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Radiolysis of TcO_4^- in Alkaline, Nitrate Solutions: Reduction by NO_3^{2-}

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The radiation chemistry of pertechnetate has been examined in highly alkaline solution. In the presence of selected, organic O^- scavengers, radiolysis reduces TcO_4^- with varying radiation chemical yields, which depend on the reduction potentials of the organic radicals produced during radiolysis. When aminopolycarboxylates are used as O^- scavengers, the radiation chemical yield for pertechnetate reduction, $G(-TcO_4^-)$ is equal to 1/3 $G(e_{aq}^-)$, which strongly implies that the organic radicals produced by the reaction of O^- with aminopolycarboxylates are unreactive toward the technetium species present in solution. In the presence of excess nitrate, TcO_4^- is still efficiently reduced during radiolysis when aminopolycarboxylates are used as O^- scavengers. This observation is consistent with the reduction of TcO_4^- by NO_3^{2-}.

Introduction

The radiation chemistry of nitrate solutions has recently received increasing attention due, in part, to its relevance to the chemistry of high-level nuclear waste.[1] Specifically, the high-level nuclear waste stored in underground tanks at the Savannah River and Hanford Sites is highly alkaline and contains high concentrations of nitrate and nitrite. In these tanks, the radiation source is the decay of ^{137}Cs and ^{90}Sr.[2] In addition, certain tanks also contain lower concentrations of several organic ions including formate, oxalate, glycolate, acetate, iminodiacetate (IDA), nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA), 2-hydroxyethylethylenediaminetriacetate (HEDTA), and citrate.[2,3] Because of this variety of ions and molecules, the thermal and radiation chemistries of these tanks are complex and can produce unexpected chemical changes in the species present.

One example is the discovery of reduced technetium species in high-level waste.[4] Although the most stable form of technetium at pH > 10 is pertechnetate, TcO_4^-,[5] a large fraction of lower-valent technetium complexes was found in certain waste tanks. These tanks contain relatively high concentrations of ^{137}Cs and aminopolycarboxylates including HEDTA, NTA, and IDA. This combination has aroused suspicion that radiolysis of TcO_4^- was responsible for the presence of reduced technetium species. However, these tanks contain concentrations of nitrate and nitrite up to 5 orders of magnitude greater than that of TcO_4^-.[2] The large excess of nitrate prevents the reducing primary radiolysis product, e_{aq}^-, from reducing TcO_4^- at an appreciable rate. In addition, TcO_4^- cannot be readily reduced by organic radicals produced by radiolysis since nitrite reacts quickly with reducing organic radicals.[6] For these reasons, direct reduction of TcO_4^- by the primary radiolysis products seems unlikely in the presence of high concentrations of nitrate and nitrite. In addition, reduction of TcO_4^- by certain organic chemicals in alkaline solution can be catalyzed by the colloids of the fission products Pt, Rh, and Ru.[7]

To improve the understanding of fundamental technetium chemistry relevant to high level tank waste, the radiolysis of TcO_4^- was studied in highly alkaline solutions containing selected organic molecules. In addition, the radiolysis of TcO_4^- was studied in solutions containing IDA or NTA and different concentrations of nitrate. The radiation chemical yields for loss of TcO_4^-, $G(-TcO_4^-)$, reported in molecules/100 eV, was sensitive to the reduction potentials of the radicals produced during radiolysis. Surprisingly, in the presence of 0.2 M $NaNO_3$ and 0.1 M NTA or IDA, $G(-TcO_4^-)$ was large, 15−20% of the yield when NO_3^- was absent. The results support a mechanism in which TcO_4^- is reduced by NO_3^{2-} at a much greater rate than the reaction of NO_3^{2-} with water.

