= 2.55 Å, C-O = 1.15 Å, and Fe-C = 1.78 Å.

The geometry of $Fe_2(CO)_6B_2H_6$ was idealized to C_{2v} symmetry as shown in Figure 2. All BBH angles were chosen to be 110° with bond lengths of $B-H_t$ = 1.05 Å, $B-H_b$ = 1.30 Å, B-B = 1.70 Å, $Fe-H_b$ = 1.55 Å, and Fe-B = 2.22 Å. The geometry of the B_3H_7 fragment on $Fe_2(CO)_6$ was based on the crystal structure study,[6] with slight adjustments in positions of the B and H atoms in order to idealize C_s symmetry.

Basis Functions. The extended Hückel calculations employed the same orbital exponents and diagonal matrix elements for Fe, C, and O as used by Burdett.[29] For boron and sulfur we employed Slater exponents for the valence orbitals; 1.3 and 1.82, respectively. The H 1s orbital exponent was chosen to be 1.3 and its diagonal matrix −13.60 eV. The diagonal matrix elements for boron and sulfur were chosen from the work of Basch, Viste, and Gray.[30] The extended Hückel calculations were done employing the arithmetic mean Wolfsberg-Helmholz approximation with $K = 1.75$.

The Fenske-Hall calculations employed single-ζ Slater basis functions for the 1s and 2s functions of B, C, and O. The exponents were obtained by curve fitting the double-ζ functions of Clementi[31] while maintaining orthogonal functions. For hydrogen, an exponent of 1.16 was used which corresponds to the minimum energy exponent for methane.[32] The sulfur functions were used directly in their double-ζ form.[33] The iron 1s-3d functions were taken from the results of Richardson et al.[34] and were all single-ζ except the 3d function which is double-ζ and was chosen for the +1 oxidation state of iron. The 4s and 4p exponents were both chosen to be 2.0. For all of the atoms studied here, these are the basis functions typically employed by Fenske and Hall in their studies using this quantum chemical approach.[8,35,36]

Acknowledgment. The support of the National Science Foundation under Grants CHE 78-11600 and CHE 79-15220 is gratefully acknowledged. We thank the University of Notre Dame and the Calvin College Computer Centers for providing computing time.

Registry No. $Fe_2(CO)_6B_2H_6$, 67517-57-1; 1,2-$[Fe(CO)_3]_2B_3H_7$, 71271-99-3; $Fe_2(CO)_6S_2$, 14243-23-3.

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Technetium Electrochemistry. 1. Spectroelectrochemical Studies of Halogen, diars, and diphos Complexes of Technetium in Nonaqueous Media

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Received March 3, 1981

Spectroelectrochemical techniques have been used to investigate the electrochemistry of the well-characterized trans-octahedral Tc(III) complexes $[TcD_2X_2]^+$ where D = diars (*o*-phenylenebis(dimethylarsine)) or diphos (1,2-bis(diphenylphosphino)ethane) and X = Cl, or Br, or I. All complexes exhibit reversible Tc(III)/Tc(II) couples, and the diars complexes exhibit less well-characterized Tc(II)/Tc(I) couples. For the complex $[Tc(diars)_2Cl_2]^+$ in *N*,*N*-dimethylformamide with 0.5 M tetraethylammonium perchlorate as supporting electrolyte, reduction potentials for the Tc(III)/Tc(II) and Tc(II)/Tc(I) couples are −0.091 and −1.29 V vs. NaSCE, respectively. The potential of the Tc(III)/Tc(II) couple is sensitive to the nature of D and to the nature of X, varying Cl → Br, Br → I, or diars → diphos, favoring reduction to Tc(II) by 70-120 mV. These Tc(III)/Tc(II) couples are biologically accessible, and the sensitivity of reduction potential to the nature of X may be one source of the biological differentiation among $[^{99m}Tc(diars)_2X_2]^+$ complexes. Comparisons with literature data show that, independent of oxidation state, technetium complexes are 200-300 mV more easily reduced than are the corresponding rhenium complexes. Observations on the reduction of the Tc(IV) complexes TcX_6^{2-}, X = Cl or Br, and comments on the lability of Tc-X bonds are also presented.

Introduction

The chemistry of technetium is currently receiving considerable attention[1-9] primarily because of the preeminence of ^{99m}Tc in diagnostic nuclear medicine[1,10] but also because of the paucity of information currently available about this element which occupies a central position among the d-block metals. Technetium electrochemistry is especially poorly developed, despite the fact that complexes are known in which technetium exhibits oxidation states ranging from VII to −I.[11,12] This situation arises since almost all the tecnetium complexes available until very recently undergo only irreversible electrochemical behavior,[13] making it difficult to generate quantitative conclusions and comparisons. For example, Davison and co-workers[14] recently reported that the hexahalo-

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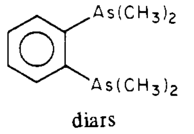
technetium(IV) complexes TcX_6^{2-} undergo only irreversible electrochemical processes in acetonitrile (and irreversibly yield only $TcO_2 \cdot xH_2O$ in aqueous media) while Mazzi and coworkers[15–17] have described the irreversible electrochemical behavior of low-valent technetium complexes with π-acceptor ligands. Reduction of pertechnetate, TcO_4^-, in the presence of complexing ligands can lead to reduced technetium species that exhibit reversible electrochemical behavior,[13,18–20] but the exact structures and compositions of these reduced species are almost invariably unknown, again making it difficult to generate quantitative conclusions and comparisons. It has only been very recently that well-characterized technetium complexes with the potential of exhibiting reversible electrochemical behavior have become available; for example, Davison and co-workers[7,8] have just reported that the Tc(III) complex $Tc(NCS)_6^{3-}$ and the series of Tc(V) complexes $TcO(dithiolato)_2^-$ undergo electrochemically reversible redox processes.

