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Behavior of Heptavalent Technetium in Sulfuric Acid under α -Irradiation: Structural Determination of Technetium Sulfate Complexes by X-ray Absorption Spectroscopy and First Principles Calculations

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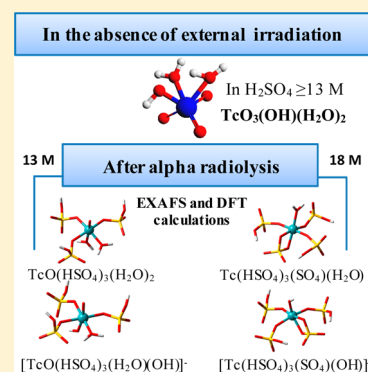
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S Supporting Information

ABSTRACT: The effect of α -radiolysis on the behavior of heptavalent technetium has been investigated in 13 and 18 M H_2SO_4 . Irradiation experiments were performed using α -particles ($^4\text{He}^{2+}$, $E = 68$ MeV) generated by the ARRONAX cyclotron. UV–visible and X-ray absorption fine structure spectroscopic studies indicate that Tc(VII) is reduced to Tc(V) under α -irradiation. Extended X-ray absorption fine structure (EXAFS) spectroscopy measurements are consistent with the presence of mononuclear technetium sulfate complexes. Experimental results and density functional calculations show the formation of $[\text{TcO}(\text{HSO}_4)_3(\text{H}_2\text{O})(\text{OH})]^-$ and/or $[\text{TcO}(\text{HSO}_4)_3(\text{H}_2\text{O})_2]$ and $[\text{Tc}(\text{HSO}_4)_3(\text{SO}_4)(\text{H}_2\text{O})]$ and/or $[\text{Tc}(\text{HSO}_4)_3(\text{SO}_4)(\text{OH})]^-$ for 13 and 18 M H_2SO_4 , respectively.



1. INTRODUCTION

The isotope ^{99}Tc ($T_{1/2} = 2.11 \times 10^5$ y) is an important fission product of the nuclear industry. In the spent fuel, technetium is present in the elemental form. In the context of spent fuel reprocessing (PUREX process), the spent fuel is dissolved in nitric acid and metallic technetium is oxidized to Tc(VII) and extracted in an organic phase. In acidic media, studying the behavior of Tc(VII) under radiation is relevant to the separation process. Although many studies have been performed under γ -irradiation, the effect of α -irradiation on the behavior of Tc species in acidic media has been less studied.¹ Previous studies investigated the effect of γ -radiolysis on the speciation of Tc in hydrochloric and sulfuric acids.^{2,3} In dilute sulfuric acid, it was shown that Tc(IV) colloids were formed under irradiation by X-rays of pertechnetate solutions.^{4,5} Under α -irradiation, the formation of colloidal species has never been reported. Even though α -radiolysis of dilute sulfuric acid solutions was studied,^{6,7} no data have been reported at high concentration of H_2SO_4 . The only radiolysis experiments in concentrated H_2SO_4 under external irradiation have been conducted in the astrochemistry field with a protons

beam to understand the atmospheric chemistry on the surface of a satellite of Jupiter (Europa).^{8,9} In previous studies, we investigated the speciation of technetium in HClO_4 , H_2SO_4 , and HNO_3 . We have shown that above 6 M H_2SO_4 and 7 M HClO_4 , the speciation of Tc(VII) is dominated by pertechnetetic acid ($\text{TcO}_3(\text{H}_2\text{O})_2(\text{OH})$) but by pertechnetate anion (TcO_4^-) in HNO_3 .

In the current work, we investigate the behavior of pertechnetetic acid in H_2SO_4 under α -irradiation ($^4\text{He}^{2+}$, $E = 68$ MeV). The speciation of technetium has been performed by UV–visible and XAFS spectroscopy, and the structure of the complexes analyzed using density functional theory (DFT) calculations. The radiolysis products of sulfuric acid have been analyzed to understand the radiolysis mechanisms.

Received: May 21, 2013

Revised: January 13, 2014

Published: January 14, 2014

2. EXPERIMENTAL AND THEORETICAL SECTION

Caution! Technetium-99 is a weak β emitter ($T_{1/2} = 2.11 \times 10^5$ y, $E_{\max} = 292$ keV). All manipulations were performed in radiochemistry laboratories designed for chemical synthesis with radionuclides using efficient HEPA-filtered fume hoods and following locally approved radioisotope handling and monitoring procedures. The solution of ammonium pertechnetate in water (0.118 M) was obtained from LEA-CERCA laboratory. All chemicals are of analytical reagent grade and were used without further purification. H_2SO_4 (95%) was provided from Merck Millipore. The TiOSO_4 powder and H_2O_2 (30% W/W) were purchased from Sigma-Aldrich.

2.1. Radiolysis Experiments. Radiolysis experiments were performed at the ARRONAX cyclotron facility (Saint-Herblain, France). The cyclotron can deliver α -particles with energy up to 68 MeV. To check that the current was constant during irradiations, the intensity of the particles beams were measured on an internal Faraday chamber located one meter upstream; the current of the beam output was recorded via a metal block connected to a current measuring device. The intensity of the beam deposited into the radiolysis cell was maintained in the range 60–70 nA.

