Reduction of pertechnetate by acetohydroxamic acid: Formation of [TcNO(AHA)$_2$(H$_2$O)]$^+$ and implications for the UREX process.

Cynthia-May S. Gong[1], Wayne W. Lukens[2], Frederic Poineau[1], and Kenneth R. Czerwinski[1].*

[1]Harry Reid Center for Environmental Studies, Nuclear Science and Technology Division, University of Nevada, Las Vegas, Las Vegas, NV, 89154-4006 [2]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720-8175

czerwin2@unlv.nevada.edu

Pertechnetate reduction by AHA.

Abstract.

Reductive nitrosylation and complexation of ammonium pertechnetate by acetohydroxamic acid has been achieved in aqueous nitric and perchloric acid solutions. The kinetics of the reaction depend on the relative concentrations of the reaction components and are accelerated at higher temperatures. The reaction does not occur unless conditions are acidic. Analysis of the x-ray absorption fine structure spectroscopic data is consistent with a pseudo-octahedral geometry with the linear Tc-N-O bond typical of technetium nitrosyl compounds, and electron spin resonance spectroscopy is consistent with a the d^5 Tc(II) nitrosyl complex. The nitrosyl source is generally AHA, but may be augmented by products of

reaction with nitric acid. The resulting low-valency *trans*-aquonitrosyl(diacetohydroxamic)-technetium(II) complex (**1**) is highly soluble in water, extremely hydrophilic, and is not extracted by tri-*n*-butylphosphate in a dodecane diluent. Its extraction properties are not pH-dependent; titration studies indicate a single species from pH 4.5 down to -0.6 (calculated). This molecule is resistant to oxidation by H_2O_2, even at high pH, and can undergo substitution to form other technetium nitrosyl complexes. The formation of **1** may strongly impact the fate of technetium in the nuclear fuel cycle.

Technetium, acetohydroxamic acid, nitrosyl, UREX, TBP extraction, XAFS, UV-vis

Introduction. Technetium, a transition metal fission product, is a major component of spent nuclear fuel. Its fate in the UREX reprocessing scheme is modeled as pertechnetate (TcO_4^-)[1-3]; however, recent work has shown that soluble, low-valency complexes can form in waste containing organic ligands[4].

Acetohydroxamic acid (AHA) is an organic ligand proposed for use in the UREX process[5]. It reduces neptunium and plutonium[6-7], and the resultant hydrophilic complexes are separated from uranium by extraction with tributylphosphate (TBP) in a hydrocarbon diluent[8-9]. Hydroxamic acids undergo irreversible hydrolysis to hydroxylamine and the pertinent carboxylic acid[10]. The reported reduction potentials of AHA and pertechnetate[6-7,11-12] indicate that it may be possible for AHA to reduce technetium, altering its fate in the fuel cycle. However, as later demonstrated for hydroxylamine[13], in these systems the electrochemistry is largely controlled by other species, especially NO, adsorbed on the Pt electrode surface, and the reported reduction potentials for AHA may not be accurate. The detailed mechanism for oxidation of AHA in solution has not been reported; however, in the gas-phase, AHA is oxidized by a single electron to AHA^+, which quickly decomposes to acetyl cation and aminoxyl radical (H_2NO)[14]. In solution, AHA may be oxidized by a single electron, yielding AHA^+, which is then hydrolyzed to yield acetic acid and aminoxyl radical (H_2NO), which quickly disproportionates to N_2 and water. The electrochemistry of AHA as well as its reaction chemistry may be complicated by the fact

that the reaction product, aminoxyl radical, is itself a good reducing agent, yielding nitroxyl (HNO) upon oxidation[15]. Previous studies of the behavior of technetium during the UREX process have not reported reduction[1], but AHA is known to react immediately with Ru(III) in aqueous solution to yield a Ru(II) nitrosyl complex[16].

More work has been done on the interaction of hydroxylamine, also a reductant, and pertechnetate. In aqueous HCl, hydroxylamine can reduce Tc(VII) to form Tc(IV) hydroxylamine and chloride complexes[17-18]. Reaction of technetium with hydroxylamine often gives a mixture of products, most notably Eakins' pink complex[19] (**2**, $[Tc^{I}(NO)(NH_3)_4]Cl_2$), the first reported technetium nitrosyl (TcNO) complex; the source of NO may be hydroxylamine or its oxidation products, H_2NO, or HNO[20]. Since its synthesis in 1963, reports on its chemistry[21] and crystal structure[22] have launched the production of an expanding number of Tc nitrosyl compounds, often by substitution[23-29], but also synthesized directly from Tc(IV) halides using hydroxylamine, $NaNO_2$, NO(g), or NO salts as the sources of nitrosyl[19,30]. Only recently have researchers exploited reductive nitrosylation of pertechnetate by hydroxylamine as a route to Tc nitrosyl complexes, including to **2**[31].

The strong π-acceptor character of the nitrosyl ligand stabilizes low valent Tc through backbonding, and few Tc(II) complexes without nitrosyl or thionitrosyl ligands are known[32-33]. Most Tc nitrosyl complexes are pseudo-octahedral Tc(I) and (II) complexes and trigonal bipyramidal Tc(III) complexes[34-36]. The strong π-acidity of nitrosyl decreases the lability of the other ligands, stabilizing the complex. Given the high hydrophilicity of known AHA complexes, this stability may affect the fate of Tc in the fuel cycle and the strategies necessary to create a final waste form.

