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## Radiolysis of $\text{TcO}_4^-$ in Alkaline, Nitrate Solutions: Reduction by $\text{NO}_3^{2-}$

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**Abstract.** The radiation chemistry of pertechnetate has been examined in highly alkaline solution. In the presence of selected, organic  $\text{O}^-$  scavengers, radiolysis reduces  $\text{TcO}_4^-$  with varying radiation chemical yields, which depend upon the reduction potentials of the organic radicals produced during radiolysis. When aminopolycarboxylates are used as  $\text{O}^-$  scavengers, the radiation chemical yield for pertechnetate reduction,  $G(-\text{TcO}_4^-)$  is equal to  $1/3 G(e_{\text{aq}}^-)$ , which strongly implies that the organic radicals produced by the reaction of  $\text{O}^-$  with aminopolycarboxylates are unreactive towards the technetium species present in solution. In the presence of excess nitrate,  $\text{TcO}_4^-$  is still efficiently reduced during radiolysis when aminopolycarboxylates are used as  $\text{O}^-$  scavengers. This observation is consistent with the reduction of  $\text{TcO}_4^-$  by  $\text{NO}_3^{2-}$ .

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**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.<sup>1</sup> 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  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ .<sup>2</sup> 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.<sup>2,3</sup> Because of this variety of ions and molecules, the thermal and radiation chemistry 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.<sup>4</sup> Although the most stable form of technetium at  $\text{pH} > 10$  is pertechnetate,  $\text{TcO}_4^-$ ,<sup>5</sup> a large fraction of lower-valent technetium complexes was found in certain waste tanks. These tanks contain relatively high concentrations of  $^{137}\text{Cs}$  and aminopolycarboxylates including HEDTA, NTA, and IDA. This combination has aroused suspicion that radiolysis of  $\text{TcO}_4^-$  was responsible for the presence of reduced technetium species. However, these tanks contain concentrations of nitrate and nitrite up to five orders of magnitude greater than that of  $\text{TcO}_4^-$ .<sup>2</sup> The large excess of nitrate prevents the reducing primary radiolysis product,  $e_{\text{aq}}^-$ , from reducing  $\text{TcO}_4^-$  at an appreciable rate. In addition,  $\text{TcO}_4^-$  cannot be readily reduced by organic radicals produced by radiolysis since nitrite reacts quickly with reducing organic radicals.<sup>6</sup> For these reasons, direct reduction of  $\text{TcO}_4^-$  by the primary radiolysis products seems unlikely in the presence of high

concentrations of nitrate and nitrite. In addition, reduction of  $\text{TcO}_4^-$  by certain organic chemicals in alkaline solution can be catalyzed by the colloids of the fission products Pt, Rh, and Ru.<sup>7</sup>

To improve the understanding of fundamental technetium chemistry relevant to high level tank waste, the radiolysis of  $\text{TcO}_4^-$  was studied in highly alkaline solutions containing selected organic molecules. In addition, the radiolysis of  $\text{TcO}_4^-$  was studied in solutions containing IDA or NTA and different concentrations of nitrate. The radiation chemical yields for loss of  $\text{TcO}_4^-$ ,  $G(-\text{TcO}_4^-)$ , reported in molecules / 100 eV, was sensitive to the reduction potentials of the radicals produced during radiolysis. Surprisingly, in the presence of 0.2M  $\text{NaNO}_3$  and 0.1M NTA or IDA,  $G(-\text{TcO}_4^-)$  was large, 15-20% of the yield when  $\text{NO}_3^-$  was absent. The results support a mechanism in which  $\text{TcO}_4^-$  is reduced by  $\text{NO}_3^{2-}$  at a much greater rate than the reaction of  $\text{NO}_3^{2-}$  with water.