Experimental Section

Caution: ^{99}Tc is a β-emitter ($E_{max} = 294$ keV, $\tau_{1/2} = 2 \times 10^5$ years). All operations were carried out in a radiochemical laboratory equipped and approved for handling this isotope. Pertechnetate, as $NH_4{}^{99}TcO_4$, was obtained from Oak Ridge National Laboratory. The solid $NH_4{}^{99}TcO_4$ was contaminated with a large amount of dark, insoluble material. Prolonged treatment of this sample with H_2O_2 and NH_4OH did not appreciably reduce the amount of dark material. Ammonium pertechnetate was separated by carefully decanting the colorless solution from the dark solid. To the colorless solution, a small amount of NaOH was added, and the volatile components were removed under vacuum. The remaining solid was dissolved in water, and the colorless solution was removed from the remaining precipitate using a cannula. The concentration of sodium pertechnetate was determined spectrophotometrically at 289 nm ($\epsilon = 2380$ M l^{-1} cm^{-1}).[8] UV−visible spectra were obtained using an Ocean-Optics ST2000 spectrometer.

All operations were carried out in air except as noted. Water was deionized, passed through an activated carbon cartridge to remove organic material, and then distilled. Iminodiacetic acid was recrystallized three times from water. All other chemicals were used as received.

Radiolysis Experiments. Solutions for radiolysis experiments were freshly prepared by weighing the appropriate amounts of sodium hydroxide, organic compound, and sodium nitrate or sodium nitrate solution into a volumetric flask then preparing the sample solution. To a known volume of sample solution,

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$NaTcO_4$ (3.9×10^{-2} M) was added to give the desired concentration of TcO_4^-; an identical volume of water was added to the reference solution. A Cu(II)/Fe(II) (Hart) dosimeter with 0.002 M Fe(II), 0.010 M Cu(II), and 0.010 M H_2SO_4, or an oxygen-saturated Fricke dosimeter was used to record the radiation dose.[9,10] A set of three tubes (sample with TcO_4^-, chemical dosimeter, sample without TcO_4^-) was positioned equidistant from a 600 Ci ^{60}Co source. In a given experiment, three or five different sets of tubes were placed at varying distances from the ^{60}Co source and irradiated for the same period of time. The tubes were contained in an aluminum box with a 0.25 in. thick polycarbonate window. For radiolysis experiments with added nitrate, the samples were purged with argon by filling the headspace (~1 mL) with argon and vigorously shaking the tube for 10 s. This process was repeated three times.

Radiolysis Data Treatment. All radiation-chemical yields are reported as molecules/100 eV. The radiation doses absorbed by the samples were determined from the Hart dosimeters and were corrected for the different compositions of the dosimeter and sample solutions, for the relative positions of the dosimeter and sample to the source. In addition, the response of the Fe(II)/Cu(II) dosimeter with a 5:1 Fe/Cu ratio was found to be slightly nonlinear in comparison to the oxygen-saturated Fricke dosimeter; this nonlinearity was corrected. At low absorbed doses, the absorbed dose was calculated using oxygen-saturated Fricke dosimeters. UV−visible spectra were collected from the pertechnetate-containing solutions, using the solutions without pertechnetate as references. The concentration of pertechnetate was determined by fitting the spectra. Unirradiated samples were used to determine the initial concentration of TcO_4^- and the position and line width of the TcO_4^- peaks. Only the heights of the TcO_4^- peaks were allowed to vary when fitting the spectra of irradiated samples. The presence of additional radiolysis products was treated by including additional peaks in the fit.

The radiation chemical yields for the primary radiolysis radicals were calculated using the method derived by Schuler.[11,12] The yield of hydrogen atoms g(H•) is 0.55. The yield of hydrated electrons $g(e_{aq}^-)$ was determined using eq 1

$$g(e_{aq}^-) = \frac{g(H\cdot)k_{H\cdot+OH-}[OH^-]}{k_{H\cdot+OH-}[OH^-] + k_{H\cdot+RH}[RH]} + 2.55 + 2.33\frac{\sqrt{\sum k[S]/\lambda}}{1+\sqrt{\sum k[S]/\lambda}} \quad (1)$$

where the left-hand term is the fraction of hydrogen atoms that react with hydroxide to form hydrated electrons ($k_{H\cdot+OH-}$ is the rate constant for the reaction of H• with OH− and $k_{H\cdot+RH}$ is the rate constant for the reaction of H• with the organic species), and the right-hand side is the yield of hydrated electrons corrected for scavenging from spurs; $k[S]$ is the rate of reaction of substrate S with hydrated electrons, and λ is 8×10^8 s^{-1}.[11] Similarly, the yield of oxide radical ions was determined using eq 2

$$g(O^-) = 2.7 + 1.5\frac{\sqrt{\sum k[S]/\lambda}}{1+\sqrt{\sum k[S]/\lambda}} \quad (2)$$

where $k[S]$ is the rate of reaction of substrate S with hydroxyl radicals, and λ is 4.7×10^8 s^{-1}.[12] Hydroxide was not included as a substrate in the calculation of $g(O^-)$.

