The autoreduction of pertechnetate in aqueous, alkaline solutions

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The autoreduction of pertechnetate ($^{99}TcO_4^-$) to Tc(IV/V) alkoxide complexes in aqueous, alkaline, solutions is described. Solutions of sodium pertechnetate (0.01M) reacted with nitrogen and oxygen donor ligands (1.0M) in 2M sodium hydroxide. Solutions containing nitrogen donor ligands (e.g., EDTA) showed the initial formation of lightly colored complexes followed by rapid decomposition in air. In contrast, stable, reduced complexes were formed within minutes of mixing pertechnetate with mono- and disaccharides in strong base, as indicated by a persistent color change. Chemical yields of these reactions were determined by thin layer chromatography or paper chromatography and radiochemically assayed with a Bioscan imaging scanner. Analysis by UV-vis spectroscopy suggested that Tc(IV) or Tc(V) complexes were produced, with the oxidation state dependent on the reducing ligand. These experiments may help explain the reduction of pertechnetate to the soluble complexes that have been found in the Hanford nuclear waste tanks.

Introduction

The safe geologic disposal of U.S. defense nuclear waste requires the separation of high-level waste from low-level waste followed by vitrification. The U.S. Department of Energy's (DOE) Hanford site is the current storage location for high-level nuclear waste from plutonium production. Approximately 200,000 m^3 of strongly alkaline waste is stored in large underground tanks as a heterogeneous mixture.[1–3] One of the major radionuclides contributing to the high level waste is ^{99}Tc.[4] There is a desire to separate the ^{99}Tc from the high level waste because of the long half-life ($T_{1/2} = 2.1 \cdot 10^5$ y) and the mobility of pertechnetate in the ground.

The tanks also contain metric tons of organic compounds including monosaccharides, disaccharides, and polyaminocarboxylates (e.g., EDTA).[5,6] The saccharides were added to the waste in the PUREX Solvent Extraction Plant to reduce the nitric acid concentration of the solution before neutralization with sodium hydroxide, whereas the polyaminocarboxylates were added to selectively remove metals. These organic compounds and their degradation products remain in the tanks today, and are a potential source of reducing equivalents for transition metals, and also a source of stabilizing ligands for the reduced metals.

Technetium-99 emerges from spent nuclear fuel processing as the pertechnetate ion (TcO$_4^-$) and is then sent to a waste tank for storage. Originally it was assumed that the technetium would remain as pertechnetate under the physical conditions of the waste storage tanks. However, SCHROEDER and co-workers[7] discovered that 50–75% of the ^{99}Tc in certain waste tanks had undergone chemical reduction to form soluble complexes. The identity of these complexes has not been determined. Furthermore, SCHROEDER and

co-workers[7–9] have shown that the complexes are difficult to separate on an anion-exchange column and are difficult to selectively oxidize back to pertechnetate. BLANCHARD and co-workers[10] obtained X-ray absorption near edge spectroscopy (XANES) data suggesting that the low-valent complexes are Tc(IV) species. Recently, LUKENS et al.,[2] using X-ray absorption fine structure (XAFS) and UV-vis spectroscopy data, have suggested the reduced, soluble complexes are binuclear Tc(IV) alkoxides.

There are at least two mechanisms by which pertechnetate can be reduced to either technetium dioxide or soluble complexes in strongly alkaline solution.[1,4,11] LUKENS et al.[11] have shown that under simulated tank waste conditions, radiolysis (^{60}Co source) of organic compounds produces radicals that are capable of generating NO$_3^{2-}$ from nitrates. The NO$_3^{2-}$ is then able to reduce pertechnetate to a lower oxidation state. In contrast, organic radicals produced from radiolysis of polyaminocarboxylates are unreactive towards pertechnetate.

We have also shown that catalytic reduction of pertechnetate by noble metals (Ru, Rh, and Pd) is a viable alternate mechanism.[4] These noble metals are products of uranium fission and are found in the tanks at low but catalytically useful concentrations. Under typical tank conditions (alkaline pH, temperature >60 °C) and in the presence of organics, these noble metals can form catalytically active zero-valent metal particles that are capable of reducing pertechnetate. Thus, we have shown that pertechnetate can be reduced to technetium dioxide and/or reduced, soluble complexes without radiolysis, in simulants containing Ru, Rh, and/or Pd in alkaline media.[4]

In our current work, we show that pertechnetate can form reduced, soluble complexes when combined with various ligands in alkaline media (2M NaOH), without the addition of any external reducing agents or radiolysis.