In this work, we demonstrate that pertechnetate undergoes reductive nitrosylation by AHA under a variety of conditions. The resulting divalent technetium is complexed by AHA to form the pseudo-octahedral $Tc^{II}(NO)(AHA)_2(H2O)^+$ (**1**, Figure 1), as characterized by extended x-ray absorption fine

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structure spectroscopy (EXAFS) - the first EXAFS reported for a Tc nitrosyl complex. This complex is the sole technetium product of the reaction and is different from the product of reaction of pertechnetate with hydroxylamine. The observed partial orders of the reagents were determined and a potential mechanism proposed. In contrast to other AHA complexes of other divalent transition metals[37-39] and divalent uranyl[40], and Cr(V)[41], **1** is very soluble in water and stable for months in a 0.235 M solution. Like the Pu and Np AHA complexes, **1** is extremely hydrophilic and does not extract into 30% TBP in dodecane, which could affect the UREX scheme. Its stability, solubility, and straightforward aqueous synthesis could allow its use as a precursor to other technetium nitrosyl complexes.
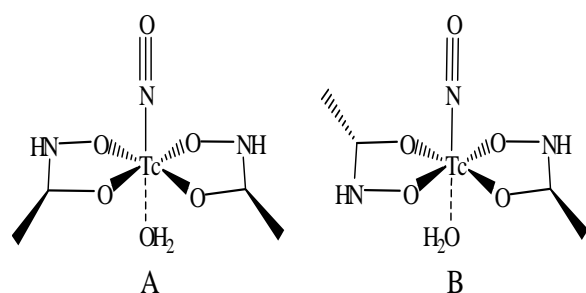
Figure 1. A, *trans*-aquonitrosyl-*cis*-diacetohydroxamic-technetium(II). B, *trans*-aquonitrosyl-*trans*-diacetohydroxamic-technetium(II).

Experimental Section

Caution! [99]Tc is a β-emitter (E_{max} = 294 keV, $t_{1/2}$ = 2 x 10^5 years). All operations were carried out in radiochemical laboratories equipped for handling this isotope.

Reagents and Solutions. Ammonium pertechnetate was purchased from Oak Ridge National Laboratory and purified as described elsewhere[42]. Water was purified to >18 MΩ by a MilliQ system. All other chemicals were used as received. A 0.18 M Tc stock solution was prepared for all studies and its concentration confirmed spectrophotometrically at 289 nm (ε = 2380 L mol^{-1} cm^{-1}) and/or *via* liquid scintillation counting (LSC) for every experiment. Amorphous TcO$_2$ was generated by adding hydrazine

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hydrate to a solution of ammonium pertechnetate, then washing the resultant black precipitate twice with ultrapure water. Stock solutions of up to 5.0 M AHA and hydroxylamine hydrochloride were generated frequently and in small batches to avoid hydrolysis. For the organic phase (30% TBP), 30 mL of tributylphosphate were diluted up to 100 mL with *n*-dodecane.

Synthesis. The effects of acid, Tc, and AHA concentrations were determined by systematically varying the initial concentrations over a series of three or more values at constant temperature (Figures S1-S2, Supporting Information). Solutions from 0.05 to 20 mM Tc in up to 4.0 M AHA and up to 2.0 M $HClO_4$ or HNO_3 were generated by diluting the Tc stock solution into AHA, then acidifying. The solutions turned from colorless to brown immediately upon addition of acid, and the color deepened with time. The Tc concentration was confirmed for each sample by UV-vis and LSC in $HClO_4$ and by LSC in HNO_3. The reactions were followed *via* UV-vis continuously for up to 12 days and intermittently up to 6 weeks (Figure S3 in Supporting Information). The complex was also generated from amorphous TcO_2 dissolved to 0.235 M in a 4.0 M solution of AHA, then acidified to 1 M H^+. Dissolution of the anionic Tc(IV) complex [(*n*-Bu)$_4$N]$_2$[TcCl$_6$] into 1.0 M AHA in dry ethanol did not generate any reaction over the period studied.

Tc-hydroxylamine. Tc-hydroxylamine compounds were generated and monitored as above, from both pertechnetate and amorphous technetium dioxide, using hydroxylamine hydrochloride instead of AHA. The addition of nitric or perchloric acid was not necessary for this reaction, though it increased the rate. The yellow Tc-hydroxylamine (**3**) was purified from the pink **2** *via* extraction with 30% TBP.