Results and Discussion

To interpret the radiation chemical yield for the reduction of pertechnetate, $G(-TcO_4^-)$, the oxidation state of the technetium radiolysis product must be identified to determine the number of reducing equivalents needed to remove a pertechnetate ion from solution. Based on known chemistry, radiolysis of TcO_4^- requires three reducing equivalents and produces Tc(IV) as the radiolysis product:[13−18]

$$TcO_4^- + e_{aq}^- \rightarrow TcO_4^{2-} \qquad k_3 = 2.5 \times 10^{10}\ M^{-1}\ s^{-1} \quad (3)$$

$$2TcO_4^{2-} \rightarrow TcO_4^- + Tc(V) \qquad k_4 = 1.5 \times 10^{5}\ M^{-1}\ s^{-1} \quad (4)$$

$$2Tc(V) \rightarrow TcO_4^{2-} + Tc(IV) \qquad k_5 = 2.4 \times 10^{3}\ M^{-1}\ s^{-1} \quad (5)$$

$$Tc(V) + TcO_4^{2-} \rightarrow Tc(IV) + TcO_4^- \quad (6)$$

Pertechnetate reacts very quickly with hydrated electrons, yielding technetate, TcO_4^{2-}.[13−15] Technetate disproportionates with a bimolecular rate constant of 1.5×10^5 M^{-1} s^{-1} in alkaline solution.[16] Similarly, in the absence of stabilizing ligands, Tc(V) is known to disproportionate rapidly with a bimolecular rate constant of 2.4×10^3 M^{-1} s^{-1}.[17] Alternatively, Tc(V) species could be reduced by TcO_4^{2-}, which is a moderately strong reducing agent, $E°(TcO_4^-/TcO_4^{2-}) = -0.64$ V vs NHE.[14,18] For these reasons, Tc(IV), as $TcO_2\cdot xH_2O$, is the likely radiolysis product in alkaline solutions in the absence of ligands capable of forming Tc(V) or Tc(IV) complexes that are stable at high pH. The supposition that Tc(IV) is the final oxidation state is strongly supported by the observation that the major radiolysis product is a dark precipitate in the absence of diolate ligands, which can form soluble, lower valent technetium complexes in highly alkaline solution.[19,20] The dark precipitate is spectroscopically identical to $TcO_2\cdot xH_2O$ produced by hydrolysis of $TcCl_6^{2-}$ as determined by X-ray absorption fine structure and electron paramagnetic spectroscopy.[21] In addition to the insoluble radiolysis product, a minor, soluble radiolysis product is usually observed. However, the principal radiolysis product is $TcO_2\cdot xH_2O$, as expected.

The effect of selected organic molecules upon the radiolytic reduction of TcO_4^- was examined in 2 M NaOH; these results, plus data previously reported by Pikaev and co-workers,[22] are reported in Table 1. In 2 M NaOH, hydroxyl radicals are rapidly converted to oxide radical anions, O^-; therefore, O^- can be treated as the primary oxidizing radical produced by radiolysis.[23] The organic molecules studied rapidly scavenge O^- radicals yielding organic radicals and preventing the oxidation of the reduced technetium species by O^-.[23] The hydrated electrons produced during radiolysis reduce TcO_4^-, removing it from solution with a radiation chemical yield, $G(-TcO_4^-)$, of 1/3 $g(e_{aq}^-)$. The deviation of $G(-TcO_4^-)$ from this value can be explained using the reduction potentials of the organic radicals.

