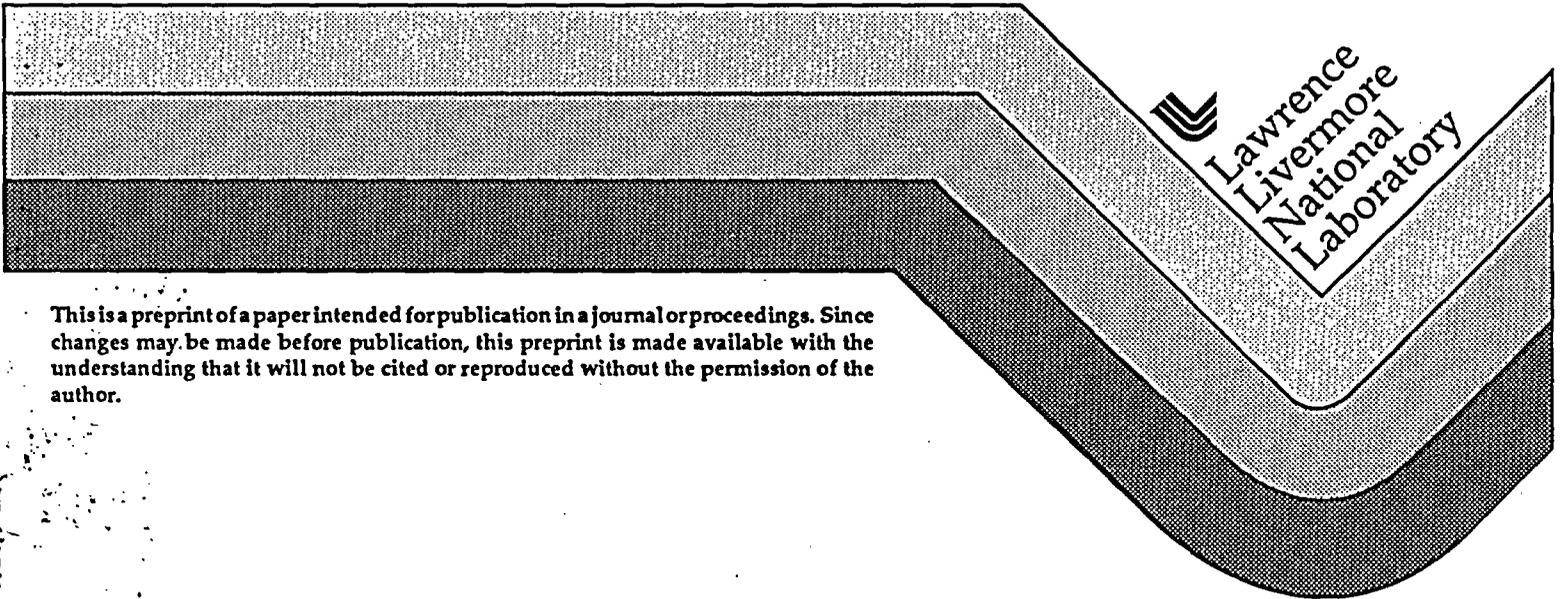


## CHEMICAL THERMODYNAMICS OF TECHNETIUM III

Joseph A. Rard

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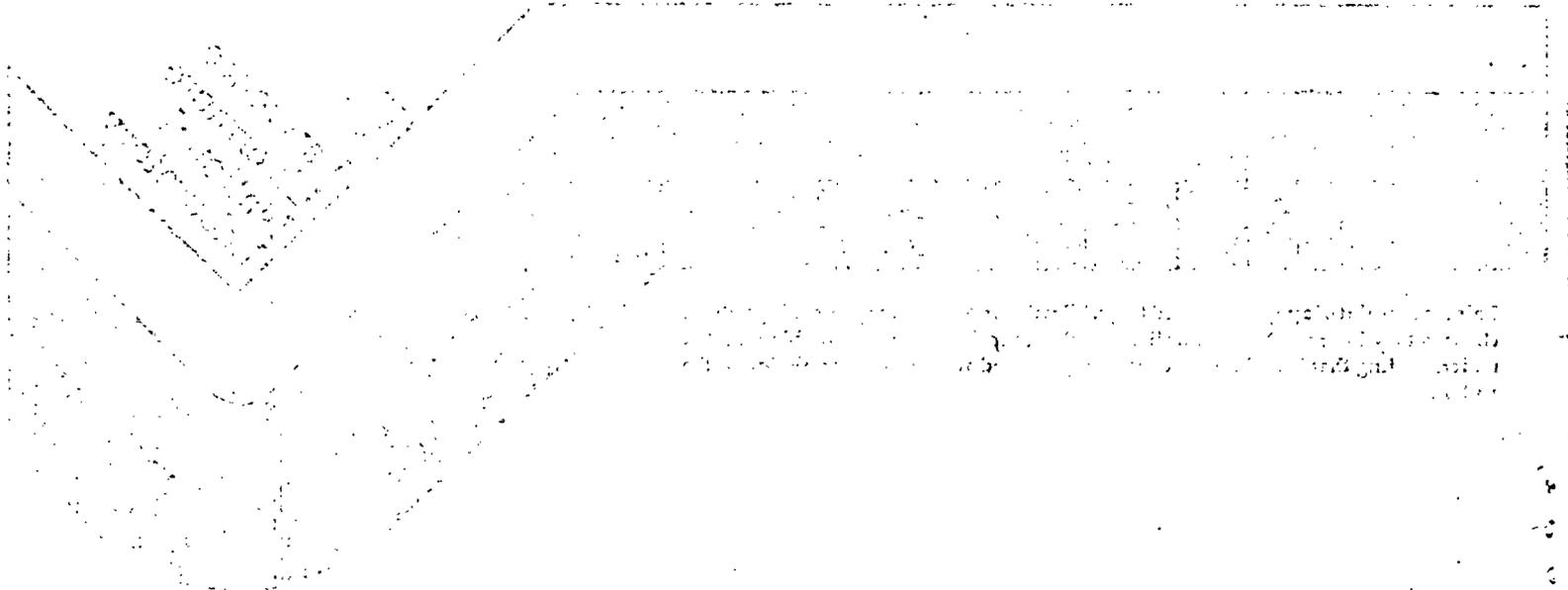
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## CHEMICAL THERMODYNAMICS OF TECHNETIUM III.

Contribution to the NEA Book on Technetium Thermodynamics: Hydroxide Compounds and Complexes Containing Other Ligands, Inorganic Carbon Complexes, and Update of UCRL-100554

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### IV. Discussion of Data Selection

#### 2. Oxide, Hydride, and Hydroxide Compounds and Complexes

#### 2.3 Hydroxide Compounds and Complexes Containing Other Ligands

The distinction of hydroxo compounds and complexes of technetium from oxo compounds and complexes is largely artificial, because in many cases it is not known to which classification a given compound or complex belongs. For example, even for the simple cases of the hydrous oxides of technetium (Section 2.1) and the hydrolyzed aqueous species of Tc(IV) (Section 2.4), it is not known for certain whether they are hydrated oxo, hydroxo, or hydroxooxo compounds or complexes, respectively. Part of this ambiguity arises because very few hydroxo compounds and complexes of technetium have been structurally characterized.

For some of the structurally characterized "hydroxo complexes," the degree of protonation of other ligands is uncertain, so the valence of the technetium may also be uncertain, and a presumed hydroxo group could actually be an oxo group. In addition, for many of the aqueous complexes, a water ligand may dissociate to form a hydroxyl as the pH is increased due to the acidic nature of hydrogens on water bound to the technetium cation. For example, in Section 10.3, we note that the aquo complexes  $\text{trans-}[\text{Tc}(\text{NH}_3)_4(\text{NO})(\text{H}_2\text{O})]^{n+}$  ( $n = 2$  or  $3$ ) exist in aqueous solutions at low pH, but they transform to  $\text{trans-}[\text{Tc}(\text{NH}_3)_4(\text{NO})(\text{OH})]^{n-1}$  as the solution pH is increased.

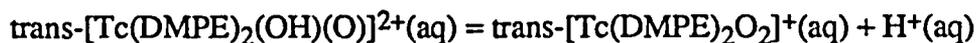
An additional possibility exists that an oxo ligand on technetium could become protonated to form a hydroxo ligand at very low pH values. For example Trop et al. [80TRO/JON] observed that aqueous solutions of  $\text{TcO}_2(\text{CN})_4^{3-}$  changed from yellow to deep blue when either concentrated  $\text{HClO}_4$  or  $\text{HCl}$  were added. They suggested that  $\text{Tc}(\text{OH})\text{O}(\text{CN})_4^{2-}$  may have formed in the highly acidic media. A number of trans-dioxo species of the type  $\text{trans-MO}_2\text{L}_4^n$  are known ( $M = \text{Tc, Re, W, Mo, Ru, Os, etc.}$ ;  $L$  denotes another ligand) [80TRO/JON], and they seem to be much more stable than their  $\text{M}(\text{OH})\text{OL}_4^{n+1}$  analogues.

This section will be restricted to known or potential hydroxo compounds and complexes that contain one or more additional ligands (those without additional ligands are covered in Sections 2.1 and 2.4). Hydroxo complexes of technetium that also contain other inorganic ligands are discussed elsewhere in this report, as are two complexes containing organic ligands. See Sections 3.3.2, 4.1.2, 5.1.1., 5.2.2.4, 6.1.2, 10.3, and 10.4. The remaining real or purported hydroxo compounds and complexes are described in this section; all of these contain organic ligands.