Analytical Techniques. Electron paramagnetic resonance (EPR) spectra were obtained at room temperature with a Varian E-12 spectrometer equipped with cryostat cooled by liquid nitrogen boil-off, an EIP-547 microwave frequency counter, and a Varian E-500 gaussmeter, which was calibrated using 2,2-diphenyl-1-picrylhydrazyl (DPPH, g = 2.0036). The low temperature spectrum was fit using a

version of the code ABVG modified to use a pseudo Voigt line shape and modified to fit spectra using the downhill simplex method. The ABVG code includes second-order effects in the calculation of the peak positions but cannot simulate anisotropic line widths, so all peaks in the simulation have the same line width.{References A} In the least squares fit, the spectrum at fields less than 2400 gauss and greater than 3900 gauss was weighted 3 times more heavily than the spectrum between 2400 and 3900 gauss due to problems caused by the narrower peaks at the center of the spectrum. The simulated solution spectra were also calculated using a downhill simplex version of ABVG in which all g and A-values were identical. For the solution spectra, the simulation used a Lorentzian line shape with the line width dependence described by Kivelson.{References B} UV-visible spectra were obtained using Varian Cary 6000i and Ocean-Optics ST2000 spectrometers. Temperature was monitored and maintained *via* a Varian Peltier thermostable multicell sample holder. Liquid scintillation counting was performed on a Perkin-Elmer Tri-Carb 3100TR instrument.

{References for EPR fitting: Set A

Bruce, S.D.; Higinbotham, J.; Marshall, I.; Beswick, P.H *J. Mag. Reson.* **2000**, *142*, 57-63.

Press, W.H.; Teukolsky, S.A.; Vetterling, W.T.; Flannery, B.P. *Numerical Recipes in Fortran 77: the Art of Scientific Computing*, 2nd ed.; Cambridge University Press: Cambridge, 1992.}

{Set B:

Daul, C.; Schläpfer, C.W.; Mohos, B.; Ammeter, J.; Gamp, E. *Comp. Phys. Commun.* **1981**, *21*, 385-395.

Press, W.H.; Teukolsky, S.A.; Vetterling, W.T.; Flannery, B.P. *Numerical Recipes in Fortran 77: the Art of Scientific Computing*, 2nd ed.; Cambridge University Press: Cambridge, 1992.

Kivelson, D. *J. Chem. Phys.* **1960**, *33*, 1094-1106.}

X-ray absorption fine structure (XAFS) spectra were acquired at the Stanford Synchrotron Radiation Laboratory (SSRL) at beamline 11-2 using a Si(220) double crystal monochromator. Higher order

harmonics were rejected by detuning the monochromator by 30%. X-ray absorption spectra were obtained in the transmission mode at room temperature using Ar-filled ionization chambers. The spectra were energy calibrated using the first inflection point of the pre-edge peak from the Tc K-edge spectrum of an aqueous solution of NH_4TcO_4, defined as 21044 eV. To determine the Tc K-edge charge state shifts, the energies of the Tc K-edges at half height were used. Extended x-ray absorption fine structure (EXAFS) data analysis was performed by standard procedures using the programs ifeffit[43] and Athena/Artemis[44]; theoretical EXAFS phases and amplitudes were calculated using FEFF7[45]; Fitting of the Tc K-edge spectrum of the reaction product of TcO_4^- with AHA was performed as previously described[43]. Statistical relevance of the EXAFS parameters was checked using the F-test.* The All ^{99}Tc samples were triply contained inside sealed polyethylene vessels.

* Downward, L.; Booth, C.H.; Lukens, W.W.; Bridges, F. *AIP Conference Proceedings* **2007**, *882*, 129-132.

Extraction. The decrease in pertechnetate was followed by UV-vis and LSC in perchloric acid and by extraction with tetraphenylarsonium chloride in chloroform[42] and LSC in nitric acid. Extraction with 30% TBP was performed by combining equal volumes organic and aqueous phases and mixing vigorously by vortexing for 60 seconds, followed by centrifugation. The technetium concentration in both phases was determined by LSC.

Results and Discussion

Synthesis and characterization. The $Tc^{II}(NO)(AHA)_2(H2O)^+$ complex, as confirmed by UV-vis spectrometry, was the only Tc species detected from the reaction of ammonium pertechnetate and AHA in acid. The reaction proceeded with concentrations as low as 0.5 M acid, 0.5 M AHA, and 0.2 mM NH_4TcO_4. $Tc^{II}(NO)(AHA)_2(H2O)^+$ can be generated consistently from ammonium pertechnetate at various temperatures: a sample generated by heating 20 mM NH_4TcO_4, 1 M HNO_3, and 4 M AHA to 95 ºC for 15 minutes, which visibly evolved gas, had the same UV-vis spectrum (Figure 2) as those generated from similar concentrations over 12 days at 20 ºC and 4 days at 30 ºC.
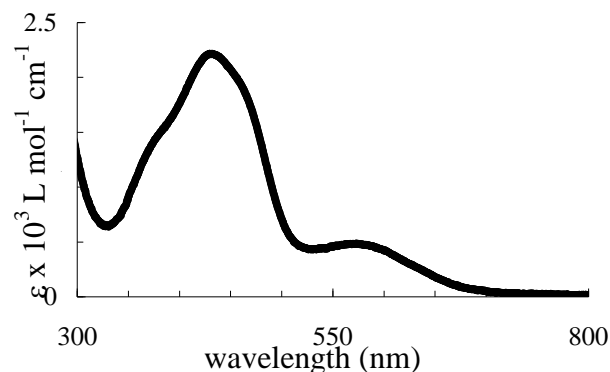
Figure 2. Basis spectrum of Tc(NO)AHA$_2$. λ_{max} = 428 nm, ε = 2216.