As part of our program to develop ^{99m}Tc heart-imaging agents, we have followed the work of Nyholm[21,22] and Fergusson[23,24]to prepare ^{99}Tc complexes of diars (*o*-phenylenebis(dimethylarsine)) and diphos (1,2-bis(diphenylphosphino)ethane). These are Tc(III) complexes of the general formula *trans*-$[TcD_2X_2]^+$ where D = diars or diphos and X = a halogen or pseudohalogen; single-crystal X-ray structural analyses have been completed for *trans*-$[Tc(diars)_2Cl_2]^+$ [5,25] and *trans*-$[Tc(diphos)_2Br_2]^+$.[26] Interestingly, the ^{99m}Tc diars complexes do function as efficacious heart-imaging agents,[27,28] the biological distributions of the complexes being sensitive to the nature of the monodentate ligand X. Since *trans*-$[TcD_2X_2]^+$ complexes are likely to exhibit reversible electrochemical behavior which could be quantitatively compared with the electrochemical behavior of diars and diphos complexes of neighboring transition metals and since the electrochemical behavior of the *trans*-$[Tc(diars)_2X_2]^+$ complexes could be one source of the biological differentiation among these complexes, we undertook the electrochemical investigation described herein. In this investigation we have relied heavily on spectroelectrochemical techniques employing an optically transparent thin-layer electrode (OTTLE)[29–31] and nonaqueous media. Use of the OTTLE in a spectropotentiostatic experiment allows simultaneous determination of redox potentials ($E°'$), the number of electrons involved in the redox process (n), and the spectra of the electrogenerated species. The advantages of these techniques, and their application to nonaqueous inorganic redox systems, have been detailed previously.[32]



diars

$(C_6H_5)_2P—CH_2CH_2—P(C_6H_5)_2$

diphos

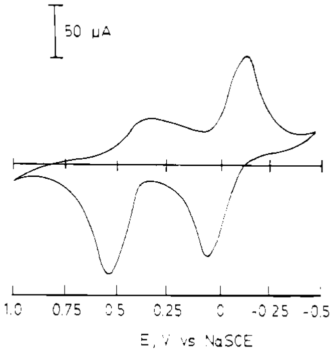


Figure 1. Thin-layer cyclic voltammogram of 0.76 mM $[Tc(diphos)_2Cl_2]^+$ (0.5 M TEAP in DMF) (scan rate 5 mV/s; initial open circuit potential 0.109 V vs. NaSCE).

Experimental Section

Reagents. All common laboratory chemicals were of reagent grade; water was triply distilled.[33] The 1,2-bis(diphenylphosphino)ethane complexes *trans*-$[Tc(diphos)_2X_2]X$ (X = Cl, Br) were prepared by a modification[26] of a reported procedure.[23],[24] The *o*-phenylenebis(dimethylarsine) complexes *trans*-$[Tc(diars)_2Cl_2]ClO_4$ and *trans*-$[Tc(diars)_2X_2]X$ (X = Br, I) were prepared by an elaboration[34] of the synthetic route reported by Nyholm.[21,22] The hexahalo complexes K_2TcX_6 (X = Cl, Br) were prepared by the method of Dalziel et al.[35] All complexes, except *trans*-$[Tc(diphos)_2Br_2]^+$, exhibited visible–UV spectrophotometric parameters in agreement with thoose reported in the literature. The identity of *trans*-$[Tc(diphos)_2Br_2]^+$ was confirmed by single-crystal X-ray structure analysis[26]. All diphos and diars complexes were purified by chromatography and were shown to be homogeneous by TLC analysis.[26,28,34]

Apparatus and Instrumentation. The design and assembly of the gold minigrid optically transparent thin-layer electrode (OTTLE) have been described.[36,37] A small wire was soldered to the minigrid and attached to the edge of quartz microscope slides with epoxy to provide electrical contact. A Telfon solution cup was used to minimize solution creep. All potentials were measured vs. a sodium saturated calomel electrode (NaSCE) which was isolated from the solution by a porous Vycor plug. The cell assembly was enclosed in a Plexiglass housing with quartz windows and inlet and outlet ports for argon. The argon purge gas was first passed through a hot copper furnace to remove residual oxygen and then bubbled through a wash tower to saturate the argon stream with solvent. Electrochemical measurements were made with a Princeton Applied Research Model 173 potentiostat/galvanostat, Model 179 digital coulometer, and a Model 175 universal programmer. Spectral measurements were made with a Harrick rapid scan spectrometer RSS-B. Spectropotentiostatic experiments were controlled by microcomputer.