Solutions were irradiated in quartz cells (Figure 1) conceived to be resistant to radiations and to concentrated acids. Each cell

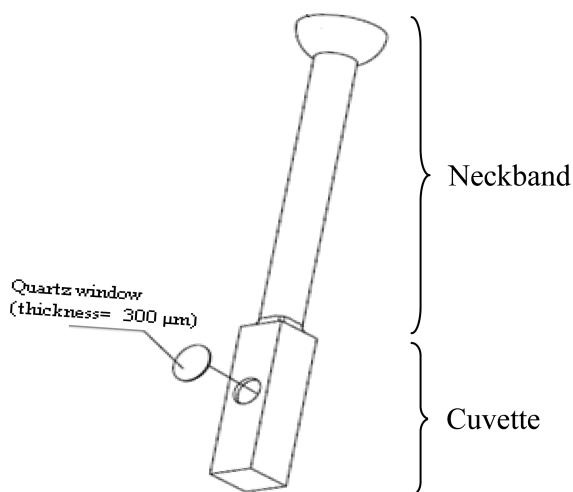


Figure 1. Quartz cell for radiolysis experiments.

consist of two compartments: the bottom compartment is a quartz cuvette (4 mL) with a quartz window (thickness = 300 μm). The top compartment is made by a neckband (10 mL) designed to facilitate the gas measurements. The solution was stirred with a magnetic stir bar and the irradiated volume was 4 mL.

The dose rate was measured using chemical Fricke dosimetry^{10,11} ($G(\text{Fe}^{3+}) = 11.7 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$).¹² The doses rates during radiolysis experiments were 6.64 ± 0.66 and $5.61 \pm 0.56 \text{ kGy} \cdot \text{min}^{-1}$.

After irradiation, UV–visible spectroscopy measurements were performed on a CARY 4000 (VARIAN) double-beam spectrophotometer.

2.2. X-ray Absorption Fine Structure spectroscopy. X-ray absorption fine structure spectroscopy (XAFS) measurements were performed on the MARS beamline at the SOLEIL synchrotron.¹³ The synchrotron ring was operated at 2.75 GeV with an average intensity of 430 mA. Measurements were

performed at the Tc–K edge (21 044 eV) using Si(220) double crystal horizontal focusing monochromator. The spectra were recorded at room temperature in fluorescence mode with a high-purity Ge multielement solid state detector using specifically adapted cells for liquids. The beam energy was calibrated by a molybdenum foil. EXAFS were recorded within the range 21 000–21 094 eV with variable energy steps depending on the scan region (5 eV at the pre-edge; 1 eV at the edge, increasing energy steps after the edge; k steps equal 0.05 \AA^{-1}).

X-ray absorption spectra were analyzed using the ATHENA/ARTEMIS softwares.¹⁴ The data were normalized and EXAFS spectra were extracted using standard procedures. The Fourier transforms (FT) were performed in the k range 2.5–13 \AA^{-1} and peaks of interest were Fourier-filtered between 1 and 3.5 \AA . The k^2 -weighed EXAFS data were fitted in R space using the scattering calculated by FEFF in the theoretical species $[\text{TcO}(\text{SO}_4)_3]^-$ and $[\text{TcO}(\text{SO}_4)(\text{HSO}_4)_2]$.

2.3. Gas Measurements. Hydrogen gas produced by α -radiolysis was measured using a μ -gas chromatograph (490-GC model from VARIAN). The gas was injected through a Swagelok connection. High purity argon was used as a gas carrier. The capillary column consists of molecular sieve A (plot column stationary phase, molecular sieve; column length, 4 m; diameter, 0.25 mm). The calibration curve of the detector was obtained by measuring argon/hydrogen mixtures at different ratios (1–500 ppm). Partial pressures are measured with a precision of 10%.

2.4. Hydrogen Peroxide Measurements. Hydrogen peroxide was determined by a colorimetric method using titanium sulfate. H_2O_2 reacts with TiOSO_4 to give a yellow peroxy complex that has a characteristic UV–visible band at 410 nm ($\epsilon = 700 \text{ M}^{-1} \cdot \text{cm}^{-1}$) (Figure S1.2, Supporting Information).¹⁵ To accurately determine the amount of H_2O_2 produced by water radiolysis, diluted standard solutions of H_2O_2 were freshly prepared and measured prior the radiolysis experiment. The calibration curve was obtained by plotting the concentrations of standards versus the absorbances of blank solutions (Figure S1.1, Supporting Information).

2.5. Computational Method. All structures were optimized using the density functional theory (DFT) approach as implemented in the Gaussian09 package.¹⁶ Calculations were performed using the hybrid B3LYP functional.¹⁷ As already used in a previous work,¹⁸ the Dunning–Huzinaga valence double- ξ basis set (D95 V)¹⁹ was used for H and O atoms, the 6-31++G** for S atoms, and the Stuttgart/Dresden effective core potentials²⁰ (SDD ECPs) for the Tc metal atom. To take into account part of the solvent effect, solvation was introduced using a dielectric continuum model of permittivity (H_2O) $\epsilon_0 = 80$. The dielectric constant of concentrated sulfuric acid is 101 at 25 $^\circ\text{C}$. The conductor-like polarizable continuum model (CPCM²¹) implemented in Gaussian09 was used.

3. RESULTS AND DISCUSSION

3.1. Radiolysis of Sulfuric Acid. To better understand the behavior of technetium in sulfuric acid under α -irradiation, the radiolysis of 13 and 18 M H_2SO_4 solution has been initially studied in the absence of technetium. The radiolytic formation of SO_2 , H_2 , and H_2O_2 was investigated by UV–visible spectroscopy and μ -gas chromatography.