A sample that had reached equilibrium at pH 3.3 was divided, and half was titrated with acid and half with base. Spectra were taken at approximately half-integral pH values (Figure S4, Supporting Information). The dilution-corrected spectrum was identical from pH -0.6 (calculated) up to pH 4, meaning that the kinetics could be tracked *via* the maximum at 428 nm, since, in contrast to the pH-sensitive spectrum of the uranium AHA complex[40], **1** exhibits the same spectrum under all reaction conditions examined. Above pH 4, the spectrum began to shift, and the sample turned green in a basic environment. Addition of acid restored the original yellow-brown color immediately, indicating that the color change is due to deprotonation of the complex.

Samples were microscale and contained only 5-100 ug Tc each *vs*. 60 mg nitrate and up to 300 mg excess AHA and acetic acid. Attempts to isolate enough of the compound for IR and crystallographic studies *via* concentration, coprecipitation, ion exchange, extraction, and thin-layer chromatography were unsuccessful. Therefore the structure of **1** was studied by solution-phase EXAFS. The EXAFS fitting parameters are given in Table 1; fitted Fourier Transform and k^3–EXAFS spectra are shown in Figure 3. The geometry and bond lengths obtained by this method are consistent, within the error of the method, with those obtained by x-ray crystallography of known Re and Tc nitrosyl compounds (Table 2). The octahedral O,O bidentate bond has been similarly seen *via* EXAFS in iron[46], and the M-N and N-O

bond distances are consistent with those of rhenium(II) nitrosyl complexes[47]. It has been shown that

AHA is an electron-donor[9,48], which may help stabilize the electron-withdrawing nitrosyl moiety.
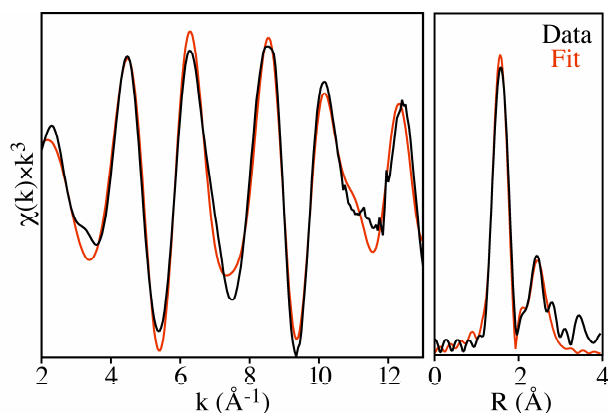
Figure 3. Data (black lines) and fit (colored lines) of the k^3- weighted EXAFS data and its Fourier

transform.

Table 1: Fitting parameters

| Neighbor	# of Neighbors	Distance (Å)	σ^2 (Å^2)	F-test (p)^b
N	1	1.77(1)	0.004(2)	2×10^{-3}
O	5	2.06(1)	0.006(1)	2×10^{-8}
O^c	1	2.95(1)	0.003(1)	5×10^{-4}

a) $S_0{}^2$=1.13 (from fitting the $TcO_4{}^-$ reference), $\Delta E_0 = 0(2)$ eV; b) Probability that improvement in the fit quality resulting from adding these atoms is due to chance; c) Nitrosyl oxygen. Includes 2 multiple scattering (MS) paths with the same parameter;

Table 2. Comparison of $Tc(NO)AHA_2$ to known TcNO complexes.

Molecule	Tc-N (Å)	N-O (Å)	Tc-L$_{trans}$ (Å)	O-N-Tc
$Tc^{II}(NO)(AHA)_2(H2O)^+$ (this study)	1.77	1.18	2.06	180 °
Eakins' pink complex $(Tc(I))^{22}$	1.716(4)	1.203(6)	2.169(4)	178.7(2)°
$Tc^ICl_2NO(HNNC_5H_4N)(PPh_3)^{23}$	1.752(4)	1.1180(5)	2.153(4)	175.1(4)°
$Tc^ICl_2NO(py-PPh_2-P,N)(PPh_2-P)^{24}$	1.743(5)	1.170(6)	2.441(2)	177.2(5)°

|				
$Tc^INOBr_2(CNCMe_3)_3$[29]	1.726(15)	1.136(17)	2.137(22)	174.9(8)°
$[Tc^ICl(\mu\text{-}Cl)(CO)_2NO]_2$[30]	1.749(14)	1.16(2)	2.455(5)	177.4(8)°
$[Tc^ICl(\mu\text{-}Cl)(CO)_2NO]_2$[30]	1.794(14)	1.15(2)	2.380(5)	174.3(9)°
$[Tc^ICl(NO)(DPPE)_2]PF_6 \cdot CH_2Cl_2$[31]	1.717(3)	1.145(3)	2.3262(7)	179.0(2)°
$[Tc^INO(NH_3)(phen)_2]^{2+}$[32]	1.739(9)	1.160(9)	n.a.	171.9(8)°
$Tc^{III}NOCl(SC_{10}H_{13})_3$[36]	1.767(6)	1.150(7)	n.a.	175.9(2)°