Procedure. Experiments were generally conducted as previously described[32] with the utilization of *N,N*-dimethylformamide (DMF, Fisher Certified) as a solvent and either tetraethylammonium perchlorate (TEAP) or tetrabutylammonium bromide (TBAB) as the supporting electrolyte. Special attention was given to maintaining anaerobic conditions. Samples of solid technetium salts were weighed

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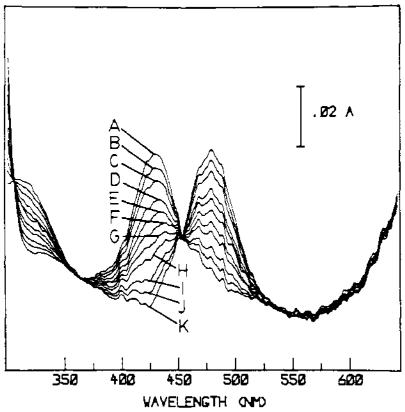

Figure 2. Spectra recorded during OTTLE spectropotentiostatic experiment on 0.76 mM $[Tc(diphos)_2Cl_2]^+$ (0.5 M TEAP in DMF). Spectra background subtracted and smoothed with 9-point Savitsky-Golay. Applied potentials in mV vs. NaSCE are as follows: (A) -500, (B) -100, (C) -80, (D) -60, (E) -50, (F) -40, (G) -30, (H) -20, (I) 0, (J) +20, (K) +300.

on a microbalance and transferred to a dry, argon-purged, glovebox for dissolution in degassed solution, and sealed with a layer of polyethylene (Glad Wrap) in the glovebox. The entire assembly was then quickly transferred into the rapid-scanning spectrophotometer and connected to the deoxygenated, solvent-saturated, purge gas. The cell was aligned with the optical beam passing through the center of the minigrid to minimize edge effects, and then standard[32] spectropotentiostatic procedures were initiated. Blank experiments showed that this procedure eliminated detectable dissolved oxygen.

Results and Discussion

diphos Complexes. Figure 1 shows a thin-layer cyclic voltammogram for $[Tc(diphos)_2Cl_2]^+$ wherein two redox couples are observed. A negative potential scan initiated at the open circuit potential (0.109 V vs. NaSCE) gives a reduction wave with $E_{p(c)} = -0.125$ V which is attributed to the following 1-equiv reduction of Tc(III) to Tc(II):

$$Tc(diphos)_2Cl_2^+ + e^- \rightarrow Tc(diphos)_2Cl_2 \qquad (1)$$

A coupled oxidation wave, $E_{p(a)} = 0.050$ V, is present on the subsequent positive scan, the peak separation, $E_{p(c)} - E_{p(a)} = 0.175$ V, being dependent on the scan rate. Large peak separations, and the dependence of peak separation on scan rate, are typical for OTTLE's used with nonaqueous solvents because of the large solution resistance inherent in this arrangement.[32] Spectra recorded for this Tc(III)/Tc(II) couple during a spectropotentiostatic experiment in an OTTLE are shown in Figure 2; the Tc(III) and Tc(II) complexes exhibit maxima at 475 and 430 nm, respectively, in good agreement with values obtained from chemically prepared materials.[24,26] Repetitive cycles between the Tc(III) and Tc(II) oxidation states yielded no detectable change in spectrophotometric properties, indicating that these complexes are stable on the time scale of several hours. Nernst plots for the data of Figure 2 (at 316, 424, and 475 nm) yield $E^{\circ\prime} = -0.040$ V vs. NaSCE and $n = 0.98$; the plot of the data at 424 nm is shown in Figure 3.

The cyclic voltammogram of Figure 1 also shows a second oxidation wave, $E_{p(a)} = 0.520$ V, with a coupled reduction wave, $E_{p(c)} = -0.040$ V, but no spectrophotometric changes accompany cycling the potential through this couple. This peak is attributed to oxidation of the gold electrode to form a gold chloride species where the source of chloride is the anion of the complex salt, $[Tc(diphos)_2Cl_2]$*Cl*. The peak height increases with addition of LiCl.

A negative potential scan beyond −1.0 V shows that the Tc(II) complex $Tc(diphos)_2Cl_2$ undergoes an irreversible reduction with $E_{p(c)} = -1.12$ V, the characteristic 430-nm absorption band of the Tc(II) complex being lost upon reduction. A positive scan does not regenerate $Tc(diphos)_2Cl_2$. The chemistry of this irreversible process has not been characterized, but $NaBH_4$ reduction of $[Tc(diphos)_2Cl_2]Cl$ yields a product which exhibits similar redox behavior, indicating that technetium complexes are involved.

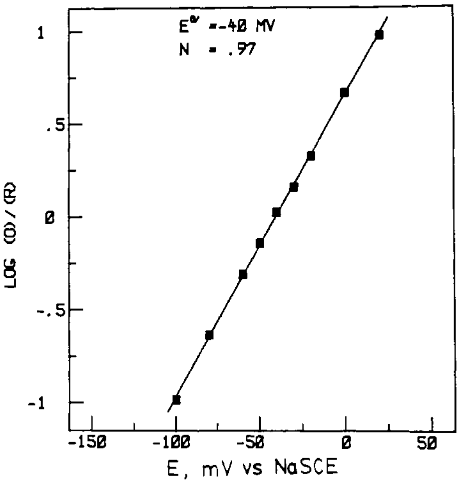

Figure 3. Nernst plot of data in Figure 2 at 424 nm. Conditions as given in Figure 2, except 5-point smooth.