3.1.1. Hydrogen Gas Measurements. The radiolytic production of hydrogen gas is a complex process; its formation depends on many parameters such as the electrolyte nature and

the acidity.^{22,23} In 13 and 18 M H₂SO₄, the quantity of H₂ was measured by μ -GC at different absorbed doses. The radiolytic yields of H₂ were obtained from curves of produced hydrogen as a function of deposited energy. Results (Table 1 and Figure

Table 1. Radiolytic (α -Radiolysis) Yields of Hydrogen ($G(\text{H}_2)$ in $\text{mol}\cdot\text{J}^{-1}$) in 13 M H₂SO₄, 18 M H₂SO₄, and Water

medium	$G(\text{H}_2)$, $\text{mol}\cdot\text{J}^{-1}$	ref
air saturated H ₂ SO ₄ (13 M)	$(7.62 \pm 0.8) \times 10^{-8}$	this work
air saturated H ₂ SO ₄ (18 M)	$(2 \pm 0.2) \times 10^{-8}$	this work
air saturated water	$(6.43 \pm 0.7) \times 10^{-8}$	23

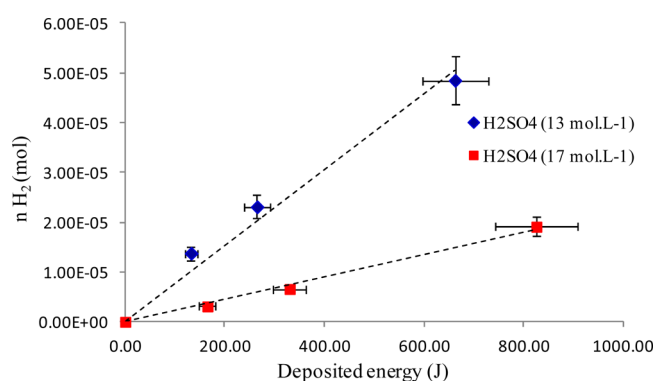
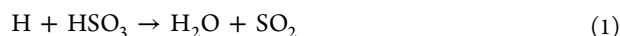


Figure 2. Quantity of H₂ (moles) produced by α -radiolysis of 13 and 18 M H₂SO₄ as a function of the deposited energy (Joules).

2) show the formation of hydrogen in both solutions. In 13 M H₂SO₄, $G(\text{H}_2)$ is slightly higher than the average measured in ultrapure water. This value is consistent with previous studies which shows that $G(\text{H}_2)$ is larger in sulfuric acid than in water.²⁴ When the concentration of sulfuric acid increases, the production of H₂ decreases (Figure 2). This production of H₂ can be correlated to the content of water in concentrated acidic media. The concentration of H₂O in 13 M H₂SO₄ is 9.67 and 2.58 M in 18 M H₂SO₄. The ratio between the [H₂O] in 13 and 18 M H₂SO₄ is 3.75; this value is consistent with H₂ production ratio between 13 and 18 M H₂SO₄ (i.e., 3.81). High acid has low water content which results in low hydrogen production. Moreover, H radicals can also undergo reactions with HSO₃ radicals to form SO₂:⁹



3.1.2. Spectroscopic Evidence for the Radiolytic Formation of SO₂ in 18 M Sulfuric Acid. The evidence of the radiolytic formation of SO₂ in 18 M H₂SO₄ was performed by optical spectroscopy. In the absence of α -irradiation, the spectrum of sulfuric acid does not exhibit absorbance in the range 200–800 nm. After irradiation, the spectrum of sulfuric acid exhibits a band at 278 nm (Figure 3), which is characteristic of SO₂. The UV–visible spectrum of sulfuric acid after irradiation is similar to the one obtained after bubbling SO₂ in 18 M H₂SO₄. These spectra are also similar to the one of S(IV) in 98% sulfuric acid.²⁵ Consequently, SO₂ is generated during α -irradiation of 18 M H₂SO₄. The radiolytic yield of soluble SO₂ produced (i.e., $G(\text{SO}_2)$) under α -irradiation in H₂SO₄ (95%) was determined at $(1.84 \pm 0.18) \times 10^{-7} \text{ mol}\cdot\text{J}^{-1}$. The radiolytic formation of

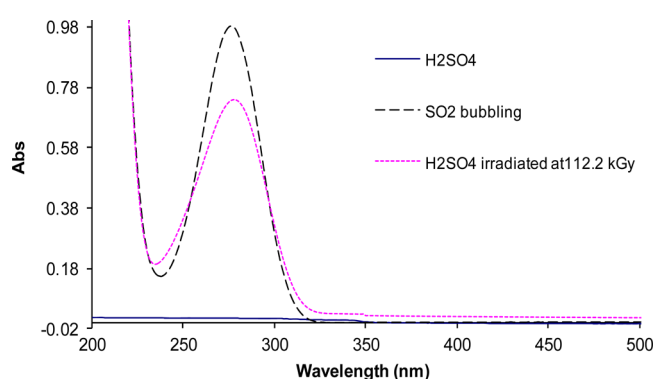


Figure 3. UV–visible spectra of 18 M H₂SO₄ (blue), 18 M H₂SO₄ after α -radiolysis (dashed-pink), and 18 M H₂SO₄ after purging with SO₂ gas (dashed-black).

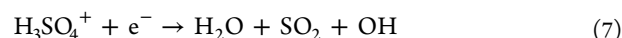
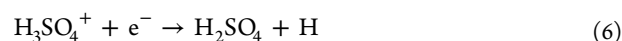
SO₂ under α -radiation can be described according to the following reactions: Excitation and ionization reactions:



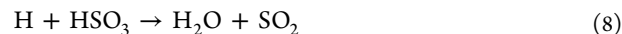
Dissociation of excited H₂SO₄* to H and HSO₄ radicals:



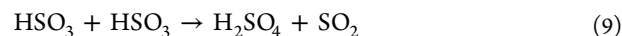
Dissociative electron capture reactions:



Recombination of H and HSO₃ radicals:



Radical disproportionation:



3.1.3. Hydrogen Peroxide Measurements. Hydrogen peroxide is a radiolysis product of water. The concentrations of H₂O₂ produced after irradiations of 13 and 18 M H₂SO₄ have been measured using the titanium method (see experimental section). In 13 M H₂SO₄, the formation of a yellow complex is consistent with the presence of hydrogen peroxide. The amount of H₂O₂ ($1.37 \times 10^{-5} \text{ mol}$) decreases as a function of the dose (Figure 4 and Figure S1.2, Supporting Information). This phenomena is probably due to the fast reaction between H₂O₂ and radiolytic SO₂ according to