The oxidation state of **1** was determined from its EPR spectrum, shown in Figure 4 in frozen solution and in Figure S10 in liquid solution. The g-values, g_1, g_2, and g_3, obtained by fitting the spectrum shown in Figure 4 are 2.041, 2.028, and 1.949, respectively, and the associated hyperfine coupling constants, A_{11}, A_{22}, and A_{33}, are 118, 108, and 259×10^{-4} cm^{-1}, respectively, with smaller, off-diagonal elements: A_{12}, A_{13}, and A_{23} are 3, 33, and 5×10^{-4} cm^{-1}, respectively. These g and A-values are similar to those of Tc(II) nitrosyl complexes as reported in Table S2. Of these complexes, the EPR parameters of **1** are most similar to those of trichloronitrosyl(acetylacetonato)-technetium, which is the only reported Tc(II) nitrosyl complex with an oxygen donor ligand that is similar to AHA. The spectroscopic data all support the proposed structure of **1** shown in Figure 1.
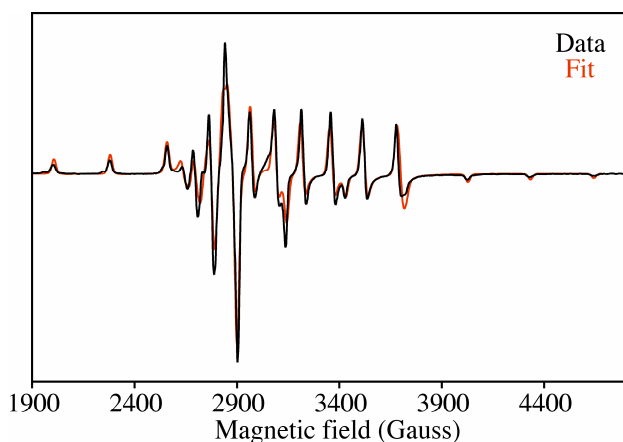
Figure 4. EPR spectrum of a frozen solution of **1**. The g-values of the simulation are 2.041, 2.028, and 1.949, and the associated hyperfine coupling constants are 118, 108, and 259×10^{-4} cm^{-1} with smaller, off-diagonal elements.

Kinetics and proposed mechanism

Unlike the reaction with AHA, the reaction of pertechnetate with hydroxylamine hydrochloride was not consistent: occasionally, different aliquots of the same mother solution of the reagents generated different complexes, and in some cases, no reaction was observed. The solutions generally turned yellow over time, indicating the formation of **3**, but in some instances reaction produced **2**, confirmed by UV-vis in comparison to literature, and even reversibly turned green upon heating (likely $TcNOCl_5$[21]). Both **2** and **3** formed more often in perchloric rather than nitric acid. The UV-vis spectrum of **3** matches the description of a Tc^{IV}-hydroxylamine complex, though its spectrum was not published[18]; it is presented here in Figure 5. The rate of Tc(VII) reduction by hydroxylamine was much slower than that by AHA, as determined by UV-vis (Table 3).
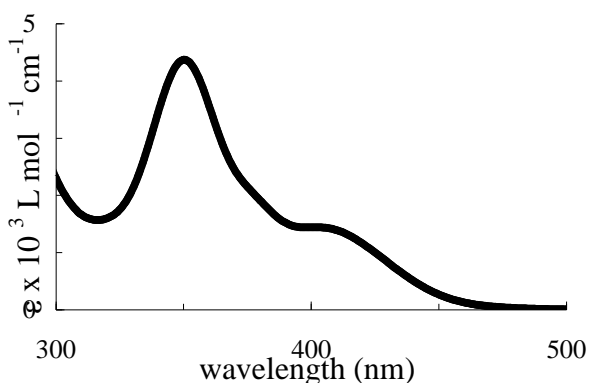
Figure 5. Basis spectrum of Tc-hydroxylamine. $\lambda_{max} = 350$ nm, $\varepsilon = 4360$.

Table 3. Decrease in pertechnetate; total [Tc] 0.55 mM.

M	Rate (ΔA_{289nm}/min)	
	Hydroxylamine	AHA
3.66	-0.00020	-0.00170
1.83	-0.00010	-0.00020
0.92	-0.00004	-0.00003

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Tc(IV) hexachloride, $TcCl_6^{2-}$, is often a starting material for synthesis of technetium nitrosyl complexes. This compound can be heated with hydroxylamine hydrochloride to form the tetrachloronitrosyl Tc(II) complex[49]. In this study, it was found that **1** can be formed from Tc(IV) as $TcO_2 \cdot xH_2O$; dissolution into AHA forms a wine-red solution with a distinct UV-vis spectrum (Figure S5), which upon acidification forms the yellow-brown **1**, reaching equilibrium within an hour. The initial red complex could not be recovered even upon the addition of base (to 1.0 M) and hydrogen peroxide (to 1.0 M). The formation of **1** from pertechnetate was much slower than from amorphous technetium oxide. The overall rate of that reaction depends on the temperature, but by holding the temperature constant over a series of trials the partial order of each reagent in the production of **1** could be ascertained by observing the reaction over time (Tables 4, S3; Figure S6).

Table 4: Partial reaction orders for the reaction of TcO_4^- with AHA in acid.