A bonafide hydroxooxo complex of  $\text{Tc}(\text{V})$  has been prepared and characterized by Vanderheyden et al. [84VAN/KET]. They reacted an aqueous solution of  $\text{NH}_4\text{TcO}_4$  in  $0.05 \text{ mol} \cdot \text{dm}^{-3}$   $\text{NaOH}$  with an ethyl alcohol solution of bis(1,2-dimethylphosphino)ethane (DMPE). The solution turned orange almost immediately, and after 10 minutes that solution was diluted with a mixture of 90% water and 10% ethyl alcohol and then separated on a cation-exchange column. After adjustment of the pH to 7, elution of the technetium containing band was done with  $0.15 \text{ mol} \cdot \text{dm}^{-3}$   $\text{LiF}_3\text{CSO}_3$ , and evaporation of the elutant gave a solid. This solid was dissolved in acetone, a mixture of 2-propanol with diethyl ether was added, and the solution was cooled to 269 K to give a precipitate of light-sensitive yellow  $\text{trans-}[\text{Tc}(\text{DMPE})_2\text{O}_2]\text{F}_3\text{CSO}_3$ . This material was then dissolved in hot 2-propanol to which  $\text{F}_3\text{CSO}_3\text{H}$  was added; subsequent addition of diethyl ether followed by cooling to 269 K gave crystals of light-stable reddish-orange  $\text{trans-}[\text{Tc}(\text{DMPE})_2(\text{OH})(\text{O})](\text{F}_3\text{CSO}_3)_2$ . This latter substance was characterized by elemental analysis, EXAFS, and visible-UV spectroscopy.

An X-ray diffraction study indicated that trans-[Tc(DMPE)<sub>2</sub>(OH)(O)](F<sub>3</sub>CSO<sub>3</sub>)<sub>2</sub> crystallized in the monoclinic space group P2<sub>1</sub>/c with unit cell parameters of a = (8.052±0.004)×10<sup>-10</sup> m, b = (11.527±0.004)×10<sup>-10</sup> m, c = (16.070±0.006)×10<sup>-10</sup> m, β = (101.96±0.04)°, and Z = 2. Because of disorder in the crystal structure, the Tc-O and Tc-OH bond lengths could not be distinguished. The average technetium-to-oxygen bond length was 1.795×10<sup>-10</sup> m [84VAN/KET].

This complex dissociated in aqueous solution as a relatively strong acid [84VAN/KET]



They reported that the pK<sub>a</sub> was (0.80±0.10) at an ionic strength of 0.5 mol • dm<sup>-3</sup>, using mixtures of HClO<sub>4</sub> and LiClO<sub>4</sub> to control ionic strengths, but the sign of pK<sub>a</sub> was probably reported incorrectly since they also reported that K<sub>a</sub> = (6.3±0.1) mol • dm<sup>-3</sup>. This value was determined using UV-visible spectrophotometry. These values were originally given in the Ph.D dissertation of Vanderheyden [85VAN]. He also reported K<sub>a</sub> = (0.109±0.110) mol • dm<sup>-3</sup> and pK<sub>a</sub> = (1.03±0.47) (which are similarly inconsistent) for the 1,2-bis(diethylphosphino)ethane analogue trans-[Tc(DEPE)<sub>2</sub>(OH)(O)]<sup>2+</sup>. Since values of K<sub>a</sub> were derived directly from the spectrophotometric measurements, they were assumed to be given correctly and the pK<sub>a</sub> values were assumed to be incorrect. These authors [85VAN, 84VAN/KET] also cited a literature value of pK<sub>a</sub> = (2.5±0.2) at I = 2.0 mol • dm<sup>-3</sup> for trans-[Tc(cyclam)(OH)(O)]<sup>2+</sup>, where cyclam denotes the 1,4,8,11-tetraazacyclotetradecane ligand. This value was attributed to Zuckman et al. [81ZUC/FRE]; although Zuckman et al. did prepare trans-[Tc(cyclam)O<sub>2</sub>]ClO<sub>4</sub> • H<sub>2</sub>O, they did not report an acidity constant. The correct reference is the Ph.D dissertation of S.S. Jurisson [82JUR].

Jurisson [82JUR] obtained K<sub>ai</sub> = (304±20) mol • dm<sup>-3</sup> at 298 K and I=2 mol • dm<sup>-3</sup> using visible-UV spectrophotometric measurements at 244, 281, and 294 nm. The ionic strength was controlled at 2.0 mol • dm<sup>-3</sup> by using mixtures of NaClO<sub>4</sub> and HClO<sub>4</sub> [90JUR]. By using spectrophotometric measurements in 8 and 12 mol • dm<sup>-3</sup> HClO<sub>4</sub>, Jurisson [82JUR] estimated that

$\log_{10}K_{a2}$  was between 0.9 and 1.1 for



Since the ionic strength was not constant, this value was not analyzed further.

Noll et al. [80NOL/SEI] prepared solid complexes of technetium with nitrilotriacetic acid ( $\text{H}_3\text{NTA}$ ). They reacted  $\text{K}_2\text{TcBr}_6$  dissolved in  $1 \text{ mol} \cdot \text{dm}^{-3}$   $\text{HBr}$  with hot saturated  $\text{H}_3\text{NTA}$  in  $0.1 \text{ mol} \cdot \text{dm}^{-3}$   $\text{HBr}$ . The solution color changed slowly from red to brown to pink, and most of the excess ligand precipitated upon cooling. The supernatant solution was extracted with mixtures of diethyl ether and ethyl alcohol to remove  $\text{HBr}$  and a yellow  $\text{NTA}$  complex. The aqueous phase was concentrated by evaporation under reduced pressure, and addition of ethyl alcohol gave a brown mixture of technetium-containing species. Repeated recrystallizations from water followed by precipitation with ethyl alcohol gave a red oxy compound and a brown material that they formulated as a hydroxy compound.

Chemical analysis indicated the presence of  $2 \text{ H}_2\text{O}$  per technetium in the brown compound, it was diamagnetic, and absorption spectra showed extinction maxima at 350 and 506 nm [80NOL/SEI]. Two  $\text{OH}^-$  were required per technetium to neutralize that complex; in contrast, a sample that was converted to the hydrogen form on an ion-exchange column required 5  $\text{OH}^-$  per technetium. This information, together with elemental analyses for  $\text{Tc}$ ,  $\text{C}$ ,  $\text{H}$ , and  $\text{N}$ , led them to formulate the compound as being  $\text{K}_3\text{H}_2[\text{Tc}_3\text{O}_2(\text{OH})_4(\text{NTA})_3] \cdot 6\text{H}_2\text{O}$ .

Gorski and Koch [70GOR/KOC] studied the reaction of aqueous  $\text{Tc}(\text{IV})$  with  $\text{NTA}^{3-}$  at  $\text{pH} = 1.5$  and  $2.0$ . Since  $\text{Tc}(\text{IV})$  is generally considered to exist as  $\text{TcO}(\text{OH})^+$  at this  $\text{pH}$  range, they formulated the aqueous complexes as  $\text{TcO}(\text{OH})(\text{NTA})^{2-}$  and  $\text{TcO}(\text{OH})(\text{NTA})_2^{5-}$ . By using ion-exchange at  $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ , they determined that  $\log_{10}K_1 = 13.8 \pm 0.4$  and  $\log_{10}K_2 = 25.7 \pm 0.4$ . Similar measurements at  $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$  with ethylenediaminetetraacetic acid  $\text{H}_4\text{EDTA}$  gave  $\log_{10}K_1 = 19.1 \pm 0.4$  for the complex  $\text{TcO}(\text{OH})(\text{EDTA})^{3-}$ , and  $\log_{10}K_1 = 20.7 \pm 0.4$  for the cyclohexanediaminetetraacetic acid  $\text{H}_4\text{DATA}$  complex  $\text{TcO}(\text{OH})(\text{DATA})^{3-}$ . Measurements for the latter complex at  $I = 0.035 \text{ mol} \cdot \text{dm}^{-3}$

by using electrophoresis gave  $\log_{10}K_1 = 20.8 \pm 0.4$ . The ionic strengths of the solutions were controlled with  $\text{NaClO}_4$ .

Gorski and Koch [70GOR/KOC] tabulated their detailed experimental results for the  $\text{NTA}^{3-}$  complexes with technetium, but they only gave equilibrium constants for the other systems. For the  $\text{Tc(IV)-NTA}^{3-}$  studies the  $\text{NTA}^{3-}$  concentration was varied enough that it was clear that equilibrium had been reached, which implies that these complexes were labile enough that the distribution coefficients represented equilibrium measurements. The presentation of more detailed results for the  $\text{EDTA}^{4-}$  and  $\text{DATA}^{4-}$  complexes would have been helpful in establishing that equilibrium had been reached for those systems also.

Crystal structures have been reported for an NTA and an EDTA complex of  $\text{Tc(IV)}$ . Anderegg et al. [83AND/MÜL] mixed aqueous  $\text{HTcO}_4$  with  $\text{Na}_2\text{H(NTA)}$ , added  $\text{HClO}_4$  to adjust the pH to about 2, and then heated the solution to between 343 and 353 K for several days while bubbling  $\text{SO}_2$  through it to reduce the  $\text{Tc(VII)}$ . The solution was then cooled to room temperature and slowly evaporated to yield a mixture of  $\text{Tc-NTA}$  complex,  $\text{NaClO}_4$ , and  $\text{H}_3\text{NTA}$ . Crystals of the technetium complex were separated mechanically and then recrystallized from  $0.01 \text{ mol} \cdot \text{dm}^{-3} \text{ HClO}_4$ . The non-hydrated potassium analogue was prepared by a similar method. Both compounds were quite hygroscopic.

The blackish sodium compound was diamagnetic, and a X-ray structural determination [83AND/MÜL] indicated that the unit cell was triclinic with space group  $\bar{P}1$ ,  $a = (6.330 \pm 0.002) \times 10^{-10}$ ,  $b = (9.512 \pm 0.004) \times 10^{-10}$ ,  $c = (11.239 \pm 0.008) \times 10^{-10} \text{ m}$ ,  $\alpha = (64.97 \pm 0.04)^\circ$ ,  $\beta = (83.00 \pm 0.04)^\circ$ ,  $\gamma = (74.74 \pm 0.04)^\circ$ , and  $Z = 1$ . Each structural unit of  $\text{Na}_2[(\text{NTA})\text{Tc(IV)}(\mu\text{-O})_2\text{Tc(IV)}(\text{NTA})] \cdot 6\text{H}_2\text{O}$  contained a four-membered  $\text{Tc}(\mu\text{-O})_2\text{Tc}$  ring, and each technetium was also coordinated to the nitrogen atom and three carboxylate oxygen atoms of an NTA.

