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Technetium Electrochemistry. 2.[1] Electrochemical and Spectroelectrochemical Studies of the Bis(tertiary phosphine) (D) Complexes *trans*-$[Tc^{III}D_2X_2]^+$ (X = Cl, Br) and $[Tc^{I}D_3]^+$

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The redox chemistry of a series of the well-characterized, robust, cationic technetium complexes *trans*-$[Tc^{III}D_2X_2]^+$ and $[Tc^{I}D_3]^+$, where D = 1,2-bis(dimethylphosphino)ethane (dmpe) and 1,2-bis(diethylphosphino)ethane (depe) and X = Cl and Br, has been investigated in nonaqueous media with use of cyclic voltammetry at 25 and -40 °C, spectroelectrochemistry with a gold-minigrid optically transparent thin-layer electrode, and thin-layer coulometry plus in aqueous media with use of normal pulse voltammetry. The $[TcD_2X_2]^+$ complexes undergo two electrochemical reactions in *N*,*N*-dimethylformamide (DMF), 0.5 M in tetraethylammonium perchlorate (TEAP), corresponding to the reduction of Tc(III) to Tc(II) and Tc(II) to Tc(I), respectively. The reduction potential, the reversibility, and the stability of the product of each process depend on the nature of both D and X. The $[TcD_3]^+$ complexes exhibit a reversible one-electron oxidation of Tc(I) to Tc(II) in water, acetonitrile, propylene carbonate, or DMF. The redox potentials for these Tc(II)/Tc(I) couples in propylene carbonate (0.5 M TEAP) are +0.330 and +0.166 V vs. Ag/AgCl for the dmpe and depe complexes, respectively. The Tc(II) complex $[Tc(dmpe)_3]^{2+}$ undergoes further, more complicated oxidation reactions in propylene carbonate. In aqueous media the $E^{\circ\prime}$ value governing the $[Tc(dmpe)_3]^{2+/+}$ couple is the same as it is in DMF, but the $E^{\circ\prime}$ values governing the $[TcD_2X_2]^{+/0}$ couples are markedly shifted to more positive potentials, reflecting the water insolubility of the neutral technetium(II) complexes $[TcD_2X_2]^0$. The Tc(III)/Tc(II) couples for the $[TcD_2X_2]^+$ complexes and the Tc(I)/Tc(II) couples for the $[TcD_3]^+$ complexes are biologically accessible, and thus the redox behavior of these monocationic complexes is relevant to their potential nuclear medicine use as ^{99m}Tc myocardial imaging agents.

Introduction

The chemistry of technetium has expanded markedly during the last several years.[3-10] This expansion has been driven to a large extent by inorganic chemists striving to obtain a basic understanding of this relatively unstudied element. However, an even greater driving force has been provided by the extensive use of ^{99m}Tc in diagnostic nuclear medicine.[3,5,9,10] Technetium electrochemistry has not been well developed, despite the fact that complexes are known in which technetium exhibits oxidation states ranging from VII to -I.[3,11-13] This situation arises since almost all the technetium complexes available until very recently are oxo compounds, such as TcO_4^-, and thus undergo primarily irreversible electrochemical processes in aqueous media, making it difficult to obtain quantitative conclusions.[14,15] Recently the electrochemical behavior of well-characterized technetium complexes *not* containing oxo groups has been investigated in aprotic solvents;[1,16-21] many of these complexes, which contain technetium in a low oxidation state, exhibit reversible electrochemical processes.