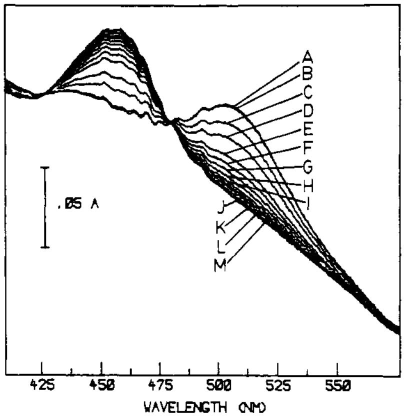

Figure 4. Spectra recorded during OTTLE spectropotentiostatic experiment on 0.601 mM $[Tc(diphos)_2Br_2]^+$ (0.5 M TEAP in DMF). No background subtraction. Applied potentials in mV vs. NaSCE are as follows: (A) 300, (B) 150, (C) 100, (D) 80, (E) 60, (F) 50, (G) 40, (H) 30, (I) 20, (J) 10, (K) -20, (L) -50, (M) -0.250.

Thin-layer cyclic voltammetry of the bromo analogue, $[Tc(diphos)_2Br_2]^+$, shows a single reversible couple ($E_{p(c)} = 0.0$ and $E_{p(a)} = 0.140$ V at a scan rate of 2 mV s^{-1}) which is attributed to the 1-equv reduction of Tc(III) to Tc(II). Figure 4 shows spectra resulting from an OTTLE spectropotentiostatic experiment; the Tc(III) and Tc(II) complexes exhibit maxima at 503 and 460 nm, respectively, in good agreement with values obtained from chemically prepared materials.[24,26] Again, repetitive cycles between the Tc(II) and Tc(III) oxidation states yield no indications of decomposition. A Nernst plot of the spectropotentiostatic data at 403 nm yields $E^{\circ\prime} = 0.068$ V vs. NaSCE and $n = 0.99$.

It was of interest to determine if a mixed-ligand species, $[Tc(diphos)_2ClBr]^{+/0}$, could result from ligand exchange between the homogeneous $[Tc(diphos)_2Cl_2]^{+/0}$ and $[Tc(diphos)_2Br_2]^{+/0}$ complexes. If such a mixed-ligand species were formed, the resultant $E^{\circ\prime}$ would be expected to lie between the $E^{\circ\prime}$ values of the homogeneous complexes. Figure 5 shows a thin-layer cyclic voltammogram obtained with use of a slow scan rate on an equimolar solution of $[Tc(diphos)_2Cl_2]^+$ and $[Tc(diphos)_2Br_2]^+$. Because the individual redox couples of

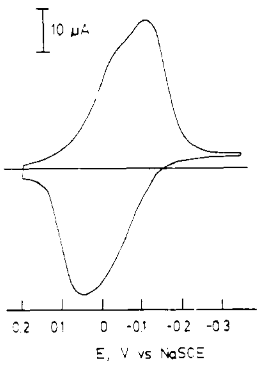

Figure 5. Thin-layer cyclic voltammogram of 1.07 mM $[Tc^{III}(diphos)_2Cl_2]^+$ and 0.97 mM $[Tc^{III}(diphos)_2Br_2]^+$ (0.5 M TEAP in DMF) (scan rate 1 mV/s).

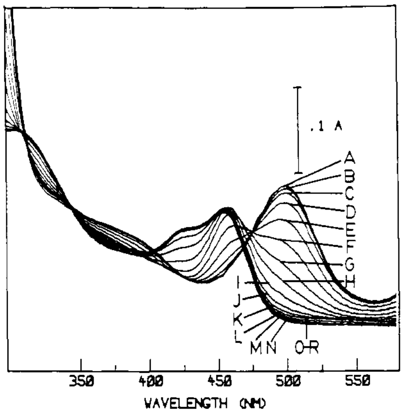

Figure 6. Spectra recorded during OTTLE spectropotentiostatic experiment on 1.07 mM $[Tc^{III}(diphos)_2Cl_2]^+$ and 0.97 mM $[Tc^{III}(diphos)_2Br_2]^+$ (0.5 M TEAP in DMF). Applied potentials in mV vs. NaSCE are as follows: (A) 200, (B) 125, (C) 100, (E) 50, (F) 25, (G) 0, (H) -25, (I) -50, (J) -75, (K) -100, (L) -125, (M) -150, (N) -175, (O) -200, (P) -225, (Q) -250, (R) -350.

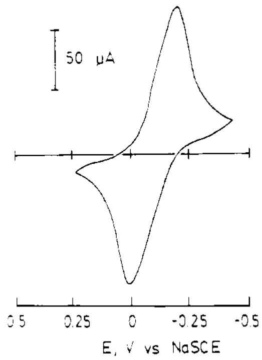

Figure 7. Thin-layer cyclic voltammogram of 0.87 mM $[Tc(diars)_2Cl_2]^+$ (0.5 M TEAP in DMF) (scan rate 2 mV/s). Initial open circuit potential is -36 mV vs. NaSCE.