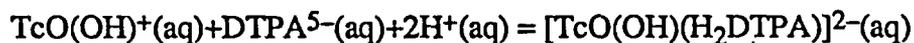
Synthesis of the EDTA complex of technetium was done under very nearly identical conditions [81BÜR/AND] except that  $\text{NaHSO}_3$  was used for a reducing agent and a two-fold excess of  $\text{Na}_2\text{H(NTA)}$  over technetium was required to prevent partial formation of hydrated  $\text{TcO}_2$ . Two of the protons of the complex are acidic with  $\text{pK} \approx 3$ , and it is diamagnetic. An X-ray structural analysis

and elemental analyses for Tc, C, H, and N showed that this red brown complex had the formula  $[(\text{H}_2\text{EDTA})\text{Tc}(\text{IV})(\mu\text{-O})_2\text{Tc}(\text{IV})(\text{H}_2\text{EDTA})] \cdot 5\text{H}_2\text{O}$ . It crystallized in the orthorhombic space group  $\text{Pna}2_1$  with unit cell parameters of  $a = (18.41 \pm 0.02) \times 10^{-10}$  m,  $b = (10.96 \pm 0.02) \times 10^{-10}$  m,  $c = (16.25 \pm 0.02) \times 10^{-10}$  m, and  $Z = 4$ . All four atoms of the  $\text{Tc}(\mu\text{-O})_2\text{Tc}$  ring are within  $\pm 0.01 \times 10^{-10}$  m of being planar.

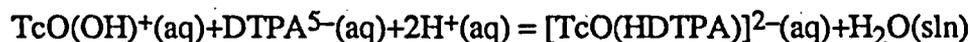
Since hydrogen atoms are not located in X-ray diffraction studies, it is possible that the valence of technetium may be different than assigned. For example, the  $\text{Tc}(\text{IV})(\mu\text{-O})_2\text{Tc}(\text{IV})$  rings could actually be  $\text{Tc}(\text{III})(\mu\text{-OH})_2\text{Tc}(\text{III})$ . However, the short technetium-to-oxygen bond lengths in the bridged rings of NTA (average of  $1.919 \times 10^{-10}$  m) and EDTA complexes ( $1.912 \times 10^{-10}$  m) favor a  $\text{Tc}(\text{IV})(\mu\text{-O})_2\text{Tc}(\text{IV})$  structure in both cases [83AND/MÜL, 81BÜR/AND].

In view of this structural information for the NTA and EDTA complexes of technetium, the exact nature of the solution species investigated by Gorski and Koch [70GOR/KOC] must remain in doubt. That is, their complexes could have been of the type  $\text{Tc}_2(\mu\text{-O})_2\text{L}_2$  rather than  $\text{TcO}(\text{OH})\text{L}$  as formulated by the authors. If the dimeric structures also form in aqueous solutions, then the experimental values of  $K_1$  and  $K_2$  should be squared to yield the correct values. It is also possible that the dimeric complexes [83AND/MÜL, 81BÜR/AND] are not structurally related to the solution species studied by Gorski and Koch, since they were prepared by different methods.

Studies have also been made of the complex between technetium and diethylenetriaminepentaacetate ( $\text{DTPA}^{5-}$ ). Levin et al. [80LEV/GRA] made liquid-liquid extraction measurements for this aqueous complex; the non-aqueous phase was thenoyltrifluoroacetone HTTA in toluene. Their  $\text{Tc}(\text{IV})$  had been prepared by reduction of  $\text{TcO}_4^-$  with acidified  $\text{NaBH}_4$ , followed by extraction of  $\text{Tc}(\text{IV})$  with HTTA in toluene. Extraction measurements were done using  $I = 1.0 \text{ mol} \cdot \text{dm}^{-3}$   $\text{NaClO}_4$  to control the ionic strength; the charge on the technetium DTPA complex was found to be  $-2$  for their pH range of 0.95 to 4.20. They determined  $\log_{10}K_1 = 26.3 \pm 1.8$  at this ionic strength, and pointed out that the formation reaction could be written either as



or



Russell and Speiser [82RUS/SPE] studied the reduction of  $\text{TcO}_4^-$  in the presence of  $\text{DTPA}^{5-}$  and  $\text{EDTA}^{4-}$  by using amperometric titration with  $\text{Sn}^{2+}$ . At  $\text{pH} = 10$  reduction of  $\text{TcO}_4^-$  was  $3.0 e^-$  per technetium to  $\text{Tc(IV)}$  in both media. However, similar reductions for  $\text{DTPA}^{5-}$  solutions at  $\text{pH} = 5, 6,$  and  $7,$  and for  $\text{EDTA}^{4-}$  solutions at  $\text{pH} = 4$  and  $7$  gave  $3.6 e^-$  reductions per technetium. Thus reduction of  $\text{TcO}_4^-$  with  $\text{Sn}^{2+}$  in the presence of these ligands at neutral and acidic  $\text{pH}$  values appears to yield mixed-valence dimers of  $\text{Tc(III, IV)}$  with unknown stoichiometry. Steigman et al. [75STE/MEI] also found that potentiometric reduction of  $\text{TcO}_4^-$  with  $\text{SnCl}_2$  in  $0.4 \text{ mol} \cdot \text{dm}^{-3}$   $\text{DTPA}^{5-}$  at  $\text{pH} = 4$  involved  $3.4$  to  $3.5 e^-$  per technetium from  $298$  to  $363 \text{ K}$ .

Russell et al. [80RUS/CRI] had earlier investigated the reduction of aqueous tracer-level  $\text{TcO}_4^-$  with a mixture of  $\text{SnCl}_2$  in  $0.1 \text{ mol} \cdot \text{dm}^{-3}$   $\text{Na}_2\text{H}_2(\text{EDTA})$  that had been adjusted to  $\text{pH} = 7.0$  prior to the addition of  $\text{SnCl}_2$  and  $\text{TcO}_4^-$ . The resulting major  $\text{EDTA}^{4-}$  complex of technetium was separated by chromatography, and the net charge on this complex was determined to be  $-2$  at  $\text{pH} = 7$  by ion-exchange equilibration. By analogy with other known  $\text{EDTA}$  complexes, they assumed that all  $\text{EDTA}$  nitrogens were coordinated with the technetium, and that all unbounded carboxyl groups were ionized at this  $\text{pH}$ . Depending on the valence of technetium present, they concluded that either  $\text{Tc(III)(OH)(EDTA)}^{2-}$ ,  $\text{Tc(IV)O(EDTA)}^{2-}$ , or  $\text{Tc(V)O(OH)(EDTA)}^{2-}$  were possible. However, given the later results of Russell and Speiser [82RUS/SPE] a mixed-valence dimeric complex of  $\text{Tc(III,IV)}$  is also possible.

Steigman et al. [75STE/MEI] also studied the reduction of aqueous  $\text{TcO}_4^-$  by  $\text{SnCl}_2$  from their reaction in a  $1:6$  mole ratio in  $0.4 \text{ mol} \cdot \text{dm}^{-3}$   $\text{DTPA}^{5-}$  at  $\text{pH} = 4$ . Polarographic oxidation of the excess  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  was used to determine the technetium valence in the technetium complex with  $\text{DTPA}^{5-}$ . The technetium valence was  $3.17$  after  $3$  minutes of reaction between  $\text{TcO}_4^-$  and  $\text{Sn}^{2+}$ , but the

valence was constant at 3.0 after 45 minutes and longer. No further reduction of technetium was observed.

Russell et al. [80RUS/CRI] did similar experiments with  $\text{DTPA}^{5-}$ , but at both  $\text{pH} = 4.6$  and  $7.0$ . The  $\text{TcO}_4^-$  reduced by  $\text{Sn}^{2+}$  formed a complex with  $-2$  net charge at both  $\text{pH}$  values. They concluded that either  $\text{Tc(III)(DTPA)}^{2-}$ ,  $\text{Tc(IV)(OH)(DTPA)}^{2-}$ , or  $\text{Tc(V)O(DTPA)}^{2-}$  were possible. From the results of Steigman et al. [75STE/MEI], a  $\text{Tc(III)}$  complex is most likely. However (as for  $\text{EDTA}^{4-}$ ) the actual species could also have been a mixed valence dimeric complex of  $\text{Tc(III,IV)}$  [82RUS/SPE].

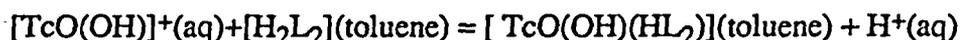
In the absence of tin, polarographic reduction [82RUS/SPE] of  $\text{TcO}_4^-$  in the presence of  $\text{EDTA}^{4-}$  gave a  $4 e^-$  reduction per technetium to  $\text{Tc(III)}$  from  $\text{pH} \approx 4$  to  $7$ ,  $3 e^-$  per technetium to  $\text{Tc(IV)}$  at  $\text{pH} = 10$ , and  $2 e^-$  per technetium to  $\text{Tc(V)}$  at  $\text{pH} = 12$ . For  $\text{TcO}_4^-$  in the presence of  $\text{DTPA}^{5-}$ , a  $4 e^-$  reduction per technetium occurred to  $\text{Tc(III)}$  for  $\text{pH} < 6$ ; two reoxidation waves were observed corresponding to about  $1/2 e^-$  per technetium. This suggests that formation of  $\text{Tc(III, IV)}$  and possibly  $\text{Tc(IV,IV)}$  dimers occurred during reoxidation. However, at higher  $\text{pH}$  values, reduction of  $\text{TcO}_4^-$  in the presence of  $\text{DTPA}^{5-}$  gave  $3 e^-$  per technetium to  $\text{Tc(IV)}$  by  $\text{pH} = 10$  and  $2 e^-$  per technetium to  $\text{Tc(V)}$  at  $\text{pH} = 12$ . At  $\text{pH}$  values from  $7$  to  $9$ , reduction of  $\text{TcO}_4^-$  in  $\text{DTPA}^{5-}$  solutions gave mixtures of  $\text{Tc(III)}$  and  $\text{Tc(IV)}$ . No speculations were made by these authors as to the stoichiometry of their complexes.