**Experimental Caution:**  *$^{99}\text{Tc}$  is a  $\beta$ -emitter ( $E_{max} = 294 \text{ keV}$ ,  $\tau_{1/2} = 2 \times 10^5 \text{ years}$ ).* All operations were carried out in a radiochemical laboratory equipped and approved for handling this isotope. Pertechnetate, as  $\text{NH}_4^{99}\text{TcO}_4$ , was obtained from Oak Ridge National Laboratory. The solid  $\text{NH}_4^{99}\text{TcO}_4$  was contaminated with a large amount of dark, insoluble material. Prolonged treatment of this sample with  $\text{H}_2\text{O}_2$  and  $\text{NH}_4\text{OH}$  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  $\text{NaOH}$  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 ( $\epsilon = 2380 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>8</sup> 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,  $\text{NaTcO}_4$  ( $3.9 \times 10^{-2} \text{ M}$ ) was added to give the desired concentration of  $\text{TcO}_4^-$ ; an identical volume of water was added to the reference solution. A Cu(II)/Fe(II) (Hart) dosimeter with 0.002M Fe(II), 0.010M Cu(II), and 0.010M  $\text{H}_2\text{SO}_4$ , or an oxygen-saturated Fricke dosimeter was used to record the radiation dose.<sup>9,10</sup> A set of three tubes (sample with  $\text{TcO}_4^-$ , chemical dosimeter, sample without  $\text{TcO}_4^-$ ) was positioned equidistant from a 600 Ci  $^{60}\text{Co}$  source. In a given experiment, three or five different sets of tubes were placed at varying distances from the  $^{60}\text{Co}$  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 non-linear in comparison to the oxygen-saturated Fricke dosimeter; this non-linearity 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  $\text{TcO}_4^-$  and the position and linewidth of the  $\text{TcO}_4^-$  peaks. Only the heights of the  $\text{TcO}_4^-$  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.<sup>11,12</sup> The yield of hydrogen atoms  $g(\text{H}\bullet)$  is 0.55. The yield of hydrated electrons  $g(e_{aq}^-)$  was determined using equation (1) where the left-hand term is

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

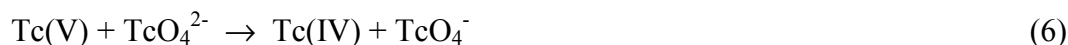
the fraction of hydrogen atoms that react with hydroxide to form hydrated electrons ( $k_{\text{H}\bullet+\text{OH}^-}$  is the rate constant for the reaction of  $\text{H}\bullet$  with  $\text{OH}^-$ , and  $k_{\text{H}\bullet+\text{RH}}$  is the rate constant for the reaction of  $\text{H}\bullet$  with the organic species), and the right-hand side is the yield of hydrated electrons corrected for scavenging from spurs;  $k[\text{S}]$  is the rate of reaction of substrate S with hydrated electrons, and  $\lambda$  is  $8 \times 10^8 \text{ s}^{-1}$ .<sup>11</sup> Similarly, the yield

of oxide radical ions was determined using equation (2) where  $k[S]$  is the rate of reaction of

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

substrate S with hydroxyl radicals, and  $\lambda$  is  $4.7 \times 10^8 \text{ s}^{-1}$ .<sup>12</sup> 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,  $G(-\text{TcO}_4^-)$ , 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 upon known chemistry, radiolysis of  $\text{TcO}_4^-$  requires three reducing equivalents and produces Tc(IV) as the radiolysis product:<sup>13-18</sup>



Pertechnetate reacts very quickly with hydrated electrons yielding technetate,  $\text{TcO}_4^{2-}$ .<sup>13-15</sup> Technetate,  $\text{TcO}_4^{2-}$ , disproportionates with a bimolecular rate constant of  $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  in alkaline solution.<sup>16</sup> Similarly, in the absence of stabilizing ligands, Tc(V) is known to disproportionate rapidly with a bimolecular rate constant of  $2.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>17</sup> Alternatively, Tc(V) species could be reduced by  $\text{TcO}_4^{2-}$ , which is a moderately strong reducing agent,  $E^0(\text{TcO}_4^-/\text{TcO}_4^{2-}) = -0.64 \text{ V vs. NHE}$ .<sup>14,18</sup> For these reasons, Tc(IV), as  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ , 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 the 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.<sup>19,20</sup> The dark precipitate is spectroscopically identical to  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$  produced by hydrolysis of  $\text{TcCl}_6^{2-}$  as determined by X-ray absorption fine structure and electron paramagnetic spectroscopy.<sup>21</sup> Besides the insoluble radiolysis product, a minor, soluble radiolysis product is usually observed. However, the principal radiolysis product is  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ , as expected.