When the organic scavengers are primary or secondary alcohols, α-hydroxyalkyl radicals are produced by H-abstraction from the alcohol. These radicals are strongly reducing, e.g., $E°[(CH_3)_2CO,H^+/(CH_3)_2C^{\bullet}OH] = -1.7$ V, and are even more strongly reducing when deprotonated.[24] In fact, 2-hydroxy-2-propyl radical reduces TcO_4^- with a rate constant of 7×10^8 M^{-1} s^{-1}.[15] Since these radicals reduce TcO_4^-, the predicted value of $G(TcO_4^-)$ is $1/3[g(e_{aq}^-) + g(R\cdot)]$, where g(R•) is the yield of organic radicals produced from H-abstraction by O^- and H•. The first two entries in Table 1 show that the observed $G(-TcO_4^-)$ values are in good agreement with this prediction.

TABLE 1: Observed Radiation-Chemical Yields for the Loss of TcO_4^- in the Presence of Selected Organic Molecules

organic	$[TcO_4^-]$ mM	[organic] M	$G_{obs}(-TcO_4^-)$	$G_{calc}(-TcO_4^-)$	ref
ethanol	5	0.1	2.7	2.4[a]	22
methanol	5	0.1	2.5	2.5[a]	22
EDTA	5	0.04	1.2	1.2[b]	22
NTA	0.2	0.1	1.0	1.0[b]	this work
IDA	0.2	0.1	0.9	1.0[b]	this work
acetate	1.2	0.5	0.1		this work
citrate	1.2	0.5	0.5		this work
ethylene glycol	1.2	0.5	0.4		this work

[a] $G_{calc}(-TcO_4^-) = (g(e_{aq}^-) + g(R\cdot))/3$ [b] $G_{calc}(-TcO_4^-) = g(e_{aq}^-)/3$

TABLE 2: Observed and Calculated Radiation-Chemical Yields for the Loss of TcO_4^- in 2 M NaOH, 0.1 M IDA or NTA at Various Nitrate Concentrations

$[NO_3^-]$	$G(-TcO_4^-)$ NTA[a,b]	$G(-TcO_4^-)$ IDA[a,b]
0.20	-	0.13(1)
0.10	0.16(1)	0.12(2)
0.05	0.17(3)	0.13(1)
0.01	0.22(1)	0.17(1)
0.005	0.29(7)	0.21(1)
0.001	0.50(3)	0.50(3)
0	1.0(1)	0.90(3)

[a] Standard error from fitting the radiolysis data is given in parentheses. [b] Radiation-chemical yields in ions/100 eV.

On the other hand, if the organic radicals are capable of oxidizing reduced technetium species, the observed $G(-TcO_4^-)$ values will be smaller than 1/3 $g(e_{aq}^-)$. For example, the calculated standard potential of the radical produced by H-abstraction from acetate, $E°(\cdot CH_2CO_2^-,H^+/CH_3CO_2^-) = 1.7$ V,[25] is similar to that of O^-.[26] Consequently, this radical can oxidize reduced technetium species. As a result, $G(-TcO_4^-)$ will be smaller than 1/3 $g(e_{aq}^-)$, although the value of $G(-TcO_4^-)$ cannot be predicted without knowing the rates of reaction of the organic radicals with each other and with the reduced technetium species. As shown by the lower entries in Table 1, H-abstraction from certain organic molecules produces radicals capable of oxidizing reduced technetium species. The fact that radicals produced from citrate are oxidizing is not surprising since the carbon-centered radical of citrate is α to the carboxylate group as in the acetate radical. Similarly, the 1,2-dihydroxyethyl radical, produced by H-atom abstraction from ethylene glycol, rapidly dehydrates in alkaline solution to form the oxidizing formylmethyl radical.[27]

The radicals produced by the reaction of O^- with the aminopolycarboxylates EDTA, IDA, and NTA appear to be unreactive toward both pertechnetate and reduced technetium species. In the presence of these molecules, the $G(-TcO_4^-)$ can be attributed to reduction by e_{aq}^- alone, as shown in Table 1. However, a similar radiation-chemical yield could be obtained if radicals produced from the aminopolycarboxylates both reduced TcO_4^- and oxidized reduced technetium species. Such a scenario is suggested by the known radiation chemistry of glycine.[28]