Volkert et al. [82VOL/TRO] studied reactions of the  $\text{Tc-DTPA}$  complex produced by  $\text{Sn}^{2+}$  reduction of  $\text{TcO}_4^-$  in the presence of  $\text{DTPA}^{5-}$ . Addition of cyclam, 1,5,8,12-tetraazadodecane (TA), or ethylenediamine (EN) to solutions in  $0.7 \text{ mol} \cdot \text{dm}^{-3}$   $\text{DTPA}$  caused no destruction of the  $\text{Tc-DTPA}$  complex for  $\text{pH} < 9$ , but essentially complete exchange occurred with each of those ligands by and above  $\text{pH} = 11$ .

A monomeric  $\text{EDTA}$  complex of technetium has been described [82BAN/MAZ; unpublished data of Deutsch, Elder, and Packard cited therein]. This is the salt  $\text{Ba}[\text{TcO}(\text{EDTA})]_2$ , which contains  $\text{Tc(V)}$ . It consists of discrete monomeric anions that are bridged with barium cations. It was prepared by ligand

exchange between  $\text{TcOCl}_4^-$  and  $\text{H}_4\text{EDTA}$  in anhydrous dimethylsulfoxide, and it is not likely to be relevant to aqueous situations.

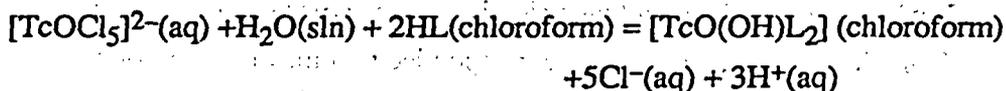
The liquid-liquid extraction of Tc(IV) between water and benzene or toluene in the presence of bis-(2-ethylhexyl)phosphoric acid HDEHP has been reported by Guénnec and Guillaumont [73GUÉ/GUI], and Jovtschev et al. used toluene, benzene, or  $\text{CCl}_4$  as the organic phase [80JOV/KUP]. Both noted that HDEHP is monomeric in the aqueous phase, but it formed a mixture of monomer and dimer in toluene. Both found that the extractions proceeded by



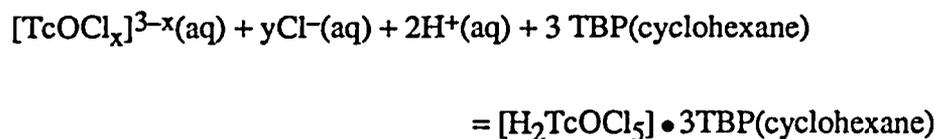
where  $\text{H}_2\text{L}_2$  denotes the dimer of HDEHP. Guénnec and Guillaumont [73GUÉ/GUI] varied the pH from about -0.4 to 2.0 by using  $\text{HClO}_4$ , whereas Jovtschev et al. [80JOV/KUP] did measurements at  $I = 1 \text{ mol} \cdot \text{dm}^{-3}$  with pH varied from 0 to 4.86 and the total HDEHP concentration ranging from  $10^{-2}$  to  $1 \text{ mol} \cdot \text{dm}^{-3}$ . No equilibrium constant was reported in these studies.

Rajec et al. [79RAJ/MIK] investigated the liquid-liquid extraction of Tc(V) from aqueous mixtures of HCl and LiCl. They prepared aqueous  $\text{TcOCl}_5^{2-}$  by reaction of  $\text{TcO}_4^-$  with concentrated aqueous HCl for 10 minutes followed by cooling the solution and dilution to  $6 \text{ mol} \cdot \text{dm}^{-3}$  HCl. This solution was mixed with variable amounts of  $6 \text{ mol} \cdot \text{dm}^{-3}$  HCl and LiCl to obtain solutions of different acidity with  $I = 6 \text{ mol} \cdot \text{dm}^{-3}$ . The extraction systems were 5,7-dichloroxine in chloroform, tributyl phosphate (TBP) in cyclohexane, and 1-phenyl-3-methylbenzoylpyrazolone (PMBP) in chloroform. Some of the TBP extractions were done at higher HCl concentrations.

Their analysis of the extraction data for Tc(V) using 5,7-dichloroxine in chloroform at  $I = 6 \text{ mol} \cdot \text{dm}^{-3}$  with variable  $\text{H}^+$  contraction indicated that complex formation produced 3  $\text{H}^+$  per technetium [79RAJ/MIK]. They thus proposed that



This mechanism applied for 3.15 to 6 mol • dm<sup>-3</sup> H<sup>+</sup>; additional hydrolysis of Tc(V) occurred below 3.15 mol • dm<sup>-3</sup> H<sup>+</sup>. In contrast, for TBP in cyclohexane with 4.5 to 9 mol • dm<sup>-3</sup> HCl, their proposed reaction was



Grossmann and Muenze (Münze) [82GRO/MUE] studied complex formation between various aliphatic carboxylic acids and Tc(IV). Samples of ligand were dissolved in water and 20 mg of K<sub>2</sub>TcBr<sub>6</sub> was then added for final ligand-to-technetium ratios of 1:1, 2:1, 3:1, 5:1, 10:1, and 100:1. Unsubstituted carboxylic acids yielded a precipitate of hydrated TcO<sub>2</sub> in all cases, so their complexes with Tc(IV) were relatively weak. However the α-hydroxycarboxylic acids - tartaric acid, malic acid, and α-hydroxyisobutyric acid formed mixtures of soluble brown and red-violet species with Tc(IV); higher ligand-to-technetium ratios favored formation of the red-violet complexes. These soluble complexes were partially characterized by spectrophotometric measurements, electrophoresis, and gel-chromatography. All of these complexes migrated as anions during electrophoresis for pH = 1 to 10, and the red-violet complexes migrated faster than the brown complexes both during electrophoresis and gel-chromatographic elution. Since a maximum of three of these ligands would complete the coordinate sphere of Tc(IV) but would yield a cation of the type TcL<sub>3</sub><sup>+</sup> rather than an anion, hydroxo cores of TcO(OH)<sup>+</sup> may be present instead; they would give anionic complexes upon complex formation with ligands.

Omori et al. [87OMO/YAM] studied kinetics of the hydrolysis of cis-dihalobis(acetylacetonato)technetium(IV) complexes cis-TcCl<sub>2</sub>(acac)<sub>2</sub> and cis-TcBr<sub>2</sub>(acac)<sub>2</sub> using spectrophotometric measurements. Kinetic measurements were mainly done in aqueous acetonitrile in the presence of air or nitrogen at 298 K. These complexes were resistant to attack by mineral acids, but were hydrolyzed by aqueous hydroxide. The initially brown acetonitrile solution of cis-TcCl<sub>2</sub>(acac)<sub>2</sub> first became red-violet and then slowly became colorless after addition of aqueous alkali. The initial color change corresponded to removal of chloride from the complex, and the later color change to oxidation of Tc(IV) to TcO<sub>4</sub><sup>-</sup>. The hydrolysis data at early times followed the rate law

$$-d[\text{TcCl}_2(\text{acac})_2]/dt = k_1[\text{TcCl}_2(\text{acac})_2][\text{OH}^-]$$

for  $[\text{OH}^-] > 0.02 \text{ mol} \cdot \text{dm}^{-3}$ , with  $k_1 = (1.5 \pm 0.4) \times 10^{-4} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ . The intermediate species could possibly contain hydroxo and acac ligands. They noted that Y. Yamada [Thesis, 1985, Tohoku University; cited in 87OMO/YAM] suggested that  $\text{TcO}(\text{OH})(\text{acac})_2$  was an intermediate involved in the alkali hydrolysis of Tc(V) acetylacetonates.

Münze [77MÜN1] investigated the formation of purple-violet complexes of Tc(IV) with ethylene glycol and glycerol in aqueous alkali. The Tc(IV) was added directly as  $\text{K}_2\text{TcBr}_6$  or prepared from  $\text{TcO}_4^-$  reduced with  $\text{Sn}^{2+}$ . With glycerol, for example, hydrated  $\text{TcO}_2$  precipitated for  $\text{pH} < 6$ . They suggested that  $\text{Tc}(\text{OH})_4(\text{C}_3\text{H}_6\text{O}_3)^{2-}$  formed from  $\text{pH} = 8$  to 10.5, and  $\text{Tc}(\text{OH})_2(\text{C}_3\text{H}_6\text{O}_3)_2^{2-}$  at higher pH values. The higher pH values were required to dissociate two hydrogens from each glycerol, which then could complex through two of their oxygen atoms. Obviously, some of the hydroxo groups directly coordinated to Tc(IV) could actually be oxo groups. If this were the case,  $\text{Tc}(\text{OH})_2(\text{C}_3\text{H}_6\text{O}_3)_2^{2-}$  would be rewritten as  $\text{TcO}(\text{C}_3\text{H}_5\text{O}_3)_2^{2-}$ . Electrophoresis and spectroscopic measurements indicated that ethylene glycol formed complexes with Tc(IV) similar to the ones with glycerol.

Steigman et al. [77STE/HWA] briefly described formation of a pink technetium-ethylene glycol complex formed by reduction of  $\text{TcO}_4^-$  with excess  $\text{SnCl}_2$  at  $\text{pH} = 12$ . Upon acidification, the pink complex immediately disproportionated to yield hydrated  $\text{TcO}_2$  and  $\text{TcO}_4^-$  in a 2:1 ratio. This confirms that technetium was present as Tc(V) in the pink complex, and suggests the possibility that the valence of technetium in some of Münze's complexes [77MÜN1] may have been different than claimed by him.

Münze and Grossmann [77MÜN/GRO] studied the reaction between  $\text{K}_2[\text{TcBr}_6]$  and aqueous potassium citrate  $\text{K}_3\text{Cit}$  at technetium-to-citrate ratios of 1:1 to 1:100. Oxidation of the complexes by  $\text{Ce}^{4+}$  in  $I = 1 \text{ mol} \cdot \text{dm}^{-3}$  aqueous  $\text{H}_2\text{SO}_4$  indicated that the technetium oxidation state in these complexes was 4.0 to 4.2. At the lower technetium-to-citrate ratios formation of blue-violet-colored monomeric species predominated, whereas for ratios around 1:1 the polymeric

species were favored. By using equivalent weight determinations, potentiometric pH-titrations, and IR spectroscopic measurements for various chromatographically separated fractions, they concluded that the isolated compounds were polymeric  $\{K_2[Tc(OH)_3(Cit)] \cdot nH_2O\}_x$  where  $n = 3, 2, 1$ , or  $0$ ; polymeric  $\{K_4[Tc(OH)_2(HCit)_2]\}_x$ ; and monomeric  $K_6 [Tc(OH)_2(Cit)_2]$ .