As part of our program to develop ^{99m}Tc heart-imaging agents for use in diagnostic nuclear medicine,[22-24] we have synthesized and characterized cationic ^{99}Tc bis(tertiary phosphine) and bis(tertiary arsine) complexes having the general formula *trans*-$[Tc^{III}D_2X_2]^+$, where D represents a chelating bis(tertiary phosphine) or bis(tertiary arsine) ligand and X represents a halogen or pseudohalogen.[1,16] Single-crystal X-ray structural analyses have been completed for complexes with D = 1,2-bis(dimethylarsino)benzene (diars) and X = Cl,[25] D = 1,2-bis(dimethylphosphino)ethane (dmpe) and X = Cl,[26] and D = 1,2-bis(diphenylphosphino)ethane (dppe) and X = Br.[16] In previous papers we described the spectroelectrochemistry of $[Tc(diars)_2X_2]^+$ and $[Tc(dppe)_2X_2]^+$ [1] and the cyclic voltammetry of $[TcD_2X_2]^+$ complexes.[16] In this paper we report on the electrochemical behavior of $[Tc^{III}D_2X_2]^+$ complexes, where D represents dmpe or the ethyl analogue depe (1,2-bis(diethylphosphino)ethane) (X = Cl, Br), and the

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novel cationic technetium(I) complexes $[Tc^ID_3]^+$ (D = dmpe and depe). The techniques employed include cyclic voltammetry, spectroelectrochemistry with a gold-minigrid optically transparent thin-layer electrode (OTTLE), and thin-layer coulometry in nonaqueous media, plus pulse voltammetry in aqueous media. Spectroelectrochemical techniques using the OTTLE are very useful for characterizing coordination complexes. By taking advantage of rapid electrolysis rates and small cell volumes, these techniques allow simultaneous determination of formal redox potentials ($E^{\circ\prime}$), electron stoichiometries (n), and spectra of electrogenerated species,[27-34] using very small quantities of material. These aspects of OTTLE spectroelectrochemistry are particularly useful in characterizing new technetium complexes, which, because of the radioactivity of ^{99}Tc, are often available in only very limited amounts.

Abbreviations and Acronyms

Ligands: D, 1,2-bis(dialkylphosphino)ethane; dmpe, 1,2-bis(dimethyphosphino)ethane; depe, 1,2-bis(diethylphosphono)ethane; dppe, 1,2-bis(diphenylphosphino)ethane; diars, 1,2-bis(dimethylarsino)benzene; X, halide.

Electrolytes: TEAP, tetraethylammonium perchlorate; (TEA)Cl, tetraethylammonium chloride; (TBA)Br, tetrabutylammonium bromide.

Solvent: DMF, *N*,*N*-dimethylformamide.

Electrodes: OTTLE, optically transparent thin-layer electrode; PDE, platinum-disk electrode; GCE, glassy-carbon electrode.

Experimental Section

General Considerations. Technetium-99 emits a low-energy (0.292-MeV) β particle with a half-life of 2.12×10^5 years. When this material is handled in milligram amounts, it does not present a serious health hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or by Guelph Chemical Laboratories, Ltd., Guelph, Ontario, Canada. Visible–UV spectra were recorded on a Cary 210 spectrophotometer. IR spectra were obtained on a Perkin-Elmer 224 grating infrared spectrometer.

Reagents. Unless otherwise noted, all chemicals were of reagent grade. The dmpe and depe ligands were obtained from Strem Chemical Co. and were used without further purification. Ammonium pertechnetate was obtained from Oak Ridge National Laboratory and purified as previously described.[16] All technetium complexes were purified by column chromatography and were shown to be homogeneous by TLC or HPLC analysis.[16,35] The *trans*-dihalogenobis(1,2-bis(dialkylphosphino)ethane)technetium(III) complexes *trans*-$[Tc(depe)_2Cl_2]CF_3SO_3$, *trans*-$[Tc(dmpe)_2Br_2]Br$, *trans*-$[Tc(depe)_2Cl_2]Cl$, and *trans*-$[Tc(depe)_2Br_2]Br$ were prepared as previously described.[16] The tris(1,2-bis(dimethylphosphino)ethane)technetium(I) complex $[Tc(dmpe)_3]Y$ (Y = $CF_3SO_3^-$, PF_6^-) was prepared from TcO_4^- and excess dmpe ligand as previously detailed.[35]

Table I. Formal Redox Potentials of the Ferrocenium/Ferrocene Couple in Various Nonaqueous Media

solvent	electrolyte	$E^{\circ\prime}$, V vs. Ag/AgCl[a]
N,*N*-dimethylformamide	0.5 M TEAP	+0.506
N,*N*-dimethylformamide	0.5 M (TEA)Cl	+0.530
N,*N*-dimethylformamide	0.4 M (TBA)Br	+0.56[b]
acetonitrile	0.5 M TEAP	+0.398
propylene carbonate	0.5 M TEAP	+0.371

[a] $E^{\circ\prime} = (E_{p,a} + E_{p,c})/2$; cyclic voltammetry on a platinum-disk electrode. [b] Overlap with bromide oxidation.