The effect of selected organic molecules upon the radiolytic reduction of  $\text{TcO}_4^-$  was examined in 2M NaOH; these results, plus data previously reported by Pikaev and coworkers,<sup>22</sup> are reported in Table 1. In 2M NaOH, hydroxyl radicals are rapidly converted to oxide radical anions,  $\text{O}^-$ ; therefore,  $\text{O}^-$  can be treated as the primary oxidizing radical produced by radiolysis.<sup>23</sup> The organic molecules studied rapidly scavenge  $\text{O}^-$  radicals yielding organic radicals and preventing the oxidation of the reduced technetium species by  $\text{O}^-$ .<sup>23</sup> The hydrated electrons produced during radiolysis reduce  $\text{TcO}_4^-$ , removing it from solution with a radiation chemical yield,  $G(-\text{TcO}_4^-)$ , of  $1/3g(e_{\text{aq}}^-)$ . The deviation of  $G(-\text{TcO}_4^-)$  from this value can be explained using the reduction potentials of the organic radicals.

When the organic scavengers are primary or secondary alcohols,  $\alpha$ -hydroxyalkyl radicals are produced by H-abstraction from the alcohol. These radicals are strongly reducing, e.g.  $E^0[(\text{CH}_3)_2\text{CO}, \text{H}^+ / (\text{CH}_3)_2\text{C}^{\bullet}\text{OH}] = -1.7 \text{ V}$ , and are even more strongly reducing when deprotonated.<sup>24</sup> In fact, 2-hydroxy-2-propyl radical reduces  $\text{TcO}_4^-$  with a rate constant of  $7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>15</sup> Since these radicals reduce  $\text{TcO}_4^-$ , the predicted value of  $G(\text{TcO}_4^-)$  is  $1/3[g(e_{\text{aq}}^-) + g(\text{R}^{\bullet})]$ , where  $g(\text{R}^{\bullet})$  is the yield of organic radicals produced from H-abstraction by  $\text{O}^-$  and  $\text{H}^{\bullet}$ . The first two entries in Table 1 show that the observed  $G(-\text{TcO}_4^-)$  values are in good agreement with this prediction.

On the other hand, if the organic radicals are capable of oxidizing reduced technetium species, the observed  $G(-\text{TcO}_4^-)$  values will be smaller than  $1/3g(e_{\text{aq}}^-)$ . For

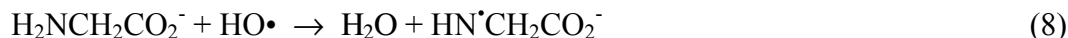
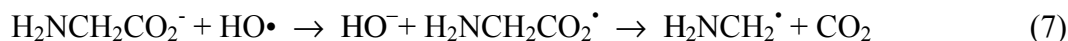


example, the calculated standard potential of the radical produced by H-abstraction from acetate,  $E^0(\bullet\text{CH}_2\text{CO}_2^-, \text{H}^+/\text{CH}_3\text{CO}_2^-) = 1.7 \text{ V}$ ,<sup>25</sup> is similar to that of  $\text{O}^-$ .<sup>26</sup> Consequently, this radical can oxidize reduced technetium species. As a result,  $G(-\text{TcO}_4^-)$  will be smaller than  $1/3g(e_{\text{aq}}^-)$ , although the value of  $G(-\text{TcO}_4^-)$  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  $\alpha$  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.<sup>27</sup>