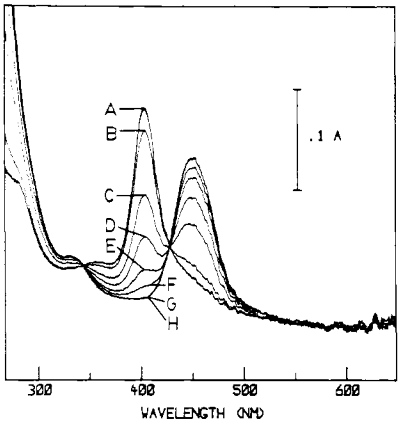

Figure 8. Spectra recorded during OTTLE spectropotentiostatic experiment on 0.87 mM $[Tc(diars)_2Cl_2]^+$ (0.5 M TEAP in DMF). Applied potentials in mV vs. NaSCE are as follows: (A) -250, (B) -150, (C) -100, (D) -75, (E) -50, (F) 25, (G) 100, (H) 250.

the homogeneous complexes are separated by only 0.108 V, the peaks of the mixture are not expected to be completely resolved. However, Figure 5 shows that sufficient resolution exists to allow observation of the two individual component peaks. This separation of component peaks is evident during the first and subsequent scans, made both before and after the spectropotentiostatic experiment, over a span of more than 2 h. The spectra resulting from the spectropotentiostatic experiment are shown in Figure 6. At +0.200 V (spectrum A), the broad band is composed of the absorptions of $[Tc^{III}(diphos)_2Br_2]^+$ at 503 nm and $[Tc^{III}(diphos)_2Cl_2]^+$ at 475 nm. As the potential is stepped in the negative direction, an isosbestic point is observed until a potential of 0.0 V (spectrum G) is attained. From the Nernst equation it can be calculated that at this potential 98.4% of the bromo species is in the reduced form while 82.7% of the chloro species remains in the oxidized form. Eventually, as the equilibrium potential is stepped beyond the reduction potential of $[Tc^{III}(diphos)_2Cl_2]^+$, the absorption at 424 nm becomes apparent; the isosbestic point is lost, and the peak around 470 nm due to the sum of the absorptions of $Tc^{II}(diphos)_2Br_2$ and $[Tc^{III}(diphos)_2Cl_2]^+$ shifts to 460 nm as the concentration of $[Tc^{III}(diphos)_2Cl_2]^+$ diminishes. Finally, only the absorption maxima of the two individual reduced species are present. This experiment yields no evidence for the existence of the mixed-ligand species $[Tc(diphos)_2ClBr]^{+/0}$, providing further evidence for the stability of the homogeneous complexes on a time scale of hours.

diars Complexes. The electrochemical behavior of the diars complexes resembles that of the analogous diphos complexes, especially with respect to the presence of a reversible Tc(III)/Tc(II) couple. Figure 7 shows a thin-layer cyclic voltammogram for $[Tc(diars)_2Cl_2]^+$ which exhibits a reduction wave at -0.200 V and a coupled oxidation wave at +0.010 V. The results of a spectropotentiostatic experiment are shown in Figure 8; the Tc(III) and Tc(II) complexes exhibit maxima at 440 and 400 nm, respectively, in good agreement with values obtained from chemically prepared materials.[21,22,34] The well-defined isosbestic points indicate that the $[Tc(diars)_2Cl_2]^{+/0}$ complexes are stable for over 2 h within the potential range +0.40 to -0.50 V. A Nernset plot of the data at 403 nm yields $E°' = -0.091$ V vs. NaSCE and $n = 0.99$.

The Tc(II) complex $Tc(diars)_2Cl_2$ undergoes further reduction in a process that appears to be reversible only within times less than about 1 min. During this reduction, the 400-nm peak characteristic of $Tc(diars)_2Cl_2$ fades, but it is regenerated upon rapid reoxidation; further oxidation generates $[Tc(diars)_2Cl_2]^+$. When scans are conducted rapidly, the height of the peak at -0.200 V (reduction of Tc(III) to Tc(II)) is comparable to the height of the peak at -1.375 V, and thus this more negative wave ($E°'$ ca. -1.3 V vs. NaSCE) is tentatively attributed to the one-equivalent reduction of Tc(II) to Tc(I). Neither the Tc(I) complex nor the products of the competing chemical reactions which cause the Tc(II)/Tc(I) couple to be irreversible has been identified. However, the cyclic voltammogram shown in Figure 9 demonstrates that the reduced byproducts can be reoxidized to $[Tc(diars)_2Cl_2]^+$. After the potential was stepped from -1.750 to -0.900 V during an unsuccessful attempt to collect spectropotentiostatic data, the potential was scanned in the negative direction starting at -0.900 V; the initial Tc(II)/Tc(I) wave is small (see Figure 9) since the bulk of the material is in the form of

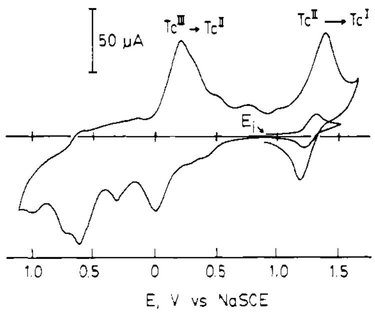

Figure 9. Thin-layer cyclic voltammogram of 0.87 mM [Tc(diars)$_2$Cl$_2$]$^+$ (0.5 M TEAP in DMF). Voltammogram recorded after OTTLE spectropotentiostatic experiment on redox couple at −1.3 V (scan rate 5 mV/s). First negative scan initiated at −900 mV.