Tris(1,2-bis(dimethylphosphino)ethane)technetium(II) Hexafluorophosphate, $[Tc(dmpe)_3](PF_6)_2$. The technetium(I) analogue, $[Tc(dmpe)_3]PF_6$ (150 mg, 0.22 mmol), was dissolved in 1.0 mL of acetonitrile. To this solution was added 0.2 mL of a saturated aqueous solution of NH_4PF_6, then 2 drops of 30% H_2O_2, and then 2 drops of concentrated HPF_6. Upon addition of the acid, the solution turned deep purple. Addition of ca. 25 mL of water generated a flocculent purple precipitate, which was collected and washed successively with 5-mL portions of cold water, cold 95% ethanol, and diethyl ether. Recrystallization of this material from acetonitrile yielded 150 mg (82%) of translucent, square, purple crystals. Anal. Calcd for $TcC_{18}H_{48}P_8F_{12}$: C, 25.76; H, 5.76; P, 29.52; F, 27.16. Found: C, 26.20; H, 5.70; P, 30.03; F, 28.43. Visible–UV (CH_3CN; λ, nm (ϵ, $M^{-1}\ cm^{-1}$)): λ_{max} 569 (810), 520 sh, 366 (340), 270 sh (2440), 239 (6460); λ_{min} 339, 232. (These extinction coefficients are lower limits since this complex suffers some decomposition on standing.) IR (KBr pellet; ν, cm^{-1} (intensity): 350 (m), 450 (m), 550 (vs), 605 (w), 635 (m), 695 (s), 720 (m), 830 (vs), 925 (vs), 1300 (m), 1376 (s), 1410 (m), 1620 (m), 2000 (w).

Tris(1,2-bis(diethylphosphino)ethane)technetium(I) and Tris(1,2-bis(diethylphosphino)ethane)technetium(II) Hexafluorophosphates, $[Tc(depe)_3]PF_6$ and $[Tc(depe)_3](PF_6)_2$. Ammonium pertechnetate (100 mg, 0.55 mmol), dissolved in 1.0 mL of water, was added to an anaerobic solution of 1.1 mL of depe (4.6 mmol) in 7.9 mL of absolute ethanol. The reaction vial was then capped with a Teflon stopper, sealed with a crimper, and heated at 130 °C for 1 h. After the vial was cooled, to room temperature, a solution of 5 mg of $NaBH_4$ (0.13 mmol) in 1 mL of H_2O was added dropwise to the reaction solution. Subsequent addition of 0.2 mL of a saturated aqueous solution of NH_4PF_6 and 3 drops of concentrated HPF_6 yielded a white precipitate of the technetium(I) complex, which was collected and washed successively with absolute ethanol and diethyl ether. Contact with the air caused the exposed surfaces of this white material to slowly turn purple. However, under anaerobic conditions, at −10 °C, both the white solid and the acetonitrile solutions of this solid are stable indefinitely. Conversion to the purple Tc(II) analogue was effected in acetonitrile by H_2O_2 oxidation as outlined above, the yield of recrystallized Tc(II) product being 84%. Visible–UV (CH_3CN; λ, nm (ϵ, $M^{-1}\ cm^{-1}$)): λ_{max} 574 (980), 520 sh (315), 373 (290), 270 sh (4610), 249 (7370); λ_{min} 352, 230. IR (KBr pellet; ν, cm^{-1} (intensity): 430 (m), 470 (w), 555 (s), 600 (w), 670 (m), 720 (m), 750 (s), 830 (vs), 1025 (s), 1410 (m), 1450 (s), 2880 (w), 2920 (m), 2960 (m).