The radicals produced by the reaction of  $\text{O}^-$  with the aminopolycarboxylates EDTA, IDA, and NTA appear to be unreactive towards both pertechnetate and reduced technetium species. In the presence of these molecules, the  $G(-\text{TcO}_4^-)$  can be attributed to reduction by  $e_{\text{aq}}^-$  alone, as shown in Table 1. However, a similar radiation-chemical yield could be obtained if radicals produced from the aminopolycarboxylates both reduced  $\text{TcO}_4^-$  and oxidized reduced technetium species. Such a scenario is suggested by the known radiation chemistry of glycine.<sup>28</sup>

Strongly reducing  $\text{H}_2\text{N}-\text{CH}_2^\bullet$  radicals result from decarboxylation of the  $\text{H}_2\text{N}^{+\bullet}-\text{CH}_2-\text{CO}_2^-$  radical produced by oxidation of glycine anion, equation 7, and oxidizing  $\text{HN}^\bullet-\text{CH}_2-\text{CO}_2^-$  radicals are produced by H-atom abstraction from the amino group, equation 8. However, the reduction potential for the  $\text{H}_2\text{N}^{+\bullet}-\text{CH}_2-\text{CO}_2^-$  radical is calculated to be  $1.6 \text{ V}$ ,<sup>29</sup> which is much greater than the  $0.94 \text{ V}$  reduction potential of  $\text{O}^-$  in  $2\text{M NaOH}$ .<sup>26</sup> Therefore, reaction 7 will not occur at high pH where  $\text{O}^-$ , rather than  $\text{HO}^\bullet$ , is present. The calculated reduction potential of the principal radical produced

during radiolysis of glycine,  $\text{H}_2\text{N}-\text{C}^*\text{H}-\text{CO}_2^-$ , equation 9, is 0.26 V in 2M NaOH, which is insufficient to reduce  $\text{TcO}_4^-$ .



**Radiolysis of  $\text{TcO}_4^-$  in the presence of  $\text{NO}_3^-$ .** Since the C-centered radicals produced during radiolysis of IDA and NTA are unreactive towards 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 equations 10-12.<sup>1,30,31</sup> In solutions containing both  $\text{NO}_3^-$  and  $\text{TcO}_4^-$ ,  $\text{NO}_3^-$  acts as a scavenger of  $e_{\text{aq}}^-$ ,

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in competition with  $\text{TcO}_4^-$ . Since the reaction rates for  $\text{NO}_3^-$  and  $\text{TcO}_4^-$  with  $e_{\text{aq}}^-$  are known, the fraction of  $e_{\text{aq}}^-$  which react with  $\text{TcO}_4^-$  can be determined.

The observed radiation chemical yields for  $\text{TcO}_4^-$  reduction in solutions of 2M NaOH, 0.1M NTA or IDA, and various concentrations of nitrate are listed in Table 2. At high nitrate concentrations,  $G(-\text{TcO}_4^-)$  is much larger than can be explained by the reaction of  $\text{TcO}_4^-$  with  $e_{\text{aq}}^-$ . For example, in 0.1M  $\text{NaNO}_3$ , and 0.1M NTA,  $G(-\text{TcO}_4^-)$  is 0.19; if only  $e_{\text{aq}}^-$  were reducing  $\text{TcO}_4^-$ , 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  $\text{TcO}_4^-$  is  $\text{NO}_3^{2-}$  ( $E^0(\text{NO}_3^-/\text{NO}_3^{2-}) = -0.89 \text{ V}$ ),<sup>1</sup> equation 13.