26,27

Study performed in 18 M H₂SO₄ indicates the absence of Ti peroxo complexes. This observation is consistent with previous studies who have shown that $G(\text{H}_2\text{O}_2)$ decreases linearly with increasing H₂SO₄.²⁸

3.2. Speciation of Technetium under α -Irradiation.

3.2.1. UV–Visible Spectroscopy. Solutions of heptavalent technetium in 1, 3, 6, 9, 13, 14, 16, and 18 M sulfuric acid were prepared with the TcO₄[−] stock solution. For H₂SO₄ < 9 M, the solutions are colorless whereas a yellow color is observed for H₂SO₄ > 13 M. Previous studies have shown that

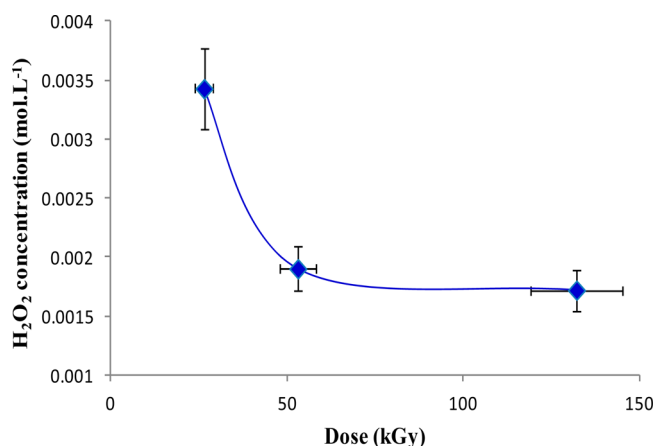


Figure 4. H_2O_2 concentration (M) as a function of the dose (kGy) in 13 M H_2SO_4 .

for $\text{H}_2\text{SO}_4 < 7$ M, Tc(VII) is present as TcO_4^- , whereas pertechnetic acid (i.e., $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$) begins to form in 7 M H_2SO_4 and becomes the predominant species for $\text{H}_2\text{SO}_4 > 13$ M.²⁹ The prepared solutions were placed in radiolysis cells and irradiated by α -particles at the cumulative dose of 132.9 ± 13 kGy. After irradiation, blue-green solutions were obtained in the range 13–16 M H_2SO_4 whereas an intense green color was observed in 18 M H_2SO_4 (Figure S2, Supporting Information). UV–visible spectra (Figure 5, Table 2) of the solution in 13,

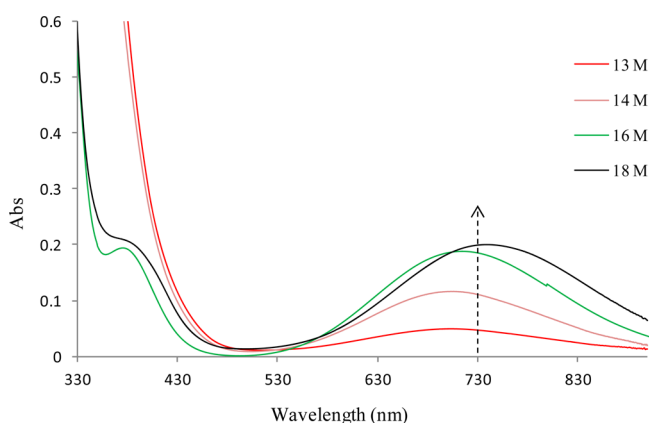


Figure 5. UV–visible spectra after irradiation of Tc(VII) solutions in 13, 14, 16, and 18 M H_2SO_4 (132.9 ± 13 kGy). $[\text{Tc(VII)}] = 5.9 \times 10^{-3}$ M.

Table 2. Position of the Absorption Band (nm) after α -Irradiation (132.9 ± 13 kGy) of Tc(VII) in 13, 14, 16, and 18 M H_2SO_4 , $[\text{Tc(VII)}] = 5.9 \times 10^{-3}$ M

$[\text{H}_2\text{SO}_4]$ (M)	wavelength (nm)
13 (sample 1)	703
14	714
16	726
18 (sample 2)	739

14, 16, and 18 M exhibit an absorption band in the range 600–800 nm. Spectrophotometric measurements show that the position of this band is shifted to larger values as a function of H_2SO_4 concentration. Therefore, the reactivity of Tc(VII) under α -irradiation depends on the acid concentration.

For $\text{H}_2\text{SO}_4 < 9$ M, the solutions remained colorless and no bands were observed in the region 600–800 nm (Figure S3, Supporting Information). These results indicate that Tc(VII) is stable under α -radiation for $\text{H}_2\text{SO}_4 < 9$ M.

In 13 M H_2SO_4 , the spectrum after radiolysis is similar to the one of $\text{TcO}(\text{HSO}_4)_2(\text{OH})(\text{H}_2\text{O})$ obtained from the chemical reduction of HTcO_4 with methanol in 13 M H_2SO_4 .¹⁸ This indicates that in 13 M H_2SO_4 , Tc(VII) is unstable under α -radiation and is reduced to Tc(V) .

In 18 M H_2SO_4 , a shift of the band from 703 to 739 nm is observed. Similarly to 13 M H_2SO_4 , it is expected that reduced Tc complexes are present for $\text{H}_2\text{SO}_4 > 13$ M. The nature of these complexes will be investigated by XAFS spectroscopy and permanganate titration.

3.2.2. XANES Spectroscopy. The XANES spectra of irradiated Tc(VII) solutions in 13 and 18 M H_2SO_4 have been recorded (Figure 6). The energy position of the absorption edge (Table 3) is consistent with the presence of reduced Tc species.