DMF, propylene carbonate, and acetonitrile from Burdick & Jackson Laboratories, Inc., were used in electrochemical experiments. Tetraethylammonium perchlorate (G. F. Smith polarographic grade) and tetraethylammonium chloride (Eastman) were dried over P_2O_5 in vacuo at 60 °C. Tetrabutylammonium bromide (Eastman) was recrystallized three times from ethyl acetate and dried over P_2O_5 in vacuo at 100 °C. No significant electrochemical impurities were detected in the above solvent and supporting electrolyte systems. Table I lists the formal redox potentials of the ferrocenium/ferrocene couple observed in various nonaqueous media by cyclic voltammetry on a platinum-disk electrode. This couple was used as an internal standard to estimate the difference in liquid-junction potential in respective solvent and supporting electrolyte systems.[36]

Electrochemical Instrumentation. Electrochemical measurements were made with a Bioanalytical Systems Inc. CV-1A. Potentials were monitored with a Fluka 8030A multimeter. Normal pulse voltammetry was conducted with an IBM EC/225 voltammetric analyzer with 2.0-s pulse interval and 2 mV/s scan rate. Voltammograms were recorded

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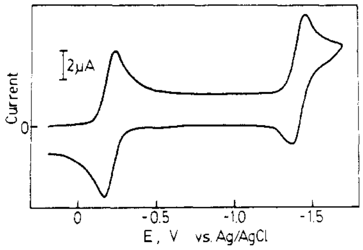

Figure 1. Cyclic voltammogram of 1.01 mM $[Tc(dmpe)_2Cl_2]^+$ in 0.5 M TEAP/DMF at a PDE, with scan rate 100 mV/s.

on a Hewlett-Packard 7015B x-y recorder, and coulograms were recorded with a Hewlett-Packard 3373B integrator. Visible spectra were recorded on a Cary 210 spectrophotometer, the cell compartment being modified to accommodate electrical leads and an inert-gas inlet. The working electrode for conventional cyclic voltammetry was a PDE (Bioanalytical Systems Inc. MF2013) with a surface area of 0.0244 cm^2 as determined by chronoamperometry of a standard potassium ferricyanide solution. An OTTLE working electrode was constructed with 500 wires/in. gold minigrid as previously described.[29,37] The cell volume and the optical thickness were calibrated by coulometry and spectrophotometry[29] and were 38 μL and 0.023 cm, respectively. A glassy-carbon electrode (Bioanalytical Systems Inc. FM2012) with a surface area of 0.0883 cm^2 was used in aqueous media. An aqueous Ag/AgCl/NaCl (3 M) electrode and a platinum wire were used as reference and auxiliary electrodes, respectively. The Ag/AgCl electrode was isolated from the solution by a porous Vycor plug. In the experiments at −40 °C an Ag wire was used as a pseudo reference electrode. All potentials reported here are vs. the Ag/AgCl/NaCl (3 M) electrode.

Electrochemical Procedures. Experiments were generally conducted as previousy described.[1,33] The time required for complete electrolysis within the OTTLE depends on the diffusion coefficient of the electroactive species. Each spectrum in the spectropotentiostatic experiments was recorded 3 min after potential application in 0.5 M TEAP/DMF and 5 min after application in 0.5 M TEAP/propylene carbonate. These times were found to be sufficient to attain equilibrium values of [O]/[R].