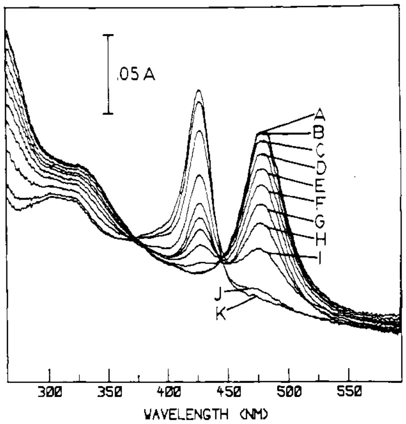

Figure 10. Spectra recorded during OTTLE spectropotentiostatic experiment on 0.80 mM [Tc(diars)$_2$Br$_2$]$^+$ (0.5 M TBAB in DMF). Applied potentials in mV vs. NaSCE are as follows: (A) 350, (B) 100, (C) 50, (D) 25, (E) 10, (F) 0, (G) −10, (H) −25, (I) −50, (J) −100, (K) −400.

reduced byproducts, but after scanning through the Tc(III)/Tc(II) couple the Tc(II)/Tc(I) wave becomes equivalent in size to the Tc(III)/Tc(II) wave, indicating that all the reduced byproducts had been reoxidized to [Tc(diars)$_i$Cl$_2$]$^+$. This behavior is in contrast to the Tc^{II}(diphos)$_2$Cl$_2$ system (vide supra) wherein electrochemical reduction yields products which cannot be reoxidized to the starting material.

Thin-layer cyclic voltammetry of the bromo analogue [Tc(diars)$_2$Br$_2$]$^+$ shows the Tc(III)/Tc(II) couple centered at −0.010 V. While the Tc(II) complex Tc(diars)$_2$Br$_2$ is stable during the voltammetry experiment (ca. 500 s), it is not sufficiently stable in DMF/TEAP to permit a spectropotentiostatic experiment; when the potential is stepped from −0.500 V to +0.400 V, the 420-nm peak characteristic[21,22,34] of Tc(II) disappears, but very little of the 474-nm peak characteristic[21,22,34] of Tc(III) appears. However, when the supporting electrolyte is changed from a perchlorate medium (0.5 M TEAP) to a bromide medium (0.4 M TBAB), Tc(diars)$_2$Br$_2$ is stabilized to the point that a spectropotentiostatic experiment can be conducted. The resulting spectra are shown in Figure 10; a Nernst plot of the data at 426 nm yields $E^{\circ\prime}$ = −0.022 V vs. NaSCE and n = 1.01. Stabilization in a bromide medium implies that Tc(diars)$_2$Br$_2$ decomposes at least partially by loss of bromide ligands.

Analogous to the chloro complex, Tc^{II}(diars)$_2$Br$_2$ exhibits a second redox couple centered at −1.15 V vs. NaSCE which is tentatively ascribed as resulting from reduction of Tc(II) to Tc(I).

Thin-layer cyclic voltammetry of the iodo analogue [Tc(diars)$_2$I$_2$]$^+$ shows a Tc(III)/Tc(II) redox couple centered about 0.105 V vs. NaSCE and a presumed Tc(II)/Tc(I) couple centered about −1.01 V vs. NaSCE. The limited solubility of [Tc(diars)$_2$I$_2$]I in DMF/TEAP precluded investigation of these couples by thin-layer spectroelectrochemistry.

Table I. Formal Reduction Potentials for Some Tc(III)/Tc(II) and Tc(II)/Tc(I) Couples in *N,N*-Dimethylformamide[a]

Tc(III) complex	$E^{\circ\prime}$-[Tc(III)/Tc(II)]	$E^{\circ\prime}$-[Tc(II)/Tc(I)]
Tc(diphos)$_2$Cl$_2$$^+$	−0.040	
Tc(diphos)$_2$Br$_2$$^+$	+0.068	
Tc(diars)$_2$Cl$_2$$^+$	−0.091	−1.29[b]
Tc(diars)$_2$Br$_2$$^+$	−0.010[b]	−1.15[b]
Tc(diars)$_2$Br$_2$$^+$	−0.022[c]	−1.20[b,c]
Tc(diars)$_2$I$_2$$^+$	+0.105[b]	−1.01[b]

[a] Given in volts vs. NaSCE. The supporting electrolyte is 0.5 M tetraethylammonium perchlorate unless otherwise noted. $E^{\circ\prime}$ values determined by Nernstian analysis of spectropotentiostatic data unless otherwise noted. [b] $E^{\circ\prime}$ determined by averaging $E_{p(a)}$ and $E_{p(c)}$ of cyclic voltammogram. [c] The supporting electrolyte is 0.4 M tetrabutylammonium bromide.