Münze and Grossmann [75MÜN/GRO2] have investigated the stoichiometry of the reaction of  $TcBr_6^{2-}$  and  $H_3Cit$  by using absorption spectrophotometry and potentiometric titration. The ionic strength was controlled at  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  with  $NaClO_4$  and the  $Tc(IV)$  concentration was  $(2 \text{ to } 3) \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ ; the pH was varied from about 1 to 10. At  $pH > 3$   $TcBr_6^{2-}$  hydrolyzed with about 4  $OH^-$  per  $Tc(IV)$ . The stoichiometry of the citrate complexes was written as  $Tc(OH)_{4-n}H_{3-m}Cit$  (they actually wrote citric acid as  $H_4Cit$  since its hydroxyl ligand can be dissociated at very high pH values). For pH values of 6 to 8, there was an average of 3  $OH^-$  per  $Tc(IV)$ , but this increased to 4  $OH^-$  at  $pH=3$  and  $pH=11$ .

Reduction of  $TcO_4^-$  with  $Sn^{2+}$  in the presence of  $Na_3Cit$  at  $pH = 7$  yielded a  $Tc(V)$  complex, since one mole of  $TcO_4^-$  was reduced per mole of  $Sn^{2+}$  consumed [77MÜN2]. This pale blue-green citrate complex was used as an intermediate in the synthesis of other  $Tc(V)$  complexes [78JOH/SYH]. Its stoichiometry is unknown. A more detailed investigation of the reduction of  $TcO_4^-$  by  $Sn^{2+}$  in the presence of citrate was done by Steigman et al. [75STE/MEI]. In all of their experiments the citrate concentration was  $0.4 \text{ mol} \cdot \text{dm}^{-3}$  and the pH was 7. Direct potentiometric titration of  $TcO_4^-$  with  $SnCl_2$  in this medium gave a  $2 e^-$  reduction to a  $Tc(V)$  citrate complex, in agreement with Münze's observation [77MÜN2]. However when  $TcO_4^-$  was mixed with  $SnCl_2$  in a 1:6 mole ratio, then the oxidation state of technetium in the citrate complex depended on reaction time [75STE/MEI]. Polarographic reoxidation of the excess  $Sn^{2+}$  shortly after the  $SnCl_2$  was added indicated that technetium was present as  $Tc(V)$  in the complex, but after 90 minutes and longer it had changed to a  $Tc(IV)$  complex. Thus both reaction conditions and time can affect the type of complex formed between technetium and citrate.

Münze [80MÜN] subsequently did a polarographic study of complexes produced by  $SnCl_2$  reduction of  $TcO_4^-$  in citrate solutions over the much wider pH

range of 2.0 to 9.0. The citrate concentration was kept at  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  in most of the experiments, the  $\text{TcO}_4^-$  concentration at  $1.68 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ , and the ionic strength was either controlled with the citrate or by use of  $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ NaClO}_4$ . The initial reduction of  $\text{TcO}_4^-$  by  $\text{SnCl}_2$  gave a bis(citrato)Tc(V) complex, followed by much slower reduction to a bis(citrato)Tc(IV) complex. This Tc(IV) complex was colorless, in contrast to the blue-violet Tc(IV) complexes prepared by ligand exchange of  $\text{TcBr}_6^{2-}$  with citrate [77MÜN/GRO]. The bis(citrato)Tc(V) complex and its dissociation products were reduced polarographically in two steps at a dropping mercury electrode to yield a bis(citrato)Tc(IV) complex followed by a bis(citrato)Tc(III) complex; approximately one  $\text{H}^+$  was consumed per technetium for each  $1 \text{ e}^-$  reduction [80MÜN].

The formulation given by Münze and Grossman [77MÜN/GRO] for two of their citrate complexes,  $\{\text{K}_4[\text{Tc}(\text{OH})_2(\text{HCit})_2]\}_x$  and  $\text{K}_6[\text{Tc}(\text{OH})_2(\text{Cit})_2]$ , must be incorrect since they would contain Tc(II) and not Tc(IV). However, this discrepancy would disappear if these complexes were reformulated as  $\{\text{K}_4[\text{TcO}_2(\text{HCit})_2]\}_x$  and  $\text{K}_6[\text{TcO}_2(\text{Cit})_2]$ . Another possibility, at least for the monomeric complex  $\text{K}_6[\text{Tc}(\text{OH})_2(\text{Cit})_2]$ , would be for the hydroxy group of  $\text{Cit}^{3-}$  to dissociate to form a  $\text{Cit}^{4-}$  complex.

Table 1 contains a summary of the various equilibrium constants mentioned in this section, along with the corresponding extrapolated values using the specific-ion interaction approach. Ionic strengths for three of the studies were controlled with  $\text{NaClO}_4$  [70GOR/KOC, 80LEV/GRA, 82JUR], and the molarity-to-molality conversions were done using the Table II.4 conversion factors given in the NEA TDB-5.1. In the other study [85VAN, 84VAN/KET] the ionic medium was mixtures of  $\text{LiClO}_4$  and  $\text{HClO}_4$ . For most 1-1 electrolytes  $0.50 \text{ mol} \cdot \text{dm}^{-3}$  equals  $0.51 \text{ mol} \cdot \text{kg}^{-1}$ , and the same situation was assumed for mixtures of  $\text{LiClO}_4$  and  $\text{HClO}_4$ . Equilibrium constants were reported on the molar concentration scale and needed to be converted to the molal scale; in most cases the correction was negligible, but for three cases [80LEV/GRA, 85VAN, 84VAN/KET]  $\log_{10} K$  was affected by 1 in the last significant figure. Results for the nitrosyl complex were taken from Section 10.3.

Two different ionic strengths were studied for complex formation between Tc(IV) and  $\text{DATA}^{3-}$ , and our recommended value of  $\log_{10} K^\circ$  is their weighted

average. In the other cases only a single ionic strength was investigated, and no completely rigorous values can be assigned to uncertainties for extrapolated  $\log_{10}K^\circ$ . In most of the other cases the ionic strength was relatively low, 0.10 to 0.51 mol • kg<sup>-1</sup>, so the corrections to infinite dilutions are fairly small. We then make the conservative estimate that the correction to  $\log_{10}K$  from the extended Debye-Hückel equation was uncertain by  $\pm 50\%$ . However, for the complex between DTPA<sup>5-</sup> and Tc(IV) the correction is large and  $\log_{10}K^\circ$  must have considerable uncertainty.

## 6. Carbon and Silicon Compounds and Complexes

### 6.1 Inorganic Carbon Compounds and Complexes

#### 6.1.2 Inorganic Carbon Complexes

Kotegov et al. [68KOT/PAV] have discussed liquid-liquid extraction behavior of technetium, which generally is done using  $\text{TcO}_4^-$ . Addition of doubly charged anions such as  $\text{CO}_3^{2-}$ ,  $\text{MoO}_4^{2-}$ , and  $\text{SO}_4^{2-}$  generally favored the extraction of  $\text{TcO}_4^-$  from the aqueous phase, whereas singly charged anions such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{CNS}^-$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{ReO}_4^-$  tended to reduce the extraction even when present in only  $10^{-3}$  to  $10^{-2}$  mol • dm<sup>-3</sup>. This does not seem to have been due to complex formation of these anions with the technetium, but rather was due partly to enhancing the phase separation by salting out the organic phase. Organic solvents with donor atoms such as oxygen or nitrogen were required to produce a significant extraction; some of these organic solvents may have reduced the Tc(VII) to a lower valence state. Very little extraction of  $\text{TcO}_4^-$  occurred with aliphatic, aromatic, or chlorohydrocarbon solvents.

Salaria et al. [63SAL/RUL] studied the coulometric reduction of deoxygenated solutions of  $\text{TcO}_4^-$  in the presence of a mixture of 0.2 mol • dm<sup>-3</sup>  $\text{Na}_2\text{CO}_3$ , 0.1 mol • dm<sup>-3</sup>  $\text{NaHCO}_3$ , and 0.5 mol • dm<sup>-3</sup>  $\text{KCl}$  using a mercury pool cathode. The solutions were deoxygenated for 10 minutes before starting the reduction. The pH of the solution was 9.80 and a 3 e<sup>-</sup> per technetium reduction was observed at -0.51 V; alkaline solutions of  $\text{TcO}_4^-$  containing  $\text{KCl}$  and  $\text{KOH}$  or  $\text{K}_2\text{SO}_4$  and  $\text{KOH}$  underwent 3 e<sup>-</sup> reductions at a similar emf of -0.61 V.

Coulometric reduction of  $\text{TcO}_4^-$  in carbonate solutions provided no direct evidence for complex formation between carbonate and  $\text{Tc(IV)}$  under these conditions.

Russell and Cash [78RUS/CAS] studied the polarographic reduction of  $\text{TcO}_4^-$  in various ionic media from pH = 1.0 to 13.0 with use of a dropping mercury electrode. In a pH = 9.8 carbonate solution, a 3  $e^-$  per technetium reduction occurred at -0.51 V followed by an ill defined second wave at -0.86 V; half-peak potentials from cyclic voltammetry at the same pH gave the first reduction wave at -0.52 V. Reoxidation of the reduced technetium solutions with anodic-sweep pulse polarography occurred at -0.02 and +0.09 V from the first reduction wave and at -0.35 and -0.05 V from the second, and with cyclic voltammetry occurred at -0.31, -0.01, and +0.10 V. Inasmuch as the reduction and oxidation potentials were different in this study, the redox processes were irreversible. Since similar potentials were observed in carbonate solutions and in KOH and mixtures of KCl and KOH, no evidence for complex formation was obtained. They fixed the  $\text{TcO}_4^-$  concentration at  $1.5 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$  and the ionic strength at  $0.1 \text{ mol} \cdot \text{dm}^{-3}$ .