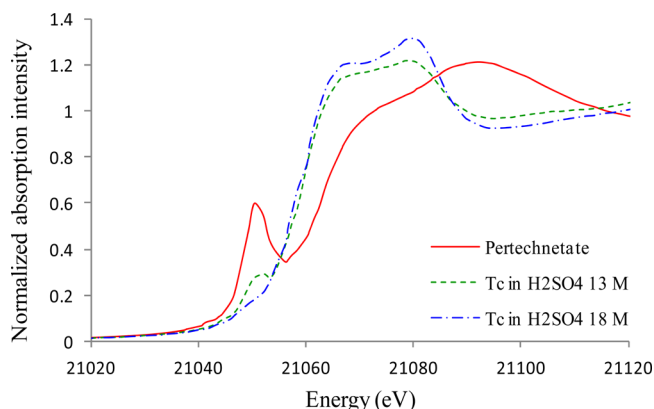


Figure 6. Tc K-edge XANES spectra of NH_4TcO_4 (solid red), after α -irradiation of Tc(VII) (132.9 ± 13 kGy) in 13 M H_2SO_4 (dashed green) and after irradiation of Tc(VII) in 18 M H_2SO_4 , $[\text{Tc(VII)}] = 5.9 \times 10^{-3}$ M.

Table 3. Position of Absorption Edges (eV) of NH_4TcO_4 in H_2O , after Irradiation of Tc(VII) in 13 M H_2SO_4 and after Irradiation of Tc(VII) in 18 M H_2SO_4 , $[\text{Tc(VII)}] = 5.9 \times 10^{-3}$ M

samples	absorption edge (eV)
NH_4TcO_4 in H_2O	21060.7
13 M H_2SO_4	21057.4
18 M H_2SO_4	21056.7

In 13 M H_2SO_4 , the XANES spectrum exhibits a preedge at 21052 eV, which indicates that Tc(VII) is still present in solution after irradiation. Therefore, the solution is probably a mixture of $\text{Tc(V)}/\text{Tc(VII)}$.

In 18 M H_2SO_4 , the XANES spectrum does not exhibit a pre-edge feature, which indicates that Tc(VII) is not present in solution. The position of the absorption edge (21056.7 eV) is slightly higher than the one reported for Tc(V) sulfato complexes (21055 eV).¹⁸ This difference (1.7 eV) is not sufficiently significant to distinguish with accuracy between Tc(V) and Tc(VI) oxidation states. Therefore, the oxidation state of the species in 18 M H_2SO_4 has been determined using manganometric titration. Results are consistent with the

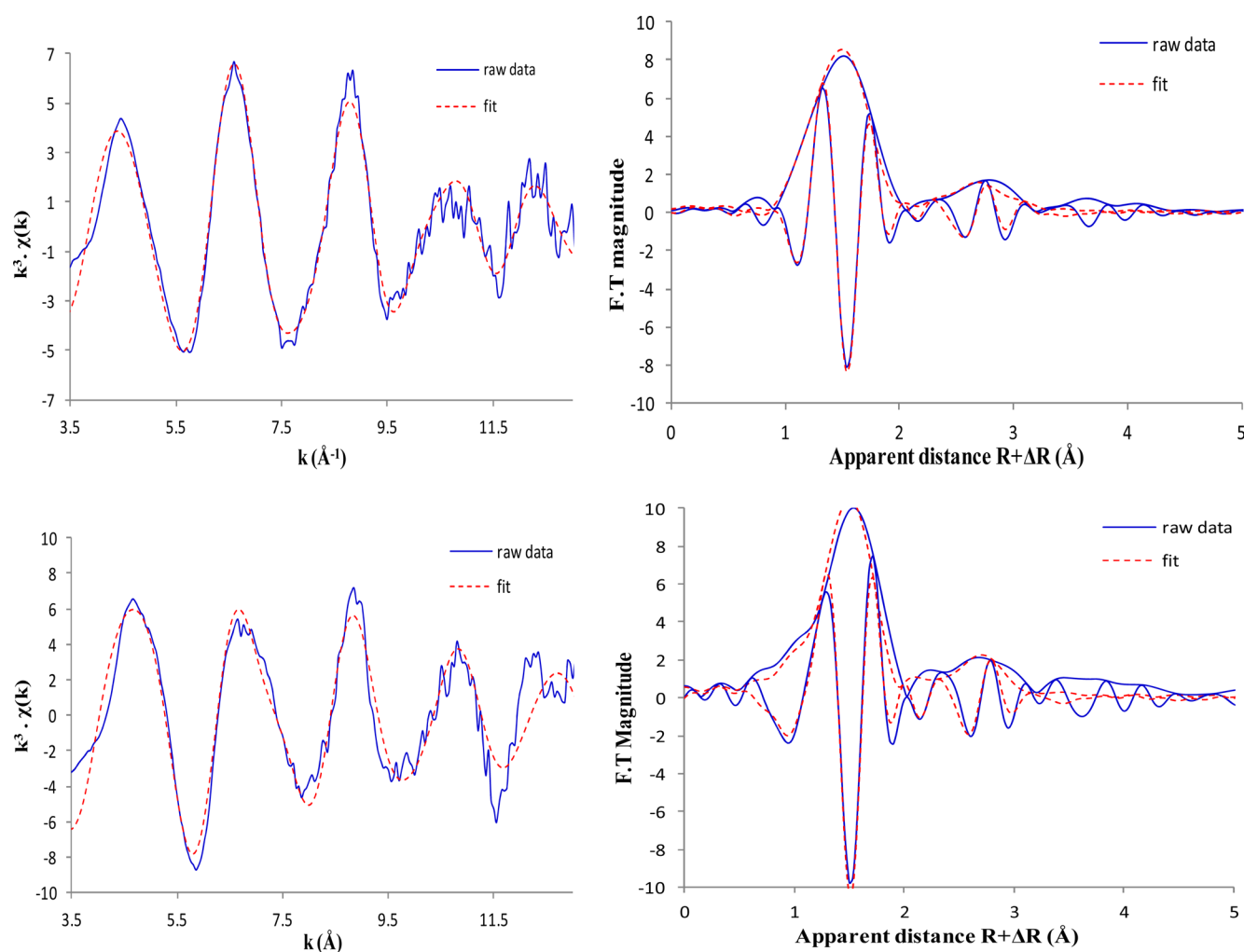


Figure 7. Fitted k^3 -weighted EXAFS spectra (left) and their corresponding Fourier transforms (right) for the products of α -radiolysis of Tc(VII) in 13 M H₂SO₄ (top) and 18 M H₂SO₄ (bottom). Fits are in red, and experimental data are in blue.