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Experimental

Safety precaution must be observed when handling ^{99}Tc because it is a weak beta-emitter ($E_{max} = 0.294$ MeV, $T_{1/2} = 2.15 \cdot 10^5$ y). All chemicals were reagent grade and used as received. Sodium pertechnetate was obtained from a stock solution (0.245M) in water. UV-vis spectroscopy and thin layer chromatography were used to determine the concentration and radiochemical purity of the pertechnetate solution, respectively. Silica gel strips (Whatman PE SIL G, 1 cm × 10 cm) on polyester support were used for thin layer chromatograpy (TLC) assays. Paper strips (Whatman Pure Cellulose Chromatography Paper, Grade 3MM Chr., 0.34 mm thick, cut to 1 cm × 10 cm) were used for paper chromatography (PC) assays. Radiochemical assays of the TLC or PC strips were performed on a Bioscan AR-2000 Imaging Scanner (Washington D.C., USA). UV-vis spectra were recorded on an Ocean Optics Inc. SD2000 system (Dunedin, FL, USA).

Typical experimental procedure

Glucose (2 mmol) was added to a scintillation vial as a solid. Water (1 ml) was added to the vial followed by sodium hydroxide solution (4M, 1 ml) to give a final concentration of 1M with respect to glucose. Sodium pertechnetate (0.245M, 82 μl) was added to the vial to give a final concentration of 0.01M technetium. The capped mixture was allowed to react at ambient temperature and pressure for up to four days.

Results and discussion

Initially, our goal was to reproduce the radiolysis method of Lukens et al.[11] at a synthetically useful scale to prepare ^{99}Tc complexes for further characterization by electrospray mass spectrometry. Without easy access to a $2.22 \cdot 10^7$ MBq ^{60}Co source, our samples containing elevated concentrations of ^{99}Tc and gluconate (0.01M and 1M, respectively) were placed next to a ^{137}Cs source (37 MBq) for irradiation. Despite the use of this weak radiation source (over five orders of magnitude smaller dose rate), the solutions turned pink within 24 hours, indicating formation of the ^{99}Tc-gluconate complex. As a control, an identical sample was allowed to react in the absence of ^{137}Cs radiation but exposed to standard laboratory lighting, and a third sample was kept in the dark for 24 hours. Both of the controls and the irradiated sample contained the ^{99}Tc-gluconate complex in approximately equal chemical yields, indicating that spontaneous reduction and complexation of ^{99}TcO$_4^-$ is possible without applying an external radiation source.

Because of this surprising result, we decided to survey the generality of this mechanism using a series of organic compounds that were intentionally added to the tank wastes during processing, as well as compounds that could be in the tanks today due to degradation. Solutions of the various ligands (1M) and ^{99}TcO$_4^-$ (0.01M) in sodium hydroxide (2M) were stored at room temperature for four days under ambient conditions. Ten microliters (approximately 1.85 MBq) of each reaction mixture was spotted onto either two TLC strips or PC strips via syringe. Each strip was developed in either water or acetone, then read with a scanning gas proportional detector (Bioscan instrument) to determine the chemical yield of the reductions.

Control experiments were performed to determine the movement of pertechnetate (^{99}TcO$_4^-$) and technetium dioxide (^{99}TcO$_2$) on both the TLC and PC strips. The strips were assayed as described above and any activity remaining at the origin of the strip developed in water was determined to be technetium dioxide. Pertechnetate activity was found to migrate to the top of the strips when developed in either water or acetone. When the reaction mixtures were developed, however, a third species was often observed that migrated with the solvent front in the case of water, but stayed at the baseline in the case of acetone. This third species was quantified by ^{99}Tc radiometric assay and reported as a reduced, soluble complex.

This method of separation and analysis of the reaction indicated that the ligands (Fig. 1 and Table 1) used in this study could be divided into three categories: (1) ligands that showed high reactivity (>15% yield of reduced complex), (2) ligands with slight reactivity (1–15% yield), and (3) ligands with no reactivity. The ligands that showed the greatest reactivity were in general mono- and disaccharides (Fig. 1). A typical chromatogram of a technetium complex developed by TLC and analyzed by the Bioscan is shown in Fig. 2. The ligands that showed slight reactivity were typically polyaminocarboxylates (Table 1). For this category of ligands, the exact radiochemical yield was difficult to determine. The reaction mixtures were slightly colored indicating some reactivity, but the products were unstable in air and repeated chromatography runs indicated re-oxidation of the complex to pertechnetate. This is consistent with the literature that indicate ^{99}Tc complexes of polyaminocarboxylates are unstable in air and at high pH.[8]