If only  $\text{NO}_3^{2-}$  and  $e_{\text{aq}}^-$  reduce  $\text{TcO}_4^-$  the mechanism for radiolysis of  $\text{TcO}_4^-$  is simple:  $\text{TcO}_4^-$  and  $\text{NO}_3^-$  compete for  $e_{\text{aq}}^-$ , and  $\text{TcO}_4^-$  and  $\text{H}_2\text{O}$  compete for  $\text{NO}_3^{2-}$ . The expected radiation chemical yield  $G(-\text{TcO}_4^-)$  is then given by equation 14 where  $k_n$  is the rate constant for the reaction given in equation n.

$$G(-\text{TcO}_4^-) = \frac{g(e_{\text{aq}}^-)}{3(k_3[\text{TcO}_4^-] + k_{10}[\text{NO}_3^-])} \left\{ k_3[\text{TcO}_4^-] + k_{10}[\text{NO}_3^-] \frac{k_{13}[\text{TcO}_4^-]}{(k_{13}[\text{TcO}_4^-] + k_{11}[\text{H}_2\text{O}])} \right\} \quad (14)$$

The results in Table 2 are presented graphically in Figure 1 along with a least squares fit of the data to equation 14 using  $k_{13}$ , the rate constant for the reaction of  $\text{TcO}_4^-$  with  $\text{NO}_3^{2-}$ , as the only variable. The agreement between the data and the fit are good; however, the two sets of experiments give slightly different values for  $k_{13}$ . Radiolysis in the presence of NTA gives  $k_{13} = 2.9(2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  while radiolysis in the presence of IDA gives the slightly lower value of  $2.2(2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ; the standard errors are in parentheses. Although these experiments do yield slightly different rate constants, rate constants derived from  $\gamma$ -radiolysis data are inherently less accurate and less precise than rates determined using pulse radiolysis.<sup>23</sup> For this reason, the rates are not sufficiently different to warrant discussion.

The reduction of  $\text{TcO}_4^-$  by  $\text{NO}_3^{2-}$  is considerably slower than the reduction of  $\text{TcO}_4^-$  by 2-hydroxy-2-propyl radical.<sup>15</sup> The slower rate is consistent with the smaller

equilibrium constant of reaction 13, based upon the reduction potentials of the species involved, and with the fact that reaction 13 involves two negatively charged substrates. The reaction of  $\text{NO}_3^{2-}$  with  $\text{TcO}_4^-$  may also be compared with other reactions of  $\text{NO}_3^{2-}$ .  $\text{NO}_3^{2-}$  reduces  $\text{O}_2$ , benzoquinone, and methylviologen with rate constants of  $2.3 \times 10^8$ ,  $7.6 \times 10^8$ , and  $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.<sup>31</sup> Again, these rate constants are considerably greater than  $k_{13}$ , for the reasons noted above.

Although the reaction of  $\text{NO}_3^{2-}$  with  $\text{TcO}_4^-$  is considerably slower than the other electron transfer reactions of  $\text{NO}_3^{2-}$ , the reaction of  $\text{NO}_3^{2-}$  with  $\text{TcO}_4^-$  is much faster than the hydrolysis of  $\text{NO}_3^{2-}$ .<sup>1,31</sup> The main effect of this difference in rate is the relatively high efficiency of the reduction of  $\text{TcO}_4^-$  in concentrated nitrate solution provided that molecules capable of scavenging  $\text{O}^-$  are present. When  $[\text{NO}_3^-] \gg [\text{TcO}_4^-]$  and  $k_{11}[\text{H}_2\text{O}] \gg k_{13}[\text{TcO}_4^-]$ ,  $G(-\text{TcO}_4^-)$  can be approximated using equation 15.<sup>32</sup>

$$G(-\text{TcO}_4^-) \approx \frac{g(e_{aq}^-)k_{13}[\text{TcO}_4^-]}{3k_{11}[\text{H}_2\text{O}]} \quad (15)$$

**Conclusion.** The  $\gamma$ -radiolysis of  $\text{TcO}_4^-$  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 towards 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  $\text{O}^-$  scavengers, radiolysis of  $\text{TcO}_4^-$  in nitrate solutions proceeds through reduction of  $\text{TcO}_4^-$  by  $\text{NO}_3^{2-}$ .

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



**Table 1:** Observed radiation-chemical yields for the loss of  $\text{TcO}_4^-$  in the presence of selected organic molecules.

