppm, integrations reported as % of whole spectrum)							
	δ , ppm $\text{M}^{\text{V}}\text{O-}\alpha_2$ ($\text{M} = {}^{99}\text{Tc, Re}$)		δ , ppm α_2 ligand		δ , ppm intermediate		δ , ppm $\text{P}_2\text{W}_{18}\text{O}_{62}$	
	Integral	Integral	Integral	Integral	Integral	Integral	Integral	Integral
4 mM solution (1:1.2 $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{10-}$: TcO_4^- without added Na_2SO_4)								
16 hrs	-11.84, -13.29	9.06	-8.51, -12.58	61.3	-14.50	23.16	-12.70	6.47
24 hrs	-11.79, -13.24	94.07	-12.45	3.19	-	-	-12.68	2.77
4 mM solution (1:1.2 $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{10-}$: TcO_4^- containing Na_2SO_4)								
16 hr	-11.84, -13.29	33.00	-12.58	18.88	-14.50	48.00	-	-
24 hours	-11.79, -13.29	57.11	-	-	-14.45	42.88	-	-
72 hours p.i.	-11.79, -13.29	100	-	-	-	-	-	-
4 mM solution (1:1 $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{10-}$: TcO_4^- containing Na_2SO_4)								
16 hr		0		59		41	-	-
5hr p.i.		8		60		32		
19 hr p.i.		18		57		25		
24 hr p.i.								
4 mM solution (1:1.2 $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{10-}$: ReO_4^- containing Na_2SO_4)								
	δ , ppm $\text{Re}^{\text{V}}\text{O-}\alpha_2$	Integral	δ , ppm α_2 ligand	Integral	δ , ppm intermediate	Integral	δ , ppm $\text{P}_2\text{W}_{18}\text{O}_{62}$	Integral
16hr	-12.21, -13.21	100	-	-	-	-	-	-

Table 2: EXAFS fitting parameters for the Tc/P containing intermediate

Neighbor	# of Neighbors	Distance (Å)	s^2 (Å ²)	$p(F)^b$	Distances in Tc ^V O- α 2
O	1.1(2)	1.728(6)	0.002 ^c	<0.001	1.638(4)
O	4.0(8)	2.01(1)	0.008(2)	<0.001	1.996(4)
W	2.0(9)	3.35(2)	0.008(2) ^d	0.005	3.43(2)
O	6(3)	3.9(2)	0.008(2) ^d	0.038	3.97(2)

a) $S_0^2=1$ (fixed), $DE_0 = 3(3)$ eV.

b) Probability that the improvement to the fit of including this shell is due to random error.

c) Fixed at 0.002.

d) Constrained to equal the Debye-Waller parameter of the second oxygen shell.

Scheme 1. Possible mechanisms for the reduction of MO_4^- ($\text{M} = {}^{99}\text{Tc}$, Re) and incorporation of reduced M into $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$. ^a The Tc containing intermediate is observed in the ${}^{31}\text{P}$ NMR and EPR, XAS experiments suggest that this is a Tc(IV) α_2 - species. ^b While the Re reactions do not show an intermediate, expansion of the ReO_4^- coordination sphere may result in a $\text{ReO}_4^- : \alpha_2$ complex that facilitates reduction. See text for complete descriptions. The designation of “slow” denotes the rate limiting step and does not reflect the speed of the reaction.

${}^{99}\text{Tc}$:

Re:

Table of Contents Figure and Caption

Technetium-99 (^{99}Tc) (β^-_{max} : 293.7 keV; $t_{1/2}$: 2.1×10^5 years), a by-product of uranium-235 fission, is found in the environment as the mobile oxyanion pertechnetate, $^{99}\text{TcO}_4^-$. The nanometer sized soluble metal oxide, $\alpha_2\text{-[P}_2\text{W}_{17}\text{O}_{61}]^{10-}$, can be photoactivated by UV light and sunlight to reduce $^{99}\text{TcO}_4^-$ and incorporate the reduced ^{99}Tc covalently into the metal oxide framework. This strategy provides a prototype for environmental ^{99}Tc remediation as well as a platform to provide molecular level understanding of the reduction and incorporation process.

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