The ligands that show no reduction and no complex formation were, in general, the simpler alcohols, along with some polyaminocarboxylates (Table 1). Control experiments using water as the solvent also showed no reduction, indicating that alkaline solutions are needed for the reactions to occur.
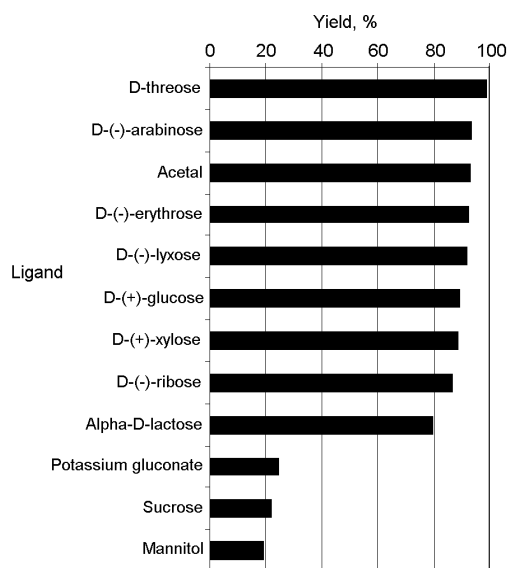
Yield, %

Fig. 1. Bar graph of ligand versus yield for the reduced, soluble ^{99}Tc complexes in greater than 15% yield

Initial experiments with potassium gluconate and sucrose indicated that mono- and disaccharides were a class of ligands with especially high reactivity. In further attempts to determine structural-activity relationships, we performed experiments with a variety of mono- and disaccharides, some of which have no known relationship to Hanford wastes. We tested the effect of non-reducing versus reducing disaccharides using sucrose and lactose. Sucrose is a non-reducing sugar because the anomeric carbon is not available for oxidation, whereas lactose has a free anomeric carbon for oxidation. Lactose produced approximately four times the amount of a reduced, soluble technetium complex as sucrose. The reduced, soluble technetium complex that was formed in the sucrose reaction (20%) can be attributed to a slow base hydrolysis of sucrose to generate the reducing monosaccharide glucose.

We investigated the effect of the number of carbon atoms and stereochemistry of the monosaccharides. One aldohexose (C_6; glucose), four aldopentoses (C_5; ribose, lyxose, xylose, and arabinose), and two aldotetroses (C_4; threose and erythrose) were run under identical conditions. There is no apparent correlation between the number of carbon atoms and the resulting yields, with all of the monosaccharides generating 90–100% of a reduced, soluble complex. We also wanted to determine the role of stereochemistry, i.e., whether certain stereoisomers would produce greater amounts of reduced technetium complexes, based upon thermodynamic stability of the chelate complexes formed. Again, there does not appear to be any correlation between yield and stereochemistry. Although we did not see any structural-activity relationships in these experiments, it is possible that more rigorous kinetic studies would reveal differential reactivity.

The last relationship we examined was the chemical form of a six-carbon monosaccharide. We compared glucose itself, an oxidized form of glucose (potassium gluconate), and glucose that is not readily accessible for oxidation without chemical break-down of a disaccharide (sucrose). Glucose, with an aldehyde carbon available for oxidation, formed the largest amount of reduced, soluble complex (89%). In contrast, sucrose and potassium gluconate showed lower reactivity, with only 22% and 24%, respectively. This lower activity can be attributed to the non-reducing nature of these saccharides. The reduction that did occur could be attributed to the decomposition of the saccharides in the alkaline solution, followed by reduction and complexation of the ^{99}Tc.

Selected samples were also analyzed by UV-vis spectroscopy. The UV-vis spectrum of the potassium gluconate reaction has a weak band at 500 nm ($\varepsilon = 80 M^{-1}$ cm^{-1}). Assuming the reaction is 25% complete as measured by TLC and PC, the weak band at 500 nm is consistent with the spectrum observed by Lukens et al.[2] who performed a similar experiment with a ^{60}Co source. These low extinction coefficients suggests that the complex is a Tc(V) diolate complex that is similar to the known bis(1,2-ethanediolato)-oxotechnetium(V), which has a weak ($\varepsilon = 60 M^{-1} \cdot cm^{-1}$) absorption at 535 nm.[12] To probe for the reactive substructures of gluconate, mannitol (C_6) and sodium acetate were separately reacted with pertechnetate. The mannitol, with only hydroxyl groups, was used to model the backbone of gluconate, while sodium acetate was a model for the carboxylate functionality. Mannitol is nearly as reactive as gluconate, reacting with TcO_4^- within four days to give 19% conversion, but no reaction was observed for acetate (Scheme 1). This suggests that the hydroxyl groups or the breakdown of the monosaccharides play a critical role in the formation of the soluble ^{99}Tc(V) complexes.