Hexahalo Complexes. The Tc(IV) complexes TcX$_6$$^{2-}$ (X = Cl, Br) rapidly hydrolyze in aqueous media to produce insoluble TcO$_2$·xH$_2$O. This can be prevented by working in concentrated solutions of HX, and indeed HX–H$_2$O solution conditions were found where the TcX$_6$$^{2-}$ complexes undergo reversible one-equivalent reduction. However, the $E^{\circ\prime}$ values governing these reductions prove to be complicated functions of X$^-$ and [H]$^+$ concentrations[38] and are therefore not readily interpretable. Hydrolysis to TcO$_2$·xH$_2$O can also be prevented by working in nonaqueous media, and Davison and co-workers have recently reported[14] on the irreversible electrochemical behavior of TcX$_6$$^{2-}$ complexes in acetonitrile. In DMF, cyclic voltammograms show that TcBr$_6$$^{2-}$ undergoes an irreversible reduction with $E_{p(c)}$ being −0.71 V vs. NaSCE when 0.5 M TEAP is the supporting electrolyte and −0.80 V vs. NaSCE when 0.5 M TBAB is the supporting electrolyte. This wave presumably corresponds to the one-equivalent Tc(IV) to Tc(III) reduction observed in aqueous HX media. The fact that it is more difficult to reduce TcBr$_6$$^{2-}$ when the supporting electrolyte contains bromide ion implies that, as in the case of the aqueous HX system,[38] bromide ion is released upon reduction.

Intercomparisons. (1) Relative Kinetic Stabilities. The Tc(III) [TcD$_2$X$_2$]$^+$ complexes are stable to halide ligand loss on the time scale of hours. However, when [Tc(diars)$_2$Br$_2$]$^+$ is reduced to Tc(diars)$_2$Br$_2$, the Tc(II) complex appears to lose bromide ligand. Similarly, when TcBr$_6$$^{2-}$ is reduced from the Tc(IV) state to the Tc(III) state, loss of bromide ligand again occurs. Thus, for both the Tc(IV)/Tc(III) and Tc(III)/Tc(II) couples, halide ligand loss occurs more readily from the lower oxidation state. This is the trend expected from the fact that the lower oxidation state has a lower positive charge density but is opposite from that expected from the fact that in these spin-paired complexes the lower oxidation state has the greater ligand field stabilization.[39] A complete explication of this phenomenon will have to await more detailed kinetic and thermodynamic studies. For the Tc(II) complexes TcD$_2$Br$_2$, bromide loss occurs more readily when D = diars than when D = diphos; this is consistent with the general synthetic chemistry observed[26,34] for these complexes and with the fact that diphos provides a stronger ligand field than does diars.[39,40]

(2) $E^{\circ\prime}$: Halogen Dependence. The data of Table I show that the Tc(III) complexes [TcD$_2$X$_2$]$^+$ are easier to reduce to

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(39) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; pp 145–158.
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Table II. Selected Reduction Potentials for Some Analogous Tc and Re Couples

electrode reaction	couple	E_{Tc}	E_{Re}	$E_{\mathrm{Tc}} - E_{\mathrm{Re}}$
$\mathrm{MO(SC(O)C(O)S)_2^-} + \mathrm{e^-}$	M(V)/M(IV)	$-0.75^{a,b}$	$-0.94^{a,b}$	0.19
$\mathrm{M(NCS)_6^{2-}} + \mathrm{e^-}$	M(IV)/M(III)	$+0.18^{a}$	-0.11^{a}	0.29
$\mathrm{M(diars)_2Cl_2^+} + \mathrm{e^-}$	M(III)/M(II)	-0.09^{c}	-0.41^{d}	0.32
$\mathrm{M(diars)_2Cl_2} + \mathrm{e^-}$	M(II)/M(I)	-1.29^{c}	-1.54^{d}	0.25

[a] Polarographic $E_{1/2}$ in volts vs. SCE. Medium is 0.1 M tetrabutylammonium perchlorate in acetonitrile. Data are from ref 7 and 8. [b] Pseudoreversible behavior observed in cyclic voltammetry.[8] [c] $E^{\circ\prime}$ in volts vs. NaSCE. Medium is 0.5 M tetraethylammonium perchlorate in *N,N*-dimethylformamide. Data are from Table I. [d] $E^{\circ\prime}$ in volts vs. NaSCE. Medium is 0.1 M tetraethylammonium perchlorate in acetonitrile. Table entry calculated from data given in ref 41 by adding 0.3 V to the reported reduction potential vs. $\mathrm{Ag/AgClO_4}$ in acetonitrile.

the Tc(II) state when X is a heavier halogen. The Tc(II) bromo complexes are 70–100 mV more accessible than the Tc(II) chloro complexes, and the Tc(II) iodo complex is ca. 120 mV more accessible than the bromo analogue. This effect presumably arises from the phenomenon of π-back-bonding, the heavier halogens stabilizing spin-paired d^5 Tc(II) over spin-paired d^4 Tc(III) by increased acceptance of t_{2g} electron density. Similarly, the Tc(II) complexes $\mathrm{Tc(diars)_2X_2}$ are easier to reduce to the Tc(I) state when X is a heavier halogen, although here the effect is only in the range of 10–15 mV.