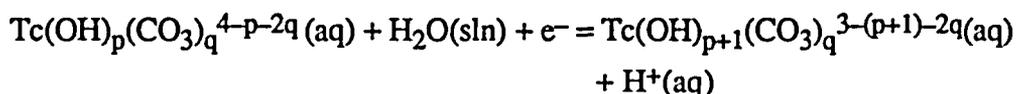
Meyer et al. [87MEY/ARN, 89MEY/ARN] have studied the solubility of hydrated  $\text{TcO}_2$  as a function of pH in various electrolyte solutions (mainly HCl or NaCl solutions). However solubility measurements were also made in  $0.01 \text{ mol} \cdot \text{dm}^{-3} \text{ NaHCO}_3$  plus  $\text{Na}_2\text{CO}_3$  at pH = 9.74 [87MEY/ARN] and at pH = 9.54 and 9.70 [89MEY/ARN] and in synthetic basaltic groundwater containing  $\text{HCO}_3^-$  at pH = 9.27 to 9.43. These solubilities are consistent with solubilities at these same pH values in NaCl-NaOH solutions, and no evidence was obtained for carbonate complexes under those conditions. Since the  $\text{Tc(IV)}$  concentrations were about  $10^{-8} \text{ mol} \cdot \text{dm}^{-3}$ , the total carbonate-to- $\text{Tc(IV)}$  ratio was about  $10^6$ .

Paquette et al. [82PAQ/LIS] reported that spectroscopic evidence was obtained by them for complex formation between carbonate ions and both  $\text{Tc(III)}$  and  $\text{Tc(IV)}$ . They noted in the absence of carbonate,  $5 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3} \text{ Tc(III)}$  disproportionated to yield  $\text{Tc(IV)}$  if pH > 4, and  $\text{Tc(IV)}$  hydrous oxide precipitated around pH = 4; in contrast, when carbonate was present, both the precipitation of  $\text{Tc(IV)}$  and the disproportionation of  $\text{Tc(III)}$  could be suppressed up to high pH. This provides significant evidence for complex formation between technetium and

carbonate, but no experimental details were provided nor were any experimental values given. Some of the details were provided in a later study [85PAQ/LAW].

A detailed study was done of the redox behavior of technetium in  $\text{HCO}_3^-$  solutions at  $\text{pH} = 8$  [85PAQ/LAW]. The ionic strength was maintained at  $I = 1 \text{ mol} \cdot \text{dm}^{-3}$  using sodium trifluoromethanesulfonate, and the  $\text{HCO}_3^-$  concentration was maintained at 0.5 to  $1.0 \text{ mol} \cdot \text{dm}^{-3}$  by use of  $\text{NaHCO}_3$  and pressurization with  $\text{CO}_2$ . The technetium concentration was generally  $1.2 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ , so the total carbonate-to-technetium ratios in their solutions were 4167 to 8333. Coulometric reduction indicated that a  $4.1 e^-$  per technetium reduction of  $\text{TcO}_4^-$  occurred between  $-0.52$  to  $-0.58 \text{ V}$ . The  $\text{TcO}_4^-$  solution was colorless, but upon reduction it rapidly turned pink and then pale blue; the pale blue  $\text{Tc(III)}$  solution was easily oxidized by oxygen in air to reform the pink species, and coulometric rereduction required  $0.9 e^-$  per technetium. Thus the pink species contained  $\text{Tc(IV)}$ .

They did a very careful study of the redox behavior of the  $\text{Tc(IV)/Tc(III)}$  couple in carbonate solutions using spectroelectrochemistry with an optically transparent electrode [85PAQ/LAW]. The redox potential was reversible or at least quasi-reversible at  $\text{pH} = 8$  in  $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{HCO}_3^-$  with a formal reduction potential of  $-0.383 \text{ V}$ . By varying the carbonate concentrations and  $\text{pH}$ , they showed that  $\text{Tc(III)}$  and  $\text{Tc(IV)}$  complexes contained the same number of carbonate ligands, whereas the  $\text{Tc(III)}$  complex had one more hydroxide than the  $\text{Tc(IV)}$  complex. Thus the redox reaction can be written as



where  $p + q > 4$ . However, since  $p$  and  $q$  are unknown, no stability constant can be derived.

We note that those studies in which no complex formation was indicated between  $\text{Tc(IV)}$  and  $\text{CO}_3^{2-}$  were done at  $\text{pH} = 9.27$  to  $9.8$ , whereas the study in which complex formation was found [85PAQ/LAW] was done at  $\text{pH} = 8$ . This suggests that carbonate complexes may be destroyed at the higher  $\text{pH}$  values, and that hydrolyzed  $\text{Tc(IV)}$  then becomes the dominant species.

## UPDATE OF UCRL-10554

### 2.2 Hydride Compounds

*(Add after sixth paragraph)*

Hileman et al. [62HIL/HUG] prepared the technetium carbonyl  $\text{Tc}_2(\text{CO})_{10}$  by direct reaction of  $\text{Tc}_2\text{O}_7$  or  $\text{TcO}_2$  with carbon monoxide. Freshly sublimed  $\text{Tc}_2(\text{CO})_{10}$  was dissolved in tetrahydrofuran at 195 K under vacuum conditions, the system was warmed to 273 K, and then a slight excess of 1% sodium amalgam was added slowly. The solution became reddish and about 5% of the CO was evolved. IR spectra of the tetrahydrofuran solution showed a species was present with carbonyl bands at 1911 and 1865  $\text{cm}^{-1}$ , which differ by only 1  $\text{cm}^{-1}$  from those for  $\text{Re}(\text{CO})_5^-$  and are presumably due to  $\text{Tc}(\text{CO})_5^-$ . The excess sodium amalgam was separated from the solution, and the tetrahydrofuran removed by distillation under high vacuum. Cyclohexane (treated previously with  $\text{LiAlH}_4$ ) was distilled into the reaction vessel, and IR spectroscopy indicated the absence of  $\text{Tc}_2(\text{CO})_{10}$  in the reaction mixture. Thoroughly degassed  $\text{H}_3\text{PO}_4$  was then added at 273 K, and about 1 1/2 mole of  $\text{H}_2$  was evolved per mole of  $\text{Tc}_2(\text{CO})_{10}$  used originally. This  $\text{H}_2$  evolution appeared to be related to partial reformation of  $\text{Tc}_2(\text{CO})_{10}$ . The more volatile components were removed by distillation at 0.02 bar, and gave a distillate that had IR bands at 2021, 2015, and 685  $\text{cm}^{-1}$ . These are close to the IR bands of  $\text{HRe}(\text{CO})_5$ , and provide strong evidence that the hydride  $\text{HTc}(\text{CO})_5$  was prepared.

Another organometallic hydride is described in Section 5.1.2.

*(Add after seventh paragraph)*

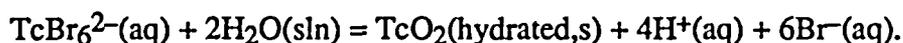
Wang and Balasubramanian [89WAN/BAL] have performed quantum mechanical calculations for  $\text{TcH}(\text{g})$  by using the state-averaged complete active space self-consistent field (CASSCF), first-order configuration interaction (FOCI), and multireference single plus double configuration interaction (MRSDCI) methodologies, and spin-orbit effects were accounted for using the relativistic configuration interaction (RCI) method. The ground state of  $\text{TcH}(\text{g})$  was predicted

to be of  $7\Sigma^+$  symmetry with an atomic distance of  $1.75 \times 10^{-10}$  m and a dissociation energy of  $254 \text{ kJ} \cdot \text{mol}^{-1}$ , which is somewhat higher than the other estimates described in the preceding paragraph. Calculations were performed for twenty seven low-lying electronic states. Dissociation limits for the lowest-lying ground states were predicted to be at 3000, 15 000, and 20 400  $\text{cm}^{-1}$ , compared to experimental values at 3277, 15 234, and 16 179  $\text{cm}^{-1}$ . Published experimental results are very incomplete. Milliken population analysis of all of the low-lying electronic states of TcH revealed they are very ionic ( $\text{Tc}^+\text{H}^-$ ), and the TcH  $\sigma$  bonds in most of these states are spd hybrids with d and s components usually dominating.

### 3.1.1 Mononuclear Halide Compounds (Binary and Ternary Systems)

*(Add before second from last paragraph)*

Münze and Grossmann [75MÜN/GRO] studied the kinetics of the hydrolysis of  $\text{TcBr}_6^{2-}$  in aqueous 0.001 to 3.0  $\text{mol} \cdot \text{dm}^{-3}$  HBr. They found that hydrolysis occurred by way of the reaction



The kinetics of this hydrolytic reaction were monitored by absorption spectra measurements, and the following rate equation was obtained.

$$-\text{d}[\text{TcBr}_6^{2-}]/\text{dt} = k[\text{TcBr}_6^{2-}]/[\text{H}^+]^2[\text{Br}_6^-]^6$$

No values of k were given, but for  $9.35 \times 10^{-5}$  mols of  $\text{K}_2[\text{TcBr}_6]$  in 5  $\text{cm}^3$  of 0.01  $\text{mol} \cdot \text{dm}^{-3}$  HBr, for example, after 90 minutes the hydrolyzed species contained 3.58  $\text{OH}^-$  per technetium .

### 3.3.1 Oxyhalides

*(Add after eleventh paragraph)*

Peacock [73PEA] has reported some additional information for  $\text{TcOF}_4$  based on unpublished measurements by A. J. Edwards. Technetium oxytetrafluoride undergoes a solid-solid phase transition at 357.7 K. The vapor

pressures of the two solid forms and liquid were given as least-squares equations, but no raw data or experimental details were given. These vapor pressure equations, after conversion to pressure in bar, are

$$\ln p = 31.718 - 12793/T$$

for the low-temperature solid from 298 to 357.7 K,

$$\ln p = 21.702 - 9210/T$$

for the higher temperature solid from 357.7 to 406 K, and

$$\ln p = 16.682 - 5844/T$$

for the liquid from 406 to 423 K. This yields an enthalpy of sublimation for the low-temperature solid of  $106.4 \text{ kJ} \cdot \text{mol}^{-1}$ , an enthalpy of sublimation of the higher temperature solid of  $76.6 \text{ kJ} \cdot \text{mol}^{-1}$ , an enthalpy of transition of  $29.8 \text{ kJ} \cdot \text{mol}^{-1}$ , an enthalpy of vaporization of  $48.6 \text{ kJ} \cdot \text{mol}^{-1}$  for the liquid, and an enthalpy of fusion of  $28.0 \text{ kJ} \cdot \text{mol}^{-1}$ . The uncertainties in these  $\Delta H$  values cannot be rigorously determined since the precision of the vapor pressures was not given, but  $\pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$  should be a conservative estimate for enthalpies of sublimation and vaporization and  $\pm 0.8 \text{ kJ} \cdot \text{mol}^{-1}$  for transition and fusion. The  $\text{TcOF}_4$  is hydrolyzed completely by water to HF,  $\text{HTcO}_4$ , and hydrated  $\text{TcO}_2$ .