The UV-vis spectra of the aldopentose and aldotetrose reactions were recorded in 2M sodium hydroxide solutions. All of the technetium complexes of the four aldopentoses show a strong bands at 266 nm ($\varepsilon = 10,000 M^{-1}$ cm^{-1}). The UV-vis spectrum of the arabinose reaction with pertechnetate is shown in Fig. 3 as a typical example. The mono- and disaccharides in 2M NaOH are themselves intensely colored, and were used as blanks for the UV-vis experiments. The absorption spectra for the five-carbon sugars agreed well with the Tc(IV) ethylene glycol complex K_2Tc (ethylene glycol)$_3$ ($\lambda_{max} = 270$ nm) prepared from K_2TcBr_6 by Alberto and co-workers.[13] K_2Tc (ethylene glycol)$_3$ was reported to be stable in aqueous solutions at pH>10–11 but hydrolyzed as the pH decreased, and is, therefore, a plausible model complex for Hanford wastes.
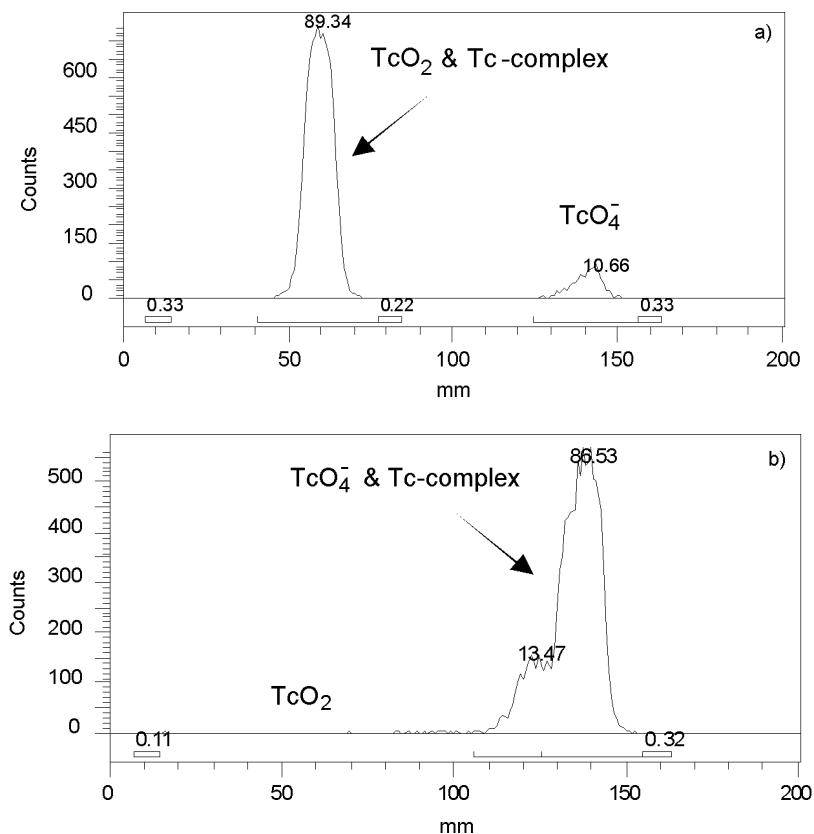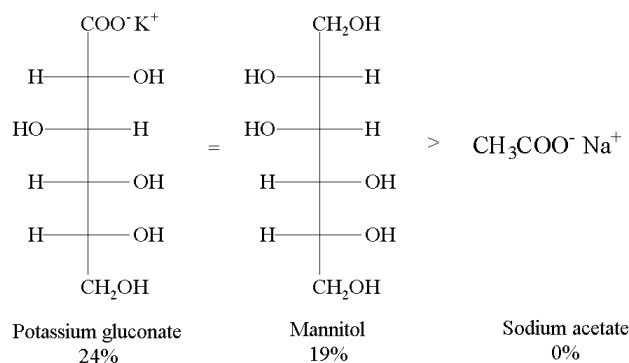
Fig. 2. Chromatograms of a solution containing 1M glucose, 0.01M TcO$_4^-$ in 2M NaOH. Chromatogram (a) is the mixture spotted on a TLC strip and developed in acetone, chromatogram (b) is a TLC strip developed in water. The strip was spotted at approximately 60 mm on this scale

Scheme 1.