Results and Discussion

Electrochemistry of *trans*-Dihalogenobis(1,2-bis(dialkylphosphino)ethane)technetium(III) Complexes. DMF was chosen as solvent for these electrochemical studies primarily because it provides sufficient solubility for both the cationic technetium(III) complexes and their neutral technetium(II) analogues. Figure 1 shows a typical bulk solution cyclic voltammogram on a PDE for $[Tc(dmpe)_2Cl_2]^+$ in DMF containing 0.5 M TEAP. A negative potential scan initiated at +0.2 V gives two reduction waves with peak potentials of −0.250 and −1.442 V, respectively. Both peak currents are proportional to the square root of the scan rate within the range of 25–200 mV/s. Reoxidation peaks corresponding to the respective reduction peaks appear on the reverse scan. At scan rates greater than 50 mV/s the ratio of anodic to cathodic peak currents is approximately unity for each process; at a scan rate of 100 mV/s the peak separations are 62 and 66 mV for the first and second reduction processes, respectively. The first process corresponds to diffusion-controlled, reversible, one-electron reduction of Tc(III) to Tc(II):

$$[TcD_2X_2]^+ + e^- \rightleftarrows [TcD_2X_2]^0 \qquad (1)$$

(in Figure 1, D = dmpe and X = Cl). The second process corresponds to diffusion-controlled, reversible, one-electron reduction of Tc(II) to Tc(I):

$$[TcD_2X_2]^0 + e^- \rightleftarrows [TcD_2X_2]^- \qquad (2)$$

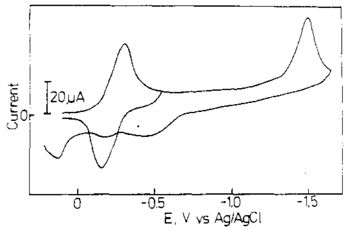

Figure 2. Thin-layer cyclic voltammogram of 1.54 mM $[Tc(dmpe)_2Cl_2]^+$ in 0.5 M TEAP/DMF at an OTTLE, with scan rate 2 mV/s.

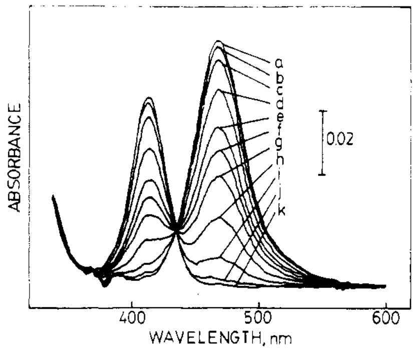

Figure 3. Spectra recorded during an OTTLE spectropotentiostatic experiment on 1.54 mM $[Tc(dmpe)_2Cl_2]^+$ in 0.5 M TEAP/DMF. Applied potentials in V vs. Ag/AgCl are as follows: (a) 0.000; (b) −0.130; (c) −0.170; (d) −0.200; (e) −0.220; (f) −0.230; (g) −0.240; (h) −0.260; (i) −0.290; (j) −0.330; (k) −0.450.

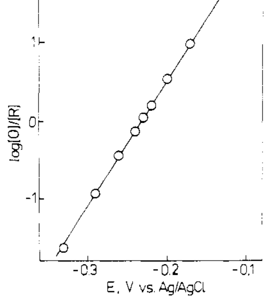

Figure 4. Nernst plot of data at 469 nm from Figure 3.

(i) $[Tc(dmpe)_2Cl_2]^+$. For $[Tc(dmpe)_2Cl_2]^+$, thin-layer cyclic voltammetry can be used to monitor the Tc(III)/Tc(II) couple but is too slow a technique to allow characterization of the Tc(II)/Tc(I) couple. The thin-layer cyclic voltammogram in Figure 2 shows a negative potential scan initiated at +0.1 V, with a scan rate of 2 mV/s, resulting in two reduction peaks that correspond to eq 1 and 2. When the first scan is reversed at −0.5 V, where $[Tc(dmpe)_2Cl_2]^+$ is fully reduced to $[Tc(dmpe)_2Cl_2]^0$, a reoxidation peak to $[Tc(dmpe)_2Cl_2]^+$ is observed, and repetitive cycles of the scan between +0.1 and −0.5 V exibit the same thin-layer cyclic voltammograms as observed in the first cycle of the scan. The large peak separation of 160 mV is due to the solution resistance of nonaqueous solvents in the OTTLE cell arrangement.[29,33] The formal reduction potential, $E^{\circ\prime}$, is calculated to be −0.231 V by averaging the anodic and cathodic peak potentials. Spectra recorded for the reversible $[Tc(dmpe)_2Cl_2]^{+/0}$ couple during a spectropotentiostatic experiment in the OTTLE are shown in Figure 3; the Tc(III) and Tc(II) complexes exhibit absorption maxima at 469 and 414 nm, respectively, and an isosbestic point is seen at 434 nm. The absorption maximum determined here for the Tc(III) complex in DMF is in fair agreement with that previously observed (460 nm) in ethanol.[16] This experiment provides the first determined absorption spectrum for the Tc(II) complex. Nernst plots at 414 and 469 nm for the data of Figure 3 yield $E^{\circ\prime} = -0.232$ V, in good agreement with the value obtained by thin-layer cyclic voltammetry, and $n = 0.95$;