Strongly reducing $H_2N-CH_2^{\bullet}$ radicals result from decarboxylation of the $H_2N^{+\bullet}-CH_2-CO_2^-$ radical produced by oxidation of glycine anion, eq 7, and oxidizing $HN^{\bullet}-CH_2-CO_2^-$ radicals are produced by H-atom abstraction from the amino group, eq 8. However, the reduction potential for the $H_2N^{+\bullet}-CH_2-CO_2^-$ radical is calculated to be 1.6 V,[29] which is much greater than the 0.94 V reduction potential of O^- in 2 M NaOH.[26] Therefore, reaction 7 will not occur at high pH where O^-, rather than $HO^{\bullet}$, is present. The calculated reduction potential of the principal radical produced during radiolysis of glycine, $H_2N-C^{\bullet}H-CO_2^-$, eq 9, is 0.26 V in 2 M NaOH, which is insufficient to reduce TcO_4^-.

$$H_2NCH_2CO_2^- + HO\bullet \rightarrow HO^- + H_2NCH_2CO_2^{\bullet} \rightarrow H_2NCH_2^{\bullet} + CO_2 \quad (7)$$

$$H_2NCH_2CO_2^- + HO\bullet \rightarrow H_2O + HN^{\bullet}CH_2CO_2^- \quad (8)$$

$$H_2NCH_2CO_2^- + HO\bullet \rightarrow H_2O + H_2NC^{\bullet}HCO_2^- \quad (9)$$

Radiolysis of TcO_4^- in the Presence of NO_3^-. Since the C-centered radicals produced during radiolysis of IDA and NTA are unreactive toward technetium species, these molecules represent excellent scavengers for use in studying the radiolysis of technetium in the presence of nitrate. The basic radiation chemistry of nitrate is given in eqs 10−12.[1,30,31]

$$NO_3^- + e_{aq}^- \rightarrow NO_3^{2-} \quad k_{10} = 9.7 \times 10^9\ M^{-1}\ s^{-1} \quad (10)$$

$$NO_3^{2-} + H_2O \rightarrow NO_2^{\bullet} + 2HO^- \quad k_{11} = 1 \times 10^3\ M^{-1}\ s^{-1} \quad (11)$$

$$2NO_2^{\bullet}\ (+\ H_2O) \rightarrow NO_3^- + NO_2^- + 2H^+ \quad k_{12} = 6 \times 10^7\ M^{-1}\ s^{-1} \quad (12)$$

In solutions containing both NO_3^- and TcO_4^-, NO_3^- acts as a scavenger of e_{aq}^-, in competition with TcO_4^-. Since the reaction rates for NO_3^- and TcO_4^- with e_{aq}^- are known, the fraction of e_{aq}^- that react with TcO_4^- can be determined.

The observed radiation chemical yields for TcO_4^- reduction in solutions of 2 M NaOH, 0.1 M NTA or IDA, and various concentrations of nitrate are listed in Table 2. At high nitrate concentrations, $G(-TcO_4^-)$ is much larger than can be explained by the reaction of TcO_4^- with e_{aq}^-. For example, in 0.1 M $NaNO_3$ and 0.1 M NTA, $G(-TcO_4^-)$ is 0.19; if only e_{aq}^- were reducing TcO_4^-, the radiation-chemical yield would be 0.01. Since the organic radicals produced from aminopolycarboxylates do not react with technetium species, the only radiolysis product capable of reducing TcO_4^- is NO_3^{2-} ($E°(NO_3^-/NO_3^{2-}) = -0.89$ V),[1] eq 13.

$$TcO_4^- + NO_3^{2-} \rightarrow TcO_4^{2-} + NO_3^- \quad (13)$$

If only NO_3^{2-} and e_{aq}^- reduce TcO_4^-, the mechanism for radiolysis of TcO_4^- is simple: TcO_4^- and NO_3^- compete for e_{aq}^-, and TcO_4^- and H_2O compete for NO_3^{2-}. The expected radiation chemical yield $G(-TcO_4^-)$ is then given by eq 14, where k_n is the rate constant for the reaction given in equation n.