The technetium complexes of the mono- and disaccharides (excluding potassium gluconate) also lacked weak bands in the 500–550 nm range that would indicate Tc(V) complexes. Based upon the absence of bands at 500–550 nm and the presence of bands in the 270 nm range, the complexes are presumed to be Tc(IV) species. This is consistent with the report by BLANCHARD and co-workers[10] indicating that the non-pertechnetate species in the tanks are Tc(IV) compounds.

Table 1. Ligands that had less than 15% of reduced soluble ^{99}Tc complex being formed. No ^{99}TcO$_2$ was detected in the reactions. All remaining activity was from ^{99}TcO$_4^-$

| Ligand	Reduced, soluble complex, %
Hydroxyethyl(ethylenediaminetriacetic acid)	12
Nitrolotriacetic acid	11
Malonic acid	9
Sodium oxalate	7
EDTA, tetrasodium salt	7
Polyethyleneimine polymer	3
2,3-Butanediol	2
Dibutylphosphate	0
Iminodiacetic acid	0
Succinic acid	0
Sodium citrate	0
N-(2-hydroxyethyl)iminodiacetic acid	0
Methyliminodiacetic acid	0
Ethanol	0
Ethylene glycol	0
Formaldehyde	0
Glycerol	0
Cis-1,2-cyclohexanediol	0
1,3-Propanediol	0
1,4-Butanediol	0
2,3-Dimethyl-2,3-butanediol	0
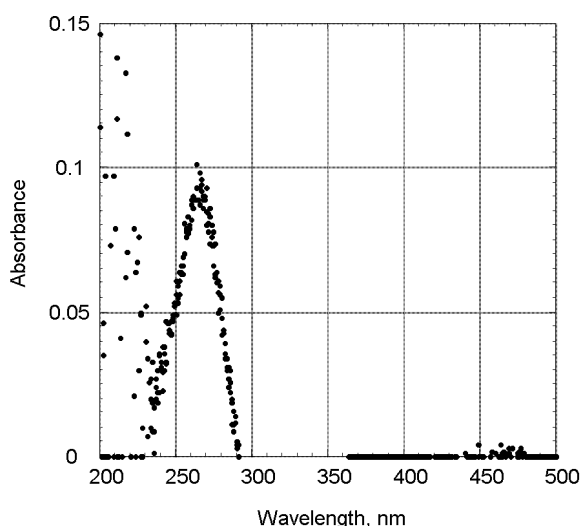
Fig. 3. Difference UV-vis spectrum of the reaction of Arabinose (1M) with pertechnetate (0.01M) in 2M sodium hydroxide. The blank is a 1M solution of Arabinose in 2M sodium hydroxide

Although our data strongly suggests that neither external radiation nor catalytic metals are needed for pertechnetate to be reduced to form soluble complexes, it could be postulated that that self-radiolysis is occurring via ^{99}Tc decay. However, there are striking differences between our experimental conditions and LUKENS'radiolysis procedures. First, our samples contained only 1.85 MBq of ^{99}Tc activity, whereas a $2.22 \cdot 10^7$ MBq ^{60}Co source was used in the radiolysis experiments, a difference of seven orders of magnitude in dose rate. To achieve the observed chemical yields in our experiments, every ^{99}Tc decay event would be required to spawn approximately 10^8 subsequent reductions of pertechnetate. Finally, LUKENS et al.[11] showed in control experiments that radiolytic reduction occurs via the NO$_3^{2-}$ intermediate, and not by direct reduction or indirectly through organic radicals. Our experiments contain no nitrate, thus it is highly improbable that the reactivity reported in this paper has any connection to radiolysis events.

Conclusions

We have shown that pertechnetate can be reduced to soluble Tc(IV/V) complexes in simple alkaline simulants of Hanford tank waste, without the addition of an external radiation source, catalytic metals, or other standard reductants such as Sn(II). The reactions of mono- and disaccharides with pertechnetate produce reduced, soluble Tc(IV) complexes in greater than 80% yield. Polyaminocarboxylates also appear to react with pertechnetate to form transiently stable complexes, while gluconate reduces pertechnetate to Tc(V). In hindsight, these reactions are not surprising considering the well known reduction ability of mono- and disaccharides. In fact, the Tollens Test for the presence of aldehydes and reducing sugars is based upon the reduction of silver nitrate to metallic silver. Thus, it appears that some of the reagents used at Hanford for denitration of acidic media can also act as direct reductants for pertechnetate under strongly basic conditions. Although the mechanism by which pertechnetate is being reduced in Hanford wastes may never be completely understood, we have shown that direct reduction, non-radiolytic reduction by known waste consituents is a viable process.

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