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Table II. Formal Redox Potentials and *n* Values for $[TcD_2X_2]^{+/0/-}$ Couples in DMF[a]

		Tc(III)/Tc(II)			Tc(II)/ Tc(I)
Tc(III) complex	medium	$E^{\circ\prime}$ [b]	$E^{\circ\prime}$ [c]	n[c]	$E^{\circ\prime}$ [d]
$[Tc(dmpe)_2Cl_2]^+$	0.5 M TEAP	−0.231	−0.232	0.95	−1.410
$[Tc(dmpe)_2Br_2]^+$	0.5 M TEAP	−0.098	−0.108	0.98	−1.268
$[Tc(depe)_2Cl_2]^+$	0.5 M TEAP	−0.260	−0.259	0.90	−1.439[e]
$[Tc(depe)_2Br_2]^+$	0.5 M TEAP	−0.131	−0.132	0.97	−1.289[e]
$[Tc(dmpe)_2Cl_2]^+$	0.5 M (TEA)Cl	−0.190	−0.186	0.96	−1.369
$[Tc(dmpe)_2Br_2]^+$	0.4 M (TBA)Br	−0.045	−0.048	0.96	−1.213

[a] $E^{\circ\prime}$ is in V vs. Ag/AgCl. [b] $E^{\circ\prime} = (E_{p,c} + E_{p,a})/2$ from thin-layer cyclic voltammetry on an OTTLE with a scan rate of 2 mV/s. [c] From Nernst plot using the spectropotentiostatic method on an OTTLE. [d] $E^{\circ\prime} = (E_{p,c} + E_{p,a})/2$ in cyclic voltammetry on a PDE. [e] At −40 °C (see text).

Table III. Spectral Data for $[TcD_2X_2]^{+/0}$ Complexes Obtained by Spectroelectrochemistry in DMF Using an OTTLE

complex	medium	$\lambda_{max}^{Tc(III)}$, nm	$\lambda_{max}^{Tc(II)}$, nm	λ_{iso}, nm
$[Tc(dmpe)_2Cl_2]^{+/0}$	0.5 M TEAP	469	414	434
$[Tc(dmpe)_2Cl_2]^{+/0}$	0.5 M (TEA)Cl	472	414	435
$[Tc(dmpe)_2Br_2]^{+/0}$	0.5 M TEAP	499	440	462, 384
$[Tc(dmpe)_2Br_2]^{+/0}$	0.4 M (TBA)Br	501	439	461, 389
$[Tc(depe)_2Cl_2]^{+/0}$	0.5 M TEAP	470	415	436
$[Tc(depe)_2Br_2]^{+/0}$	0.5 M TEAP	499	440	464, 385

a plot of the data at 469 nm is shown in Figure 4. The reverse positive scan from −1.7 V, where $[Tc(dmpe)_2Cl_2]^0$ is completely reduced to $[Tc(dmpe)_2Cl_2]^-$, does not exhibit reoxidation to $[Tc(dmpe)_2Cl_2]^0$ but gives at least three ill-defined oxidation peaks, which have not been characterized. These results indicate that both the Tc(III) and the Tc(II) complexes are much more stable than the Tc(I) analogue, which decomposes with a lifetime of ca. 10 s to as yet unidentified products.