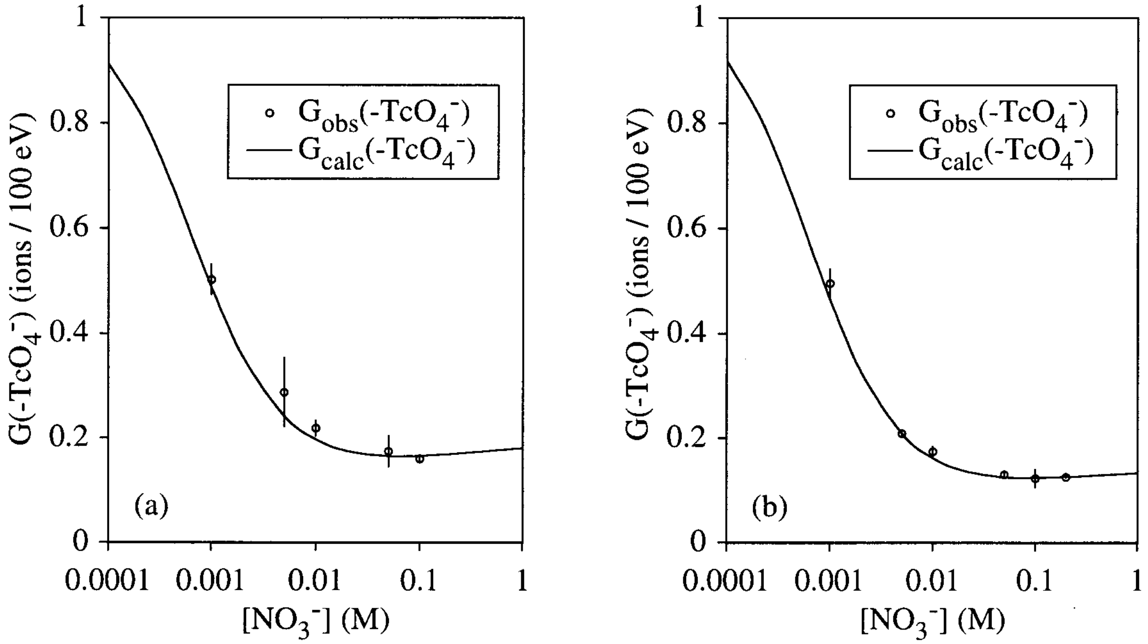

Figure 1. Radiation-chemical yield for loss of TcO_4^- in 2 M NaOH with (a) 0.1 M NTA and (b) 0.1 M IDA as a function of nitrate concentration. The data are represented by the circles with the standard error represented by vertical lines. A least-squares fit of the data to eq 14 is represented by the solid line.

$$G(-TcO_4^-) = \frac{g(e_{aq}^-)}{3(k_3[TcO_4^-] + k_{10}[NO_3^-])} \times \left\{k_3[TcO_4^-] + k_{10}[NO_3^-]\frac{k_{13}[TcO_4^-]}{(k_{13}[TcO_4^-] + k_{11}[H_2O])}\right\} \quad (14)$$

The results in Table 2 are presented graphically in Figure 1 along with a least-squares fit of the data to eq 14 using k_{13}, the rate constant for the reaction of TcO_4^- with NO_3^{2-}, as the only variable. The agreement between the data and the fit is good; however, the two sets of experiments give slightly different values for k_{13}. Radiolysis in the presence of NTA gives $k_{13} = 2.9(2) \times 10^7\ M^{-1}\ s^{-1}$, while radiolysis in the presence of IDA gives the slightly lower value of $2.2(2) \times 10^7\ M^{-1}\ s^{-1}$; the standard errors are in parentheses. Although these experiments do yield slightly different rate constants, rate constants derived from γ-radiolysis data are inherently less accurate and less precise than rates determined using pulse radiolysis.[23] For this reason, the rates are not sufficiently different to warrant discussion.

The reduction of TcO_4^- by NO_3^{2-} is considerably slower than the reduction of TcO_4^- by 2-hydroxy-2-propyl radical.[15] The slower rate is consistent with the smaller equilibrium constant of reaction 13, based on the reduction potentials of the species involved, and with the fact that reaction 13 involves two negatively charged substrates. The reaction of NO_3^{2-} with TcO_4^- may also be compared with other reactions of NO_3^{2-}. NO_3^{2-} reduces O_2, benzoquinone, and methyl viologen with rate constants of 2.3×10^8, 7.6×10^8, and $3.3 \times 10^9\ M^{-1}\ s^{-1}$, respectively.[31] Again, these rate constants are considerably greater than k_{13}, for the reasons noted above.