Organic	$[\text{TcO}_4^-]$ mM	[Organic] M	$G_{\text{obs}}(-\text{TcO}_4^-)$	$G_{\text{calc}}(-\text{TcO}_4^-)$	Reference
Ethanol	5	0.1	2.7	2.4 <sup>a</sup>	22
Methanol	5	0.1	2.5	2.5 <sup>a</sup>	22
EDTA	5	0.04	1.2	1.2 <sup>b</sup>	22
NTA	0.2	0.1	1.0	1.0 <sup>b</sup>	this work
IDA	0.2	0.1	0.9	1.0 <sup>b</sup>	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)  $G_{\text{calc}}(-\text{TcO}_4^-) = (g(e_{\text{aq}}^-) + g(\text{R}\cdot))/3$

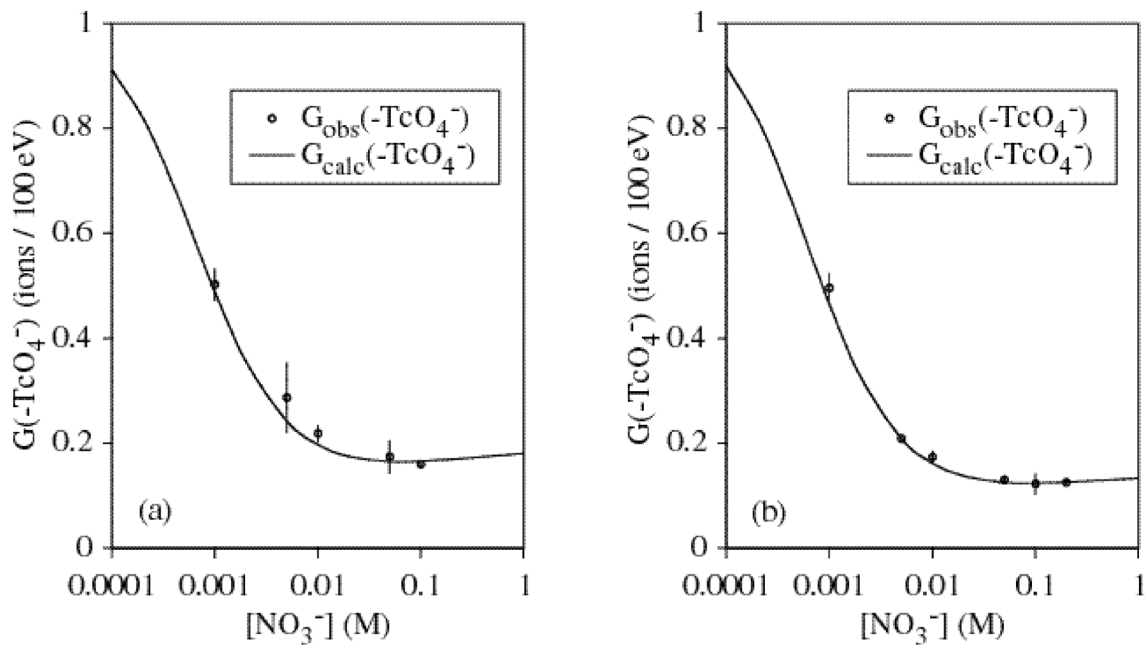
b)  $G_{\text{calc}}(-\text{TcO}_4^-) = g(e_{\text{aq}}^-)/3$

**Table 2:** Observed and calculated radiation-chemical yields for the loss of  $\text{TcO}_4^-$  in 2M NaOH, 0.1M IDA or NTA at various nitrate concentrations.

$[\text{NO}_3^-]$	$G(-\text{TcO}_4^-)$ NTA <sup>a,b</sup>	$G(-\text{TcO}_4^-)$ IDA <sup>a,b</sup>
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.



**Figure 1.** Radiation-chemical yield for loss of  $\text{TcO}_4^-$  in 2M NaOH with (a) 0.1M NTA, and (b) 0.1M 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 equation 14 is represented by the solid line.