The results of thin-layer cyclic voltammetric and spectropotentiostatic experiments on $[Tc(dmpe)_2Cl_2]^+$ in 0.5 M (TEA)Cl solution are similar to those obtained in 0.5 M TEAP (Tables II and III). The difference in $E^{\circ\prime}$ values of the Tc(III)/Tc(II) and Tc(II)/Tc(I) couples obtained in these two media (46 and 41 mV, respectively) is presumably caused largely by the same differences in liquid-junction potentials that give rise to the 24-mV difference in $E^{\circ\prime}$ of the ferrocenium/ferrocene couple (Table I). The spectroelectrochemical results obtained in 0.5 M (TEA)Cl and 0.5 M TEAP (Table III) indicate that the coordinated chloride ligands of the technetium(III) and technetium(II) complexes do not dissociate appreciably on a time scale of hours. Thus, both $[Tc(dmpe)_2Cl_2]^+$ and $[Tc(dmpe)_2Cl_2]^0$ can be characterized as robust complexes.

(ii) $[Tc(dmpe)_2Br_2]^+$. Cyclic voltammetry and thin-layer cyclic voltammetry experiments on the bromo analogue, $[Tc(dmpe)_2Br_2]^+$, in 0.5 M TEAP give results qualitatively similar to those obtained with $[Tc(dmpe)_2Cl_2]^+$ (eq 1 and 2), but the observed reduction potentials are much different. The first process corresponds to a reversible one-electron reduction of Tc(III) to Tc(II); the second one-electron reduction to Tc(I) is reversible in cyclic voltammetry at scan rates greater than 50 mV/s. Again, reduction to Tc(I) is coupled to subsequent slow chemical reaction(s). Figure 5 shows spectra resulting from a spectropotentiostatic experiment using the OTTLE. The Tc(III) and Tc(II) complexes in DMF exhibit maxima at 499 and 440 nm, respectively, in fair agreement with values observed in ethanol with use of chemically prepared materials;[16] two isosbestic points are observed at 462 and 384 nm. A Nernst plot of the spectropotentiostatic data at 499 nm yields $E^{\circ\prime} = -0.108$ V and $n = 0.98$. The electrochemical and spectroelectrochemical behavior of $[Tc(dmpe)_2Br_2]^+$ in 0.4 M (TBA)Br is essentially the same as in 0.5 M TEAP. The small difference in $E^{\circ\prime}$ values for the Tc(III)/Tc(II) and Tc(II)/Tc(I) couples obtained in these media (60 and 55 mV, respectively) is again attributed to differences in liquid-junction potential (Table I; 54 mV for ferrocenium/ferrocene).

(iii) $[Tc(depe)_2X_2]^+$. For the $[Tc(depe)_2X_2]^+$ complexes the spectropotentiostatic reductions of Tc(III) to Tc(II) are shown in Figures 6 and 7 for X = Cl and X = Br, respectively. Electrochemical and spectral results are summarized in Tables

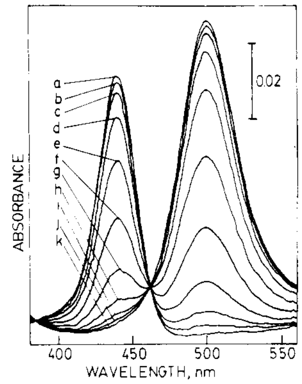

Figure 5. Spectra recorded during an OTTLE spectropotentiostatic experiment on 1.04 mM $[Tc(dmpe)_2Br_2]^+$ in 0.5 M TEAP/DMF. Applied potentials in V vs. Ag/AgCl are as follows: (a) −0.300; (b) −0.200; (c) −0.175; (d) −0.150; (e) −0.125; (f) −0.100; (g) −0.075; (h) −0.050; (i) −0.290; (j) 0.000, (k) +0.100.