presence of Tc(V) after irradiation in 18 M H₂SO₄ (Supporting Information S4).

3.2.3. EXAFS Spectroscopy. The structures of technetium complexes obtained after irradiation of Tc(VII) in 13 and 18 M H₂SO₄ have been studied by EXAFS spectroscopy and DFT calculations. The EXAFS spectra have been k^3 -weighted and their Fourier transform performed in the k range [3.5–13] Å⁻¹ (Figure 7).

For both samples, the Fourier transforms show two resolved peaks. The first peak located at $R + \Delta R \sim 1.5$ – 1.6 Å corresponds to oxygen atoms and suggests the presence of both Tc–O and Tc=O bonds.¹⁸ In 18 M H₂SO₄, this peak is shifted to 1.6 Å, which indicates a higher number of simple coordinated oxygen atoms.³⁰ The second FT peak located at $R + \Delta R \sim 2.5$ Å can be attributed to sulfur atoms of bisulfate anions.¹⁸ The Fourier transforms were fitted using the scattering calculated in the species [TcO(SO₄)₃]⁻ and [TcO(SO₄)(HSO₄)₂].

In 13 M H₂SO₄, the results (Table 4) indicate that the local environment of the Tc absorbing atoms is constituted by 0.6(1) O atom at 1.61(2) Å, 4.6(9) O atoms at 2.02(2) Å, and 3.3(7) S atoms at 3.23(3) Å. Results are consistent with the presence of the [TcO(HSO₄)₃(H₂O)₂] and/or [TcO(HSO₄)₃(H₂O)(OH)]⁻ species.

Table 4. EXAFS Fit Parameters for the Solution Obtained after Reduction of Tc(VII) under α -Irradiation in 13 M H₂SO₄, ΔE_0 (eV) = 8.74 eV, R factor = 0.00036

scattering	CN	distance (Å)	σ^2 (Å ²)
Tc=O	0.6(1)	1.61(2)	0.0022
Tc–O	4.6(9)	2.02(2)	0.0040
Tc–S _{mono}	3.3(7)	3.23(3)	0.0079

In 18 M H₂SO₄, the results (Table 5) indicate that the local environment of the Tc absorbing atoms is constituted by 5.75(11) O atoms at 1.99 Å, 0.6(1) S atom at 2.84(3) Å in monodentate mode, and 3.1(6) S atoms in bidentate mode at 3.26(3) Å. Results are in accordance with the formation of [Tc(HSO₄)₃(SO₄)(H₂O)] and/or [Tc(HSO₄)₃(SO₄)(OH)]⁻.

Table 5. EXAFS Fit Parameters for the Solution Obtained after Reduction of Tc(VII) under α -Irradiation in 18 M H₂SO₄, ΔE_0 (eV) = 9.4 eV, R factor = 0.0012

scattering	CN	distance (Å)	σ^2 (Å ²)
Tc–O	5.7(1)	1.99(2)	0.0040
Tc–S _{bid}	0.6(1)	2.84(3)	0.0077
Tc–S _{mono}	3.1(6)	3.26(3)	0.0083

Theoretical studies were performed to get more information on the nature of the species formed after irradiation of Tc(VII) in sulfuric acid. Density functional theory calculations show the stability of the proposed complexes; the optimized structures are presented in the Figure 8 for 13 M H₂SO₄ and Figure 9 for 18 M H₂SO₄. The structural parameters found by DFT are well in agreement with those found by EXAFS spectroscopy (Table 6).

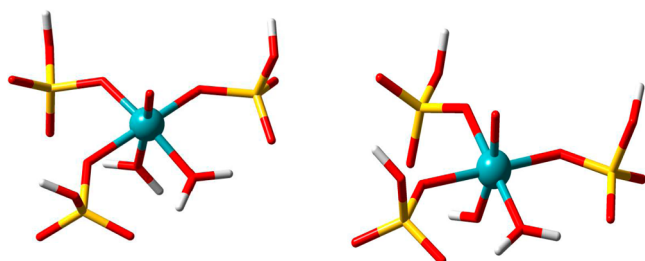


Figure 8. DFT optimized structures of the Tc(V) complexes obtained by α -radiolysis of Tc(VII) in 13 M H₂SO₄: [TcO(HSO₄)₃(H₂O)₂] (left) and [TcO(HSO₄)₃(H₂O)(OH)][−] (right). Colors of atoms: Tc in blue, O in red, S in yellow, H in white.

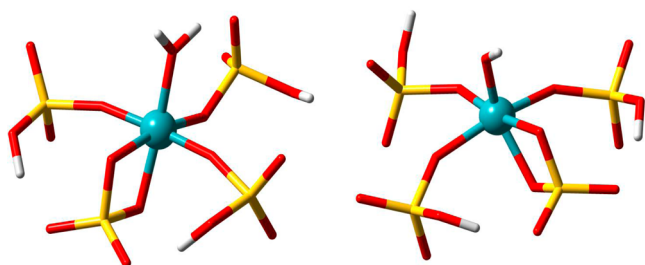


Figure 9. DFT optimized structures of the Tc(V) complexes obtained by α -radiolysis of Tc(VII) in 18 M H₂SO₄: [Tc(HSO₄)₃(SO₄)(H₂O)] (left) and [Tc(HSO₄)₃(SO₄)(OH)][−] (right). Colors of atoms: Tc in blue, O in red, S in yellow, H in white.