### 3.3.2 Hydroxohalide Salts

*(Add before last paragraph)*

Busey [60BUS] reported that zinc metal reduced  $\text{TcO}_4^-$  in aqueous HCl to produce Tc(III) chloro complexes. Presumably, oxygen was not completely excluded from his system since in the absence of oxygen this reaction produces  $\text{Tc}_2\text{Cl}_8^{3-}$  (see Section 3.1.2). The technetium in the present study was confirmed to be Tc(III) by using spectrophotometric titration with  $\text{Ce}(\text{SO}_4)_2$ . From changes in the ultraviolet spectra of the solutions as a function of HCl concentration, Busey concluded that one technetium species predominated for 3 to 6  $\text{mol} \cdot \text{dm}^{-3}$  HCl, and a different one predominated for 0.5 to 2  $\text{mol} \cdot \text{dm}^{-3}$  HCl. Busey postulated that this spectroscopic change was due to the reaction



By measuring the absorbancy at 265 nm for 0.5 to 6 mol • dm<sup>-3</sup> HCl, Busey [60BUS] obtained 11 mol • dm<sup>-3</sup> for this equilibrium constant. This K value must be regarded with some scepticism. First, as noted two paragraphs above, the more likely formula for the hydrolyzed species is Tc(OH)Cl<sub>5</sub><sup>2-</sup>. Secondly, the ionic strength was not held constant in these measurements, so this "K" value must have assimilated large changes in the activity coefficients that cannot be corrected for since the detailed experimental results were not tabulated. Consequently, we did not analyze this K value further.

### 3.3.3 Oxohalide Salts

*(Add after the fifteenth paragraph)*

A mixed-valence oxochloride of technetium has also been reported. The original references were not available to us, but it has been described in some detail by Spitsyn et al. [85SPI/KUZ]. This yellow-green K<sub>3</sub>[Tc<sub>2</sub>Cl<sub>8</sub>O<sub>2</sub>] can be prepared by refluxing K<sub>3</sub>[Tc<sub>2</sub>Cl<sub>8</sub>] • 2H<sub>2</sub>O in methyl ethyl ketone in the presence of air. The K<sub>3</sub>[Tc<sub>2</sub>Cl<sub>8</sub>O<sub>2</sub>] was sparingly soluble in organic solvents, but it dissolved readily in aqueous solutions of inorganic acids. It was rather resistant to oxidation and reduction both in the solid phase and in solution, but decomposition was more rapid in the presence of complexing agents. When K<sub>3</sub>[Tc<sub>2</sub>Cl<sub>8</sub>O<sub>2</sub>] was added to concentrated aqueous HCl, the initial decomposition was to form equivalent amounts of [TcCl<sub>6</sub>]<sup>2-</sup> and [TcOCl<sub>5</sub>]<sup>2-</sup>; this confirms that the solid was a mixed-valence Tc(IV,V) compound.

No structural results are available for K<sub>3</sub>[Tc<sub>2</sub>Cl<sub>8</sub>O<sub>2</sub>], but results from IR spectroscopy indicated that two types of non-equivalent oxygens were present, and electronic spectra indicated the absence of a bridging chlorine atom [85SPI/KUZ].

### 5.1.1 Nitrogen (Nitride and Nitrido) Compounds

*(Add right before last paragraph)*

Baldas et al. [89BAL/COL] have recently described two salts of the Tc(VII) chloronitridodiperoxo complex  $[\text{TcN}(\text{O}_2)_2\text{Cl}]^-$ . They prepared crystals of  $(\text{AsPh}_4)[\text{TcN}(\text{O}_2)_2\text{Cl}]$  and  $\text{Cs}[\text{TcN}(\text{O}_2)_2\text{Cl}]$  by addition of  $(\text{AsPh}_4)[\text{TcNCl}_4]$  or  $\text{Cs}_2[\text{TcNCl}_5]$ , respectively, to aqueous 10%  $\text{H}_2\text{O}_2$  in water, followed by evaporation of the solvent over solid KOH at room temperature in an evacuated desiccator. The resulting crystals of  $(\text{AsPh}_4)[\text{TcN}(\text{O}_2)_2\text{Cl}]$  were not very well suited for crystal structural determination because all of the ligand anions were disordered over the four co-ordination sites. Yellow-orange crystals of  $\text{Cs}[\text{TcN}(\text{O}_2)_2\text{Cl}]$  were suitable for X-ray structural analysis; they crystallized in the orthorhombic space group  $\text{P}2_12_12_1$  with  $a=(6.376\pm 0.004) \times 10^{-10}$  m,  $b=(8.552\pm 0.004) \times 10^{-10}$  m,  $c=(11.406\pm 0.006) \times 10^{-10}$  m, and  $Z=4$ . Co-ordination about the technetium atom is a distorted pentagonal pyramide with the nitrido ligand in the apical position. The technetium-to-nitrogen bond length was  $(1.63\pm 0.04) \times 10^{-10}$  m and the mean technetium-to-oxygen distance was  $1.95 \times 10^{-10}$  m.

Their [89BAL/COL]  $(\text{AsPh}_4)[\text{TcN}(\text{O}_2)_2\text{Cl}]$  had IR peaks at 653, 897, and  $1069 \text{ cm}^{-1}$  (in addition to those from the cation), and  $\text{Cs}_2[\text{TcN}(\text{O}_2)_2\text{Cl}]$  had them at 657, 894, 910, and  $1063 \text{ cm}^{-1}$ . The peaks from 894 to  $910 \text{ cm}^{-1}$  are due to O-O, the ones at 653 and 657 to Tc-(O<sub>2</sub>), and the 1063 and 1069 values to the technetium-nitrogen triple bond. Dissolution of the cesium salt in concentrated HCl caused it to be converted to the  $[\text{TcNCl}_4]^-$  anion, and dissolution of the tetraphenylarsonium salt in thionyl chloride followed by evaporation of this solvent gave  $(\text{AsPh})_4[\text{TcNCl}_4]$ . Heating the cesium salt to 383 K caused decomposition with decrepitation, followed by explosive decomposition at 433 K; in contrast  $(\text{AsPh}_4)_3[\text{TcN}(\text{O}_2)\text{Cl}]$  showed no sign of decomposition below 478 K.

### 5.1.2 Nitrogen Complexes

*(Add after sixth paragraph)*

Libson et al. [88LIB/DOY] have described a red salt of Tc(III) that contains the  $\text{H}(\text{NO}_3)_2^-$  anion. No experimental details were given for the preparation of  $\text{trans-}[\text{Tc}(\text{III})(\text{DPPE})_2\text{Cl}_2][\text{H}(\text{NO}_3)_2]$ , where DPPE denotes the

1,2-bis(diphenylphosphino)ethane ligand. It is quite likely that it was prepared by ligand exchange with trans-[Tc(DPPE)<sub>2</sub>Cl<sub>2</sub>]Cl in concentrated HNO<sub>3</sub>. This trans-[Tc(DPPE)<sub>2</sub>Cl<sub>2</sub>][H(NO<sub>3</sub>)<sub>2</sub>] crystallized in the triclinic space group  $P\bar{1}$  with  $a = (10.083 \pm 0.004) \times 10^{-10}$  m,  $b = (11.119 \pm 0.008) \times 10^{-10}$  m,  $c = (12.767 \pm 0.002) \times 10^{-10}$  m,  $\alpha = (71.80 \pm 0.02)^\circ$ ,  $\beta = (73.68 \pm 0.02)^\circ$ ,  $\gamma = (69.35 \pm 0.02)^\circ$ , and  $Z = 1$ .

*(Add right before the last paragraph)*

This complex was studied in more detail by Struchkov et al. [82STR/BAZ], who have established that it is actually the hydride complex hydridobis[1,2-bis(diphenylphosphino)ethane]dinitrotechnetium(I), HTc(N<sub>2</sub>)L<sub>2</sub>. Crystals were grown from n-hexane, and X-ray diffraction established that it crystallized in the monoclinic space group  $P2_1/n$  with  $a = (11.090 \pm 0.006) \times 10^{-10}$  m,  $b = (24.550 \pm 0.010) \times 10^{-10}$  m,  $c = (16.379 \pm 0.008) \times 10^{-10}$  m,  $\beta = (96.02 \pm 0.04)^\circ$ , and  $Z = 4$ . The technetium atom was octahedrally coordinated with the hydridic hydrogen being trans to the N<sub>2</sub> group; the presence of a hydridic hydrogen was supported by <sup>1</sup>H NMR measurements.

#### 5.2.2.4 Diphosphonate Complexes

*(Add to the end of the end of this section)*

Tji et al. [90TJI/VIN] have studied the redox behavior of technetium in oxygen-free solutions of HEDP<sup>4-</sup> and MDP<sup>4-</sup> by using potentiometric reduction of TcO<sub>4</sub><sup>-</sup> with SnSO<sub>4</sub> at various pH values. For example, in 0.1 mol • dm<sup>-3</sup> HEDP, reduction of TcO<sub>4</sub><sup>-</sup> by Sn<sup>2+</sup> involved 3e<sup>-</sup> per technetium to Tc(IV) at pH = 2.5 and 7.0, but the reduction was closer to 4e<sup>-</sup> per technetium to form a Tc(III) complex at pH=12. However, reducing the total HEDP<sup>4-</sup> concentration to 0.06 or 0.02 mol • dm<sup>-3</sup> gave about 3.3 e<sup>-</sup> reductions of TcO<sub>4</sub><sup>-</sup> at pH=2.5. Similarly, reduction of TcO<sub>4</sub><sup>-</sup> with SnSO<sub>4</sub> at pH= 7.0 and 12.0 in 0.1 mol • dm<sup>-3</sup> MDP<sup>4-</sup> also gave about 3e<sup>-</sup> per technetium to form a Tc(IV) complex. In each case, there was also some formation of hydrated TcO<sub>2</sub>, but only for MDP<sup>4-</sup> solutions at pH=12.0 was hydrated TcO<sub>2</sub> the predominant product.