Although the reaction of NO_3^{2-} with TcO_4^- is considerably slower than the other electron-transfer reactions of NO_3^{2-}, the reaction of NO_3^{2-} with TcO_4^- is much faster than the hydrolysis of NO_3^{2-}.[1,31] The main effect of this difference in rate is the relatively high efficiency of the reduction of TcO_4^- in concentrated nitrate solution provided that molecules capable of scavenging O^- are present. When $[NO_3^-] \gg [TcO_4^-]$ and $k_{11}[H_2O] \gg k_{13}[TcO_4^-]$, $G(-TcO_4^-)$ can be approximated using eq 15.[32]

$$G(-TcO_4^-) \approx \frac{g(e_{aq}^-)k_{13}[TcO_4^-]}{3k_{11}[H_2O]} \quad (15)$$

Conclusion

The γ-radiolysis of TcO_4^- in highly alkaline solution in the presence of selected organic compounds and nitrate has been examined. In highly alkaline solution, the radicals produced by radiolysis from the aminopolycarboxylates, EDTA, NTA, and IDA, are unreactive toward the technetium species present in solution. These observations strongly suggest that only unreactive C-centered radicals are produced during radiolysis of aminopolycarboxylates under these conditions. In the presence of O^- scavengers, radiolysis of TcO_4^- in nitrate solutions proceeds through reduction of TcO_4^- by NO_3^{2-}.

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References and Notes

(1) (a) Fessenden, R. W.; Meisel, D.; Camaioni, D. M. *J. Am. Chem. Soc.* **2000**, *122*, 3773. (b) Cook, A. R.; Dimitrijevic, N.; Dreyfus, B. W.; Meisel, D.; Curtiss, L. A.; Camaioni, D. M. *J. Phys. Chem. A* **2001**, *105*, 3658.

(2) Agnew, S. F.; *Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev 4.*, LA-UR-96−3860; Los Alamos National Laboratory: Los Alamos, NM, 1996.

(3) (a) Toste, A. P.; Osborn, B. C.; Polach, K. J.; Lechner-Fish, T. J. *J. Radioanal. Nucl. Chem.* **1995**, *194*, 25. (b) Meacham, J. E.; Cowley, W. L.; Webb, A. B.; Kirch, N. W.; Lechelt, J. A.; Reynolds, D. A.; Stauffer, L. A.; Bechtold, D. B.; Camaioni, D. M.; Gao, F.; Hallen, R. T.; Heasler, P. G.; Huckaby, J. L.; Scheele, R. D.; Simmons, C. S.; Toth, J. J.; Stock, L. M. *Organic Complexant Topical Report*, HNF−SD-WM-CN-058, Rev. 0, Duke Engineering Services Hanford, Inc.: Richland, WA, 1998. (c) Campbell, J. A.; Stromatt, R. W.; Smith, M. R.; Koppenaal, D. W.; Bean, R. M.; Jones, T. E.; Strachan, D. M.; Babad, H. *Anal. Chem.* **1994**, *66*, 1208A.

(4) Schroeder, N. C.; Radzinski, S.; Ball, J. R.; Ashley, K. R.; Cobb, S. L.; Cutrell, B.; Whitener; G. *Technetium Partitioning for the Hanford Tank Waste Remediation System: Anion Exchange Studies for Partitioning Technetium from Synthetic DSSF and DSS Simulants and Actual Hanford Waste (101-SY and 103-SY) Using Reillex^{tm}-HPQ Resin*, LA-UR-95−4440; Los Alamos National Laboratory: Los Alamos, NM, 1995.

(5) Meyer, R. E.; Arnold, W. D. *Radiochim. Acta* **1991**, *55*, 19.

(6) Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 253.

(7) Bernard, J. G.; Bauer, E.; Richards, M. P.; Arterburn, J. B.; Chamberlin, R. M. *Radiochim. Acta* **2001**, *89*, 59.

(8) Colton, R. *The Chemistry of Technetium and Rhenium*; Interscience Publishers: New York, 1965.