Formation of product, monitored at 428 nm		
HNO$_3$		
Reagent	Observed Partial Order	R^2
NH_4TcO_4	1.028 ± 0.003	1.000
H^+	0.991 ± 0.023	1.000
AHA	1.968 ± 0.149	0.994
HClO$_4$		
Reagent	Observed Partial Order	R^2
NH_4TcO_4	0.967 ± 0.003	1.00
H^+	1.004 ± 0.037	0.999
AHA	1.994 ± 0.193	0.991
Loss of TcO_4^-, monitored at 289 nm		
Reagent	Observed Partial Order	R^2

NH$_4$TcO$_4$	0.867 ± 0.055	0.996
H$^+$	1.066 ± 0.052	0.998
AHA	1.742 ± 0.171	0.991

All of the complexes generated from hydroxylamine are distinct from Tc^{II}(NO)(AHA)$_2$(H2O)$^+$, indicating that the ligands on **1** are not formed from the acid hydrolysis of AHA to hydroxylamine and acetic acid. Attempts to form **1** from mixtures of hydroxylamine reductant and acetic acid ligand in nitric and perchloric acids formed other distinct complexes whose UV-vis spectra varied with the ratio of hydroxylamine to acetic acid (Figure S7). The UV-vis spectrum of **1** was the same regardless of which mineral acid was used. These results strongly support the assignment of the equatorial ligands to AHA.

The slow rate of reaction of pertechnetate with AHA and the very rapid reaction of Tc(IV) with AHA, as well as the previously observed rapid reaction of Ru(III) with AHA, suggests that the technetium species reductively nitrosylated is a lower valent complex. In addition, the nitrosylating agent must be AHA itself, since the rate of reductive nitrosylation of Tc(IV) is much faster than the rate of hydrolysis of AHA to hydroxylamine. Furthermore, the observation that Tc(IV) is much more reactive than TcO$_4^-$ strongly supports a reductive nitrosylation mechanism similar to that previously proposed for the reductive nitrosylation of Ru(III) as illustrated in Scheme 1. The proposed mechanism is closely related to the previously proposed mechanism for reductive nitrosylation of V(V) by hydroxylamine studied by Wieghardt[50] and proceeds *via* a coordinated nitroxyl ligand previously observed[51]. Since the terminal oxo group of Tc(VI), Tc(V) or Tc(IV) is more nucleophilic than a terminal oxo group of TcO$_4^-$, the postulate that reductive nitrosylation proceeds by initial nucleophilic attack on the coordinated carbonyl group of AHA is consistent with the observed reactivity.
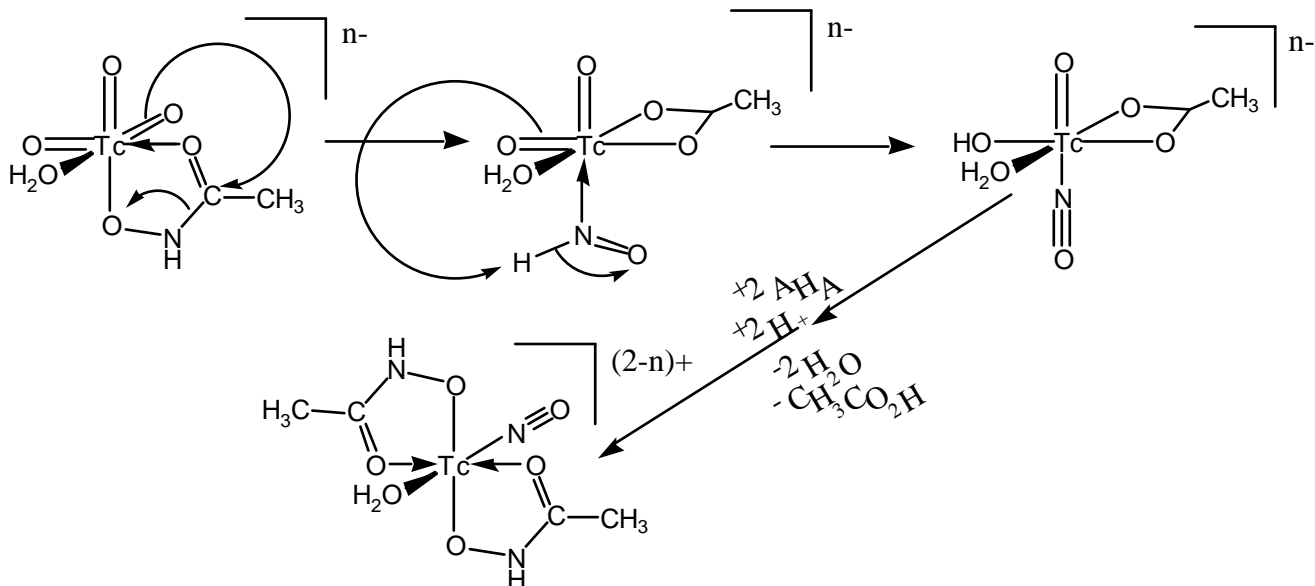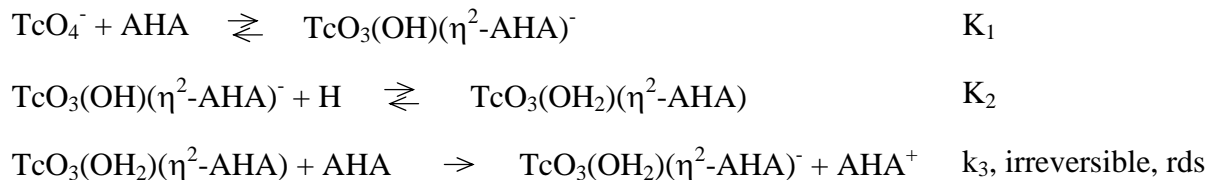
Scheme 1: Proposed mechanism for reductive nitrosylation of Tc(VI) (n=1) or Tc(V) (n=2) by AHA.