Table 6. Interatomic Distances (Å) of Tc(V) Sulfate Complexes Found by EXAFS and DFT Calculations

medium	complexes	bond	distances (Å)	
			EXAFS	DFT
13 M H ₂ SO ₄	[TcO(HSO ₄) ₃ (H ₂ O) ₂]	Tc=O	1.61	1.67
		Tc—O	2.02	2.07
		Tc—S _{mono}	3.23	3.31
	[TcO(HSO ₄) ₃ (H ₂ O)(OH)] [−]	Tc=O	1.61	1.70
		Tc—O	2.02	2.06
		Tc—S _{mono}	3.23	3.35
18 M H ₂ SO ₄	[Tc(HSO ₄) ₃ (SO ₄)(H ₂ O)]	Tc—O	1.99	1.97
		Tc—S _{bid}	2.84	2.76
		Tc—S _{mono}	3.26	3.43
	[Tc(HSO ₄) ₃ (SO ₄)(OH)] [−]	Tc—O	1.99	2.00
		Tc—S _{bid}	2.84	2.85
		Tc—S _{mono}	3.26	3.38

3.2.4. Mechanisms of Reduction of Tc(VII) under α -Radiation. Radiolytic yields for the reduction of Tc(VII) have been determined in 13 and 18 M H₂SO₄. In 13 M H₂SO₄, the spectra of the solution after irradiation (Figure 10) exhibits the band characteristic of Tc(V) at 703 nm ($\epsilon = 8.8 \text{ M}^{-1}$).

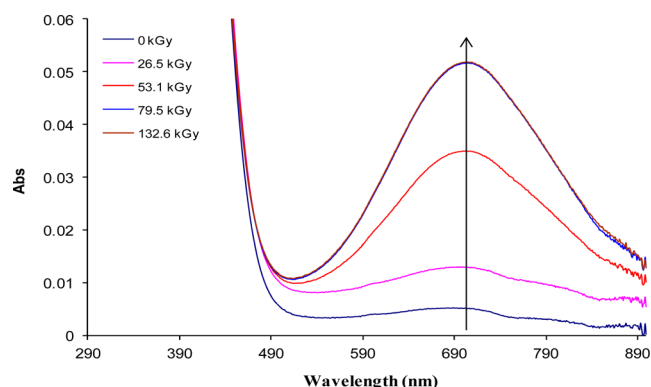


Figure 10. UV–visible spectra after the irradiation of Tc(VII) solution in 13 M H₂SO₄ as a function of the dose. [Tc(VII)] = $5.9 \times 10^{-3} \text{ M}$.

cm^{-1}); the low value of the absorbance indicates that the reduction of Tc(VII) is not complete. In 18 M H₂SO₄, the band is shifted to 739 nm (Figure 11) and the molar extinction coefficient increases to $34 \text{ cm}^{-1} \cdot \text{M}^{-1}$. The value of extinction coefficient in 18 M H₂SO₄ is consistent with the complete reduction of Tc(VII) to Tc(V).

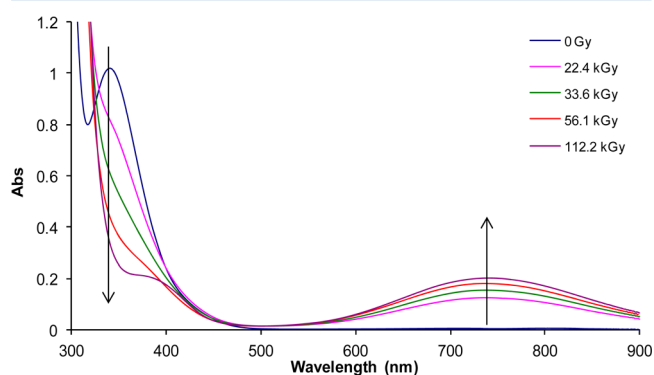
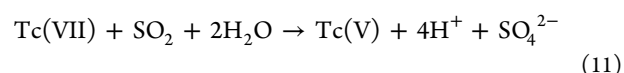


Figure 11. UV–visible spectra after the irradiation of Tc(VII) solution in 18 M H₂SO₄ as a function of the dose. [Tc(VII)] = $5.9 \times 10^{-3} \text{ M}$.

The representation of Tc(V) concentration as a function of the dose is presented in Figure 12. The slope of the curve [Tc(V)] vs Dose (at Dose = 0) allows the determination of the radiolytic yield of Tc(V). The calculated yields are respectively $G(\text{Tc(V)}) = (1.72 \pm 0.17) \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$ in 18 M H₂SO₄ and $(0.84 \pm 0.08) \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$ in 13 M H₂SO₄.

The following mechanism of α -radiolytic reduction of Tc(VII) to Tc(V) in 13 and 18 M H₂SO₄ acid is proposed:



To support this hypothesis, two experiment were performed: (1) the reduction of Tc(VII) by the gas formed during the radiolysis of H₂SO₄ and (2) the chemical reduction of Tc(VII) to Tc(V) by SO₂ gas.