(9) Hart, E. J. *Radiation Res.* **1955**, *2*, 33.

(10) Fricke, H.; Hart, E. J.; *Radiation Dosimetry*; Attix, F. H., Roesch, W. C., Eds.; Academic Press: New York, 1966; Vol II, p 186ff.

(11) Balkas, T. I.; Fendler, J. H.; Schuler, R. H. *J. Phys. Chem.* **1970**, *74*, 4497.

(12) Schuler, R. H.; Hartzell, A. L.; Behar, B. *J. Phys. Chem.* **1981**, *85*, 192.

(13) Pikaev, A. K.; Kryuchkov, S. V.; Kuzina, A. F.; Spitsyn, V. I. *Dokl. Akad., Nauk SSSR* **1977**, *236*, 1155.

(14) Deutsch, E.; Heineman, W. R.; Hurst, R.; Sullivan, J. C.; Mulac, W. A.; Gordon, S. *J. Chem. Soc., Chem. Commun.* **1978**, 1038.

(15) Lisbon, K.; Sullivan, J. C.; Mulac, W. A.; Gordon, S.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 375.

(16) Kissel, G.; Feldberg, S. W. *J. Phys. Chem.* **1969**, *73*, 3082.

(17) Koltunov, V. S.; Gomonova, T. V. *Radiokhim.* **1984**, *26*, 322.

(18) Founta, A.; Aikens, D. A.; Clark, H. M. *J. Electroanal. Chem.* **1987**, *219*, 221.

(19) Alberto, R.; Anderegg, G.; May, K. *Polyhedron* **1986**, *5*, 2107.

(20) Davison, A.; DePamphilis, B. V.; Jones, A. G.; Franklin, K. J.; Lock, C. J. L. *Inorg. Chim. Acta* **1987**, *128*, 161.

(21) Lukens, W. W.; Bucher, J. J., Edelstein, N. M.; Shuh, D. K. manuscript to be submitted to *Environ. Sci. Technol.*

(22) Pikaev, A. K.; Gogolev, A. V.; Kryutchkov, S. V.; Shilov, V. P.; Chulkov, V. N.; Belyaeva, L. I.; Astafurova, L. N. *Radiolysis of Actinides and Technetium in Alkaline Media*, WHC-EP-0901; Westinghouse Hanford Company: Richland, WA, 1996.

(23) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

(24) Schwartz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409.

(25) Yu, D.; Rauk, A.; Armstrong, D. A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2207.

(26) Kläning, U. K.; Sehested, K.; Holcman, J. *J. Phys. Chem.* **1985**, *89*, 760.

(27) (a) Bansal, K. M.; Grätzel, M.; Henglein, A.; Janata, E. *J. Phys. Chem.* **1973**, *77*, 16. (b) Steenken, S. *J. Phys. Chem.* **1979**, *83*, 595.

(28) (a) Bonifacic, M.; Stefanic, I.; Hug, G. L.; Armstrong, D. A.; Asmus, K. D. *J. Am. Chem. Soc.* **1998**, *120*, 9930. (b) Hug, G. L.; Fessenden, R. W. *J. Phys. Chem. A.* **2000**, *104*, 7021.

(29) Armstrong, D. A.; Rauk, A.; Yu, D. *J. Chem. Soc., Perkin Trans. 2* **1995**, 553.

(30) (a) Daniels, M.; Wigg, E. E. *J. Phys. Chem.* **1967**, *71*, 1024. (b) Daniels, M.; Wigg, E. E. *J. Phys. Chem.* **1969**, *73*, 3703. (c) Daniels, M. *J. Phys. Chem.* **1969**, *73*, 3710. (d) Grätzel, M.; Henglein, A.; Lilie, J. Beck, G. *Ber. der Bunsen-Ges.* **1969**, *73*, 646.

(31) Forni, L. G.; Mora-Arellano, V. O.; Packer, J. E.; Willson, R. L. *J. Chem. Soc., Perkin Trans 2* **1986**, 1.

(32) Assuming that all of the energy is absorbed, a solution containing 0.25 Ci l^{-1} of ^{137}Cs and an organic compound to scavenge O$^-$ will reduce TcO$_4^-$ with a half-life of approximately 80 days according to eq 15.