As the reaction of lower-valent Tc complexes with AHA is rapid, the initial step is most likely reduction of TcO_4^- to a lower valent complex that subsequently undergoes reductive nitrosylation. The observed partial reaction orders provide two indications about the potential mechanism. First, steps prior to the rate determining step (rds) involve one TcO_4^-, one proton, and two molecules of AHA. Second, the rate law for formation of **1** is the same as that for loss of TcO_4^-; therefore all steps prior to the rds must be reversible. This latter fact eliminates the most straightforward mechanism for the reaction of TcO_4^- with AHA: the direct reaction of TcO_4^- with AHA to produce TcO_4^{2-}, which will rapidly disproportionate to Tc(V)[52]. The reaction of TcO_4^- with AHA would be irreversible, yielding a rate law for loss of TcO_4^- equivalent to $k[TcO_4^-][AHA]$, not $k[TcO_4^-][H^+][AHA]^2$, as observed.

An alternative mechanism for reduction of TcO_4^- to Tc(VI) is suggested by the reaction of alkenes with Tc(VII) complexes[53]. In that study, TcO_4^- was unreactive, but an octahedral Tc(VII) complex, $TcO_3(AA)Cl_3$ where AA is a diamine ligand such as 1,10-phenanthroline, was sufficiently oxidizing to react with alkenes to form a coordinated diol ligand. Likewise, TcO_4^- may be insufficiently oxidizing to react with AHA, but an octahedral Tc(VII) complex is likely to be more oxidizing. The

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proposed mechanism for reduction of Tc(VII) to Tc(VI) involves a preequilibrium to form an octahedral Tc(VII) complex, as illustrated in Scheme 2. Thus, the overall proposed mechanism is formation of an octahedral Tc(VII) complex that reacts with AHA to form an octahedral Tc(VI) complex, which either is reductively nitrosylated by the coordinated AHA ligand, as illustrated in Scheme 1, or disproportionates to form an octahedral Tc(V) complex that is reductively nitrosylated by the coordinated AHA ligand.

$TcO_4^- + AHA \rightleftharpoons TcO_3(OH)(\eta^2\text{-}AHA)^- \qquad\qquad K_1$

$TcO_3(OH)(\eta^2\text{-}AHA)^- + H \rightleftharpoons TcO_3(OH_2)(\eta^2\text{-}AHA) \qquad K_2$

$TcO_3(OH_2)(\eta^2\text{-}AHA) + AHA \rightarrow TcO_3(OH_2)(\eta^2\text{-}AHA)^- + AHA^+ \quad k_3, \text{irreversible, rds}$

Scheme 2: Proposed mechanism for reduction of TcO_4^- by AHA in aqueous acid.

Extraction. In the absence of AHA, pertechnetate extraction into TBP was consistent with literature reports[54]. Pertechnetate reduction begins immediately upon contact with acidic AHA, as does the decrease in the extraction of Tc; the change in K_d with time is shown in Figure S8. The increase of **1** from an initial solution of 0.5 mM NH_4TcO_4 and 1M HNO_3, charted as a function of AHA concentration *via* its absorbance maximum, can be correlated with a decrease of the technetium distribution between the aqueous and TBP phases. Figure 6 shows this relationship after the reaction has proceeded 24 hours.
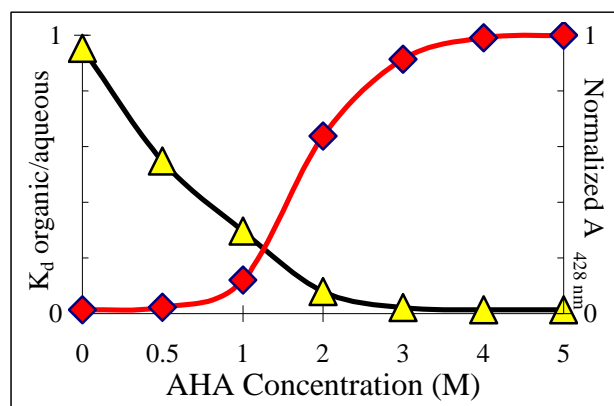
Figure 6. Correlation of absorbance of **1** at 428 nm with the distribution factor into 30% TBP-dodecane after 1 day. Triangle, K_d; diamond, A_{428nm}.