Tji et al. [90TJI/VIN] also reported the results of reverse titrations (i.e., titration of  $\text{Sn}^{2+}$  with  $\text{TcO}_4^-$ ) in  $0.1 \text{ mol} \cdot \text{dm}^{-3}$   $\text{HEDP}^{4-}$  at  $\text{pH}=2.5, 7.0,$  and  $12.0,$  and for  $0.1 \text{ mol} \cdot \text{dm}^{-3}$   $\text{MDP}^{4-}$  at  $\text{pH}=7.0.$  In each case there was a  $3.5 e^-$  reduction of  $\text{TcO}_4^-$ , possibly to a  $\text{Tc}(3.5)$  dimer. Normal titration of  $\text{TcO}_4^-$  with  $\text{Sn}^{2+}$  gave substantial  $\text{Tc(V)}$  formation before the end point was reached, but further reduction to  $\text{Tc(IV)}$  or  $\text{Tc(III)}$  occurred nearer the titration end point, as described in the preceding paragraph.

### 10.3 Nitrosyl Complexes

*(Add to the end of the second paragraph)*

It was prepared by the same procedure used by Eakins et al., except that  $\text{NaOH}$  was added to the solution to adjust the  $\text{pH}$  to  $7.0$  instead of using aqueous ammonia. Addition of an aqueous ethyl alcohol solution of  $1,10\text{-phen}$  to this solution followed by evaporation gave a residue that was next dissolved in water and then placed on a cation-exchange column. Elution with aqueous  $\text{HCl}$  gave three characteristic bands, with the first being green and the other two red. Based on characteristics of the elution, their IR and UV spectra; analyses for  $\text{Tc}, \text{C}, \text{N},$  and  $\text{Cl}$ ; and their electrochemical characteristics, they tentatively identified the first species eluted as  $[\text{Tc}(\text{NH}_3)_2(1,10\text{-phen})(\text{NO})(\text{H}_2\text{O})]^{2+},$  the second as  $[\text{Tc}(\text{NH}_3)_2(1,10\text{-phen})(\text{NO})(\text{H}_2\text{O})]^{3+},$  and the last (and major) species as  $[\text{Tc}(1,10\text{-phen})_2(\text{NH}_3)(\text{NO})]^{2+}.$

*(Add to the end of the sixth paragraph)*

Hugill and Peacock [66HUG/PEA] reported a nearly identical preparation for yellow  $(\text{NO})\text{TcF}_6$  by reaction of  $\text{TcF}_6$  with  $\text{NO}$  at  $228 \text{ K},$  but found that more than one solid compound was produced.

### 10.4 Tin Complexes

*(Add after fourth paragraph)*

In section 5.2.2.4, complex formation between technetium and  $\text{HEDP}$  was described (note:  $\text{HEDP}$  is also denoted by  $\text{EDHP}$  in the literature). Complex

formation between technetium and HEDP in the presence of tin has been investigated by van den Brand et al. [81VAN/DAS, 82VAN/DAS]. They prepared the tin-HEDP complexes first and then added technetium in tracer amounts, followed by adjustment of the pH to 7.4. The approximate stoichiometry of these technetium complexes were determined by 1) the effective molecular weight as estimated by peak position after separation with use of gel chromatography; and 2) the technetium-tin-phosphorous ratio of each complex was determined by  $\gamma$ -ray spectroscopy ( $^{99m}\text{Tc}$ ,  $^{113}\text{Sn}$ , and  $^{32}\text{P}$ ). The technetium was assumed to be Tc(IV); tin was claimed to be most likely Sn(IV) in the first paper [81VAN/DAS], but it was acknowledged later [82VAN/DAS] that either Sn(II) or Sn(IV) was possible.

A total of five technetium-containing species were separated by gel chromatography, and their empirical compositions were Tc(IV)(HEDP), Tc(IV)(HEDP)<sub>2</sub>, Tc(IV)Sn(HEDP), Tc(IV)Sn(HEDP)<sub>2</sub>, and Tc(IV)Sn(HEDP)<sub>3</sub> [81VAN/DAS, 82VAN/DAS]. The extent of hydrolysis/protonation and the charges on these complexes are unknown. The last one of these complexes was found to be rather unstable. In the 1981 report, elution of the complexes was described with pH = 7.4 aqueous solutions of HEDP or NaCl, but experiments were reported from pH = 0.5 to 11.5 in the 1982 report. Concentrations of Sn(II) were varied from  $1 \times 10^{-5}$  to  $1.6 \times 10^{-2}$  mol  $\cdot$  dm<sup>-3</sup>.

The extent of formation of Tc(IV)Sn(HEDP)<sub>2</sub> was nearly independent of pH for pH = 0.5 to about 6, but the yield of this species decreased significantly at higher pH values. For pH = 0.5 to 6.0 the yield of Tc(IV)Sn(HEDP) was approximately constant, and then became much higher for pH = 7.0 to 10.0. Typically 80 to 95% of the technetium was in these two types of complexes. The yield of Tc(IV)(HEDP) varied from 4.4 to 21.0%, but it did not seem to correlate with pH or the presence or absence of excess tin [82VAN/DAS]. It should be emphasized that the valence of tin in these complexes is unknown, as is the extent of protonation of the HEDP ligand and the extent of hydrolysis of the technetium.

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Table 1.. Experimental equilibrium constant data  
for technetium hydroxooxo complexes containing organic ligands  
and hydroxo complex containing nitrosyl and amine ligands at 298 K<sup>a</sup>

| Ionic Strength<br>mol • kg <sup>-1</sup>   | log <sub>10</sub> K | $(-\sum Z_i^2) D$  | $\log_{10} K - (\sum Z_i^2) D$<br>= log <sub>10</sub> K <sup>o</sup> | Reference   |
|--|---------------------|--------------------|--|-------------|
| trans-[Tc(DMPE) <sub>2</sub> (OH)(O)] <sup>2+</sup> (aq) = trans-[Tc(DMPE) <sub>2</sub> O <sub>2</sub> ] <sup>+</sup> (aq) + H <sup>+</sup> (aq)                                 |                     |                    |  |             |
| 0.51   | 0.81±0.10           | +0.35 <sup>b</sup> | 1.16±0.20  | [84VAN/KET] |
| trans-[Tc(DEPE) <sub>2</sub> (OH)(O)] <sup>2+</sup> (aq) = trans-[Tc(DEPE) <sub>2</sub> O <sub>2</sub> ] <sup>+</sup> (aq) + H <sup>+</sup> (aq)                                 |                     |                    |  |             |
| 0.51   | -0.95±0.31          | +0.35 <sup>b</sup> | -0.60±0.36   | [85VAN]     |
| trans-[Tc(NH <sub>3</sub> ) <sub>4</sub> (NO)(H <sub>2</sub> O)] <sup>2+</sup> (aq) = trans-[Tc(NH <sub>3</sub> ) <sub>4</sub> (NO)(OH)] <sup>+</sup> (aq) + H <sup>+</sup> (aq) |                     |                    |  |             |
| 0.01   | -7.3                | +0.09 <sup>b</sup> | -7.2±0.2   | [76ARM/TAU] |
| [Tc(cyclam)(OH)(O)] <sup>2+</sup> (aq) = [Tc(cyclam)O <sub>2</sub> ] <sup>+</sup> (aq) + H <sup>+</sup> (aq)   |                     |                    |  |             |
| 2.2  | 2.53±0.20           | +0.47 <sup>b</sup> | 3.00±0.31  | [82JUR]     |
| TcO(OH) <sup>+</sup> (aq) + NTA <sup>3-</sup> (aq) = TcO(OH)(NTA) <sup>2-</sup> (aq)   |                     |                    |  |             |
| 0.10   | 13.8±0.4            | +0.66 <sup>c</sup> | 14.5±0.5   | [70GOR/KOC] |
| TcO(OH) <sup>+</sup> (aq) + 2NTA <sup>3-</sup> (aq) = TcO(OH)(NTA) <sub>2</sub> <sup>5-</sup> (aq)   |                     |                    |  |             |
| 0.10   | 25.7±0.4            | -0.66 <sup>d</sup> | 25.0±0.5   | [70GOR/KOC] |
| TcO(OH) <sup>+</sup> (aq) + EDTA <sup>4-</sup> (aq) = TcO(OH)(EDTA) <sup>3-</sup> (aq)   |                     |                    |  |             |
| 0.10   | 19.1±0.4            | +0.87 <sup>e</sup> | 20.0±0.6   | [70GOR/KOC] |
| TcO(OH) <sup>+</sup> (aq) + DATA <sup>4-</sup> (aq) = TcO(OH)(DATA) <sup>3-</sup> (aq)   |                     |                    |  |             |
| 0.10   | 20.7±0.4            | +0.87 <sup>e</sup> | 21.6±0.6   | [70GOR/KOC] |
| 0.035  | 20.8±0.4            | +0.59 <sup>e</sup> | 21.4±0.5   | [70GOR/KOC] |
|  |                     |                    | 21.5±0.4 (Average)   |             |
| TcO(OH) <sup>+</sup> (aq) + DTPA <sup>5-</sup> (aq) + 2H <sup>+</sup> (aq) = TcO(OH)(H <sub>2</sub> DTPA) <sup>2-</sup> (aq)   |                     |                    |  |             |
| 1.05   | 26.2±1.8            | +4.93 <sup>f</sup> | 31.1±?   | [80LEV/GRA] |

a For all but the first four reactions, there is some ambiguity for the formula of the complex.

See the text for discussions of individual reactions.

b  $\Sigma Z_i^2 = -2$

c  $\Sigma Z_i^2 = -6$

d  $\Sigma Z_i^2 = +6$

e  $\Sigma Z_i^2 = -8$

f  $\Sigma Z_i^2 = -24$

## Appendix A

This report does not use any information from the Reference Information Base nor contain any candidate information for the Reference Information Base or the Site and Engineering Properties Data Base (SEPDB).

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