(3) $E^{\circ\prime}$: diphos vs. diars. The data of Table I show that for the pair of Tc(III) chloro complexes $[\mathrm{TcD_2Cl_2}]^+$ it is easier to reduce Tc(III) to Tc(II) by ca. 50 mV when D = diphos than when D = diars; for the bromo complexes, the difference is ca. 85 mV. Thus, diphos stabilizes spin-paired d^5 Tc(II) (relative to spin-paired d^4 Tc(III)) better than does diars, consistent with the established[40] fact that diphos provides a stronger ligand field than does diars. This stabilization of the d^5 center over the d^4 center by an increased ligand field is correspondingly greater when the ancillary ligands are bromide, since bromide is a weaker field ligand than is chloride. Similarly, it is easier to reduce the Tc(II) complexes $\mathrm{TcD_2Cl_2}$ to Tc(I) when D = diphos than when D = diars ($E_{\mathrm{p(c)}}$ values of −1.12 and −1.38 V vs. NaSCE, respectively), although the subsequent reactions of the Tc(I) complexes prevent full characterization of these Tc(II)/Tc(I) couples.

(4) $E^{\circ\prime}$: Tc vs. Re. Literature data on comparable, reversible Tc and Re couples are very sparse. Warren and Bennett[41] have studied a large number of diars complexes by cyclic voltammetry and include $[\mathrm{Re(diars)_2Cl_2}]^+$ in their compilation. Davison and co-workers[7,8] have recently extended the available Re/Tc data through polarographic investigation of $\mathrm{M(NCS)_6^{2-}}$ and $\mathrm{MO(dithiolato)_2^-}$ complexes. Of the latter species,[8] only the dithiooxalato complexes both exhibit at least pseudoreversible behavior and also contain an innocent ligand and therefore provide a useful comparison. The four comparable, appropriately characterized, reversible, Tc/Re redox systems known to us are listed in Table II. As expected[7,8,14] from established periodic trends,[41] it is considerably more difficult to reduce a Re complex than it is to reduce the analogous Tc complex, the effect ranging from 190 to 320 mV. The large magnitude of this effect is entirely consistent with observations made on second- and third-row elements of other groups; for example, the difference in M(III)/M(II) couples for $[\mathrm{M(diars)_2Cl_2}]^{+/0}$ is 320 mV for both the Tc/Re pair and the Ru/Os pair.[41] This effect does not appear to vary systematically with the oxiddation state of the metal center (Table II), but more data are required to better define this observation.

It is interesting to note that of all the trans-octahedral $[\mathrm{M(diars)_2X_2}]^n$ species prepared to date (complexes with at least 12 different metal centers are known[41]) only Tc and Re form anionic complexes, i.e., $\mathrm{M^I(diars)_2Cl_2^-}$. This is presumably due[41] to the great stability of the d^6 configuration of Tc(I) and Re(I) in an octahedral coordination environment.

Summary

The Tc(III) diphos and diars complexes $[trans\text{-}\mathrm{TcD_2X_2}]^+$ are stable, well-characterized species eminently suitable for electrochemical investigation. Reversible reduction to the Tc(II) state occurs at potentials that are readily accessible to biological systems—e.g., aliphatic thiols convert Tc(III) to Tc(II). The existence of this biologically accessible redox couple, perhaps combined with the tendency of the Tc(II) complexes to lose halide ligand, could be one source of the biological differentiation among the $[\mathrm{^{99m}Tc(diars)_2X_2}]^+$ complexes.[27,28] The potential of the Tc(III)/Tc(II) couple is sensitive to the nature of D and to the nature of X, the heavier halogens and diphos (relative to diars) favoring reduction to Tc(II). Technetium complexes are 200–300 mV more easily reduced than are the corresponding rhenium complexes, this effect appearing to be independent of oxidation state. Thin-layer spectroelectrochemistry is an extremely useful technique for the characterization and explication of nonaqeuous inorganic redox systems.

Acknowledgment. Financial support by the National Institutes of Health, Grant No. HL-21276 (E.D.), and the National Science Foundation, Grant No. CHE 77-04399 (W.R.H.), is gratefully acknowledged. We also thank Ms. K. Libson and Mr. K. Glavan for providing the technetium complexes used in this research.

Registry No. $\mathrm{Tc(diphos)_2Cl_2^+}$, 78656-00-5; $\mathrm{Tc(diphos)_2Br_2^+}$, 78656-03-8; $\mathrm{Tc(diars)_2Cl_2^+}$, 47512-11-8; $\mathrm{Tc(diars)_2Br_2^+}$, 78610-19-2; $\mathrm{Tc(diars)_2I_2^+}$, 78610-20-5; $\mathrm{Tc(diphos)_2Cl_2}$, 78656-02-7; $\mathrm{Tc(diphos)_2Br_2}$, 78656-01-6; $\mathrm{Tc(diars)_2Cl_2}$, 14127-29-8; $\mathrm{Tc(diars)_2Br_2}$, 75610-21-6; $\mathrm{Tc(diars)_2I_2}$, 78610-22-7; $\mathrm{Tc(diars)_2Cl_2^-}$, 78610-23-8; $\mathrm{Tc(diars)_2Br_2^-}$, 78610-24-9; $\mathrm{Tc(diars)_2I_2}$, 78610-25-0; $\mathrm{TcBr_6^{2-}}$, 19443-24-4.

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