Concerning the reduction of Tc(VII) by the gas formed during the radiolysis of H₂SO₄; the gas produced after the α -radiolysis of an 18 M H₂SO₄ solution that did not contain Tc(VII), were trapped in the neckband of the cell and transferred through a solution of Tc(VII) in 18 M H₂SO₄ using argon gas as a carrier. After passing the gas through the Tc(VII) solution, a change of color from yellow to green was observed and the UV–visible spectrum of the green solution presents the

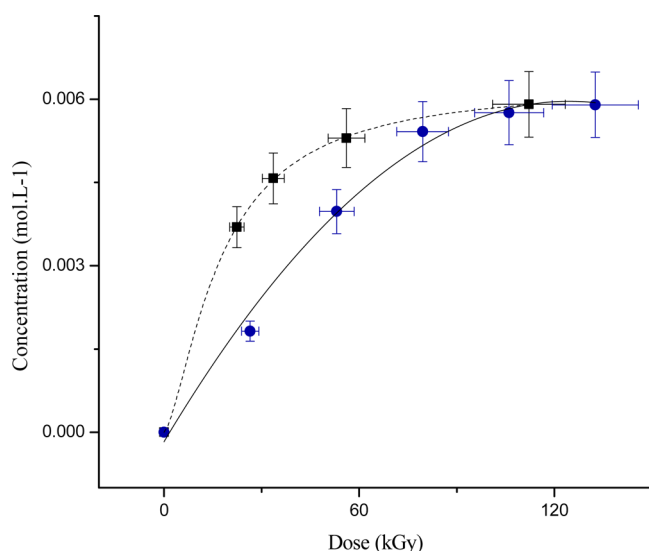


Figure 12. Concentration of Tc(V) (M) formed by α -radiolysis of Tc(VII) as a function of the dose in 13 M H₂SO₄ (blue dots, solid line) and 18 M H₂SO₄ (black dots, dashed line).

band characteristic of Tc(V). This indicates that the gas formed by radiolysis of H₂SO₄ allows the reduction of Tc(VII) to Tc(V).

In the second experiment, sulfur dioxide (from a lecture bottle) was passed through Tc(VII) solutions in 13 and 18 M H₂SO₄. A change of color from yellow to green immediately occurred and the UV–visible spectrum of the green solution exhibits bands characteristic of Tc(V) (Figure 13); this confirms that SO₂ gas allows the reduction of Tc(VII) to Tc(V).

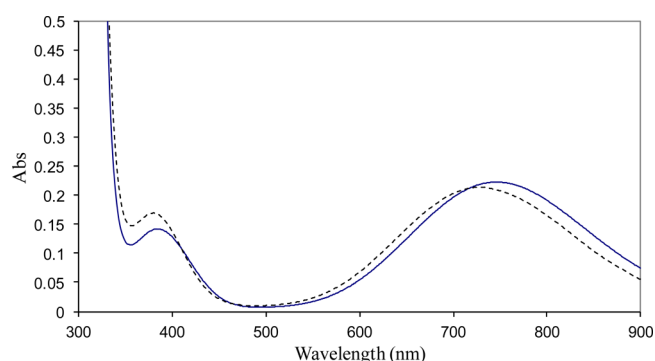


Figure 13. UV–visible spectra of the solution obtained after passing SO₂ gas through a Tc(VII) solution in 13 M H₂SO₄ (dashed curve) and 18 M H₂SO₄ (solid curve).

4. CONCLUSIONS

The behavior of Tc(VII) under α -radiation has been investigated in sulfuric acid. Under α -irradiation, pertechnetate is reduced to Tc(V) in 13 and 18 M H₂SO₄. EXAFS measurements and DFT calculations indicate that the Tc(V) species are coordinated to bisulfate ligands in both monodentate and bidentate mode; the following structures are proposed: [TcO(HSO₄)₃(H₂O)(OH)][−] and/or [TcO(HSO₄)₃(H₂O)₂] in 13 M H₂SO₄ and [Tc(HSO₄)₃(SO₄)(H₂O)][−] and/or [Tc(HSO₄)₃(SO₄)(OH)][−] in 18 M H₂SO₄. During radiolysis of H₂SO₄, results show the formation of

SO₂(g), H₂(g), and H₂O₂. The reduction mechanisms of Tc(VII) to Tc(V) were discussed, and the reduction of Tc(VII) by SO₂ gas according to $\text{Tc(VII)} + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Tc(V)} + 4\text{H}^+ + \text{SO}_4^{2-}$ was proposed.

The behavior of technetium under α -irradiation in concentrated organic acids such as trifluoromethanesulfonic acid (CF₃SO₃H) has been recently studied.³¹ However, the speciation of Tc in this acid is still not well understood. Current works are in progress and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

S1: Determination of H₂O₂ by titanium complexation. S1.1: H₂O₂ calibration curve S1.2: Qualitative and quantitative determination of H₂O₂ by UV–visible spectroscopy. S2: α -irradiated technetium solutions in H₂SO₄ 13 and 18 M. S3: Absorption spectra of α -irradiated Tc in H₂SO₄ 1–9 M. S4: Permanganate titration. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the ARRONAX staff members for their valuable assistance during α -irradiation experiments. Funding for this research at UNLV was provided by a SISGR Grant from the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. 47824B. The SOLEIL synchrotron is acknowledged for provision of beamtime, and the MARS team, in particular Bruno Sitaud, Isabelle Llorens, and Gokhan Karakurt for assistance with the EXAFS experiments.

■ ABBREVIATIONS

XAS, X-ray absorption spectroscopy; XAFS, X-ray absorption fine structure spectroscopy; XANES, X-ray absorption near edge structure; EXAFS, extended X-ray absorption fine structure; DFT, density functional theory; B3LYP, Becke three-parameter Lee–Yang–Parr; D95 V, Dunning–Huzinaga valence; SDD ECRs, Stuttgart/Dresden effective core potentials; CPCM, conductor polarized continuum model; Lee–Yang–Parr GC, gas chromatography; PUREX, plutonium and uranium refining by extraction; FT, Fourier transform; CN, coordination number; Abs, absorbance

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