The reduction and complexation of technetium by AHA, even before complete transformation to the nitrosyl complex, inhibits its extraction into TBP. Even at 0.5 M AHA and 1.0 M HNO$_3$ - conditions close to UREX+ - there is an immediate effect, culminating in a 42% reduction of the distribution constant after 1 day compared to the reaction without AHA. At 4.0 M AHA, only 1.4% of the Tc can be extracted after 1 day. When the reaction is allowed to proceed for just 4 hours, then washed 5x with TPACl to remove pertechnetate[42], only 2% of the total Tc is extracted, compared with 1.5% for the best known cationic technetium nitrosyl, Eakins' pink complex, and 2% of the red Tc-AHA complex generated from Tc(IV). When chloride is substituted for the coordinated AHA **1** by dilution into concentrated HCl (Figure S9), the anionic Tc(NO)Cl$_4^-$ complex formed is extracted into TBP with a K$_d$ of 0.92, very similar to the 0.95 of pertechnetate.

This information indicates that the formation of a Tc nitrosyl complex does not necessarily affect the extraction of Tc; rather, it is the formation of a hydrophilic AHA complex that inhibits the extraction of Tc. These complexes may take time to form at 20 °C, but at the elevated temperatures likely during reprocessing, their formation may be significantly faster.

Although the pH is changing, the distribution coefficient measured from pH -0.6 (calculated) up to 11 was the same within error (Table S4). The concentration of Tc in the organic phase was so low as to be immeasurable, and the difference in the concentration in the aqueous phase before and after extraction was within the error of the measurement; essentially no Tc is extracted into the organic phase.

Conversely, **3** extracts well into TBP, with a K$_d$ of 1.35. The UV-vis spectrum in organic solvents is identical to that in aqueous solution. For this reason, extraction can be used to separate **3** (presumably Tc(IV)(AHA)$_2$) product from **2** after the reaction of pertechnetate with hydroxylamine.

Conclusions

The observation of pertechnetate reduction by AHA under conditions similar to reprocessing, and its subsequent effect on the extraction behavior of Tc, is surprising and important. Currently, the UREX+ flowsheet indicates that AHA is added to the dilute nitric acid scrub solution, which is loaded with U, Tc, Np, and Pu, rather than the feed solution, which contains the spent fuel dissolved in concentrated nitric acid. With reduced concentrations of competing noble metal fission products, especially ruthenium, which may also be converted into nitrosyl complexes, reductive nitrosylation of techenetium needs to be considered if AHA is going to be used in the UREX+ process since.

The Tc-nitrosyl structure determined by EXAFS is consistent with previously reported TcNO and metal-AHA structures. The facile formation of this complex from AHA without side products should advance interest in the synthesis low-valency TcNO complexes directly from pertechnetate, especially if this reaction works with other substituted hydroxamic acids. More work is needed to determine whether the presence of actinides will affect the formation of these complexes, and thus the fate of technetium in the fuel cycle.

Supporting Information Available: Tables showing the kinetics and comparison of EPR data with published values; Figures showing the UV-vis spectra from pH titrations, kinetics of formation, kinetics of extraction, UV-vis characterization of Tc-hydroxylamine, Tc(IV)-AHA, and of competitive reactions with HCl.

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Synopsis artwork.

[TcNO(AHA)$_2$H$_2$O]$^+$
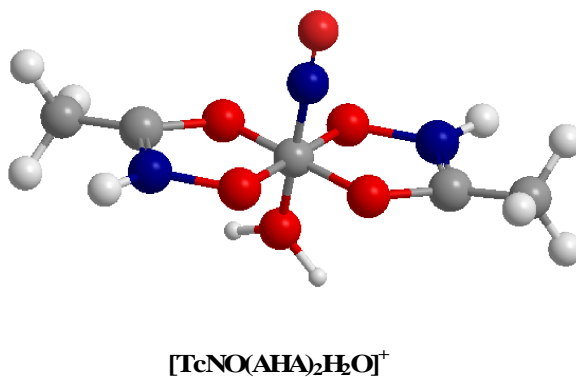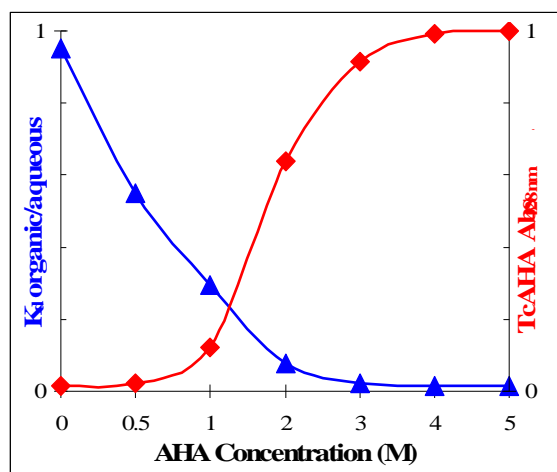
Synopsis. Ammonium pertechnetate is reduced and complexed by acetohydroxamic acid in aqueous nitric and perchloric acids under conditions close to those proposed for reprocessing spent nuclear fuel . The resulting hydrophilic technetium(II) nitrosyl complex, TcNO(AHA)$_2$ (H$_2$O), is not extracted by a solution of tri-*n*-butylphosphate in dodecane diluent. This reaction could impact the proposed nuclear fuel cycle.