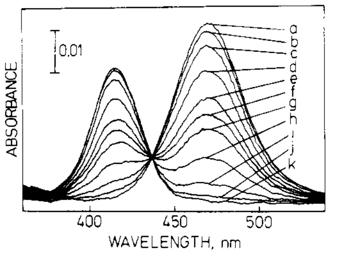

Figure 6. Spectra recorded during an OTTLE spectropotentiostatic experiment on 0.939 mM $[Tc(depe)_2Cl_2]^+$ in 0.5 M TEAP/DMF. Applied potentials in V vs. Ag/AgCl are as follows: (a) 0.000; (b) −0.160; (c) −0.200; (d) −0.230; (e) −0.250; (f) −0.260; (g) −0.270; (h) −0.290; (i) −0.320; (j) −0.360; (k) −0.500.

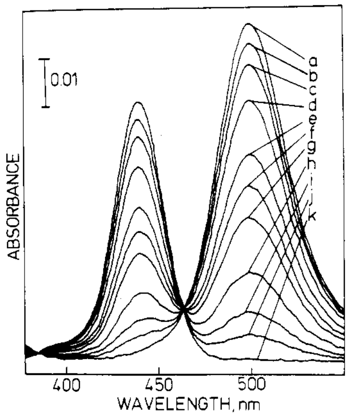

Figure 7. Spectra recorded during an OTTLE spectropotentiostatic experiment on 1.28 mM $[Tc(depe)_2Br_2]^+$ in 0.5 M TEAP/DMF. Applied potentials in V vs. Ag/AgCl are as follows: (a) +0.100; (b) −0.060; (c) −0.080; (d) −0.100; (e) −0.120; (f) −0.130; (g) −0.140; (h) −0.160; (i) −0.180; (j) −0.200; (k) −0.400.

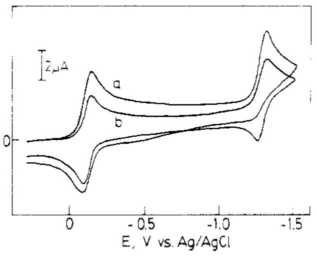

Figure 8. Cyclic voltammograms of 1.56 mM $[Tc(depe)_2Br_2]^+$ in 0.5 M TEAP/DMF at a PDE, with scan rate 100 mV/s: (a) 25 °C, (b) -40 °C.

II and III. Further reduction of Tc(II) to Tc(I), however, is so chemically irreversible that no peak corresponding to reoxidation of Tc(I) to Tc(II) appears on the reverse scan even at a cyclic voltammetry scan rate of 500 mV/s. To reduce the rate of decomposition of the Tc(I) complexes, cyclic voltammetry was conducted at -40 °C. Bulk solution cyclic voltammograms of $[Tc(depe)_2Br_2]^+$ at 25 and -40 °C are compared in Figure 8. For convenience the potential scales in Figure 8 have been superposed by assuming that $E°'$ of the ferrocenium/ferrocene couple (used as an internal standard) is constant with temperature, although this assumption is not correct.[38] The peak currents of both the Tc(III)/Tc(II) and the Tc(II)/Tc(I) processes decrease with decreasing temperature due to the increase in viscosity of the solution. The $E°'$ of the Tc(III)/Tc(II) couple at -40 °C is almost the same as it is at 25 °C, suggesting that the thermodynamic parameters governing the Tc(III)/Tc(II) reduction are similar in magnitude to those governing the ferrocenium/ferrocene couple.[38] This situation presumably occurs because both couples involve reduction of a 1+ species to a neutral species. The cathodic and anodic peak separation, 55 mV, at a scan rate of 100 mV/s is larger than the 46-mV theoretical value for a reversible one-electron process at -40 °C, reflecting the slow rate of heterogeneous electron transfer at -40 °C. The second reduction process, $[Tc(depe)_2Br_2]^{0/-}$, which is irreversible at 25 °C, becomes reversible at -40 °C (Figure 8). The ratio of anodic to cathodic peak currents increases with decreasing temperature and becomes unity at -40 °C with a scan rate of 100 mV/s. The $E°'$ governing the Tc(II)/Tc(I) reduction of $[Tc(depe)_2Br_2]^0$ at -40 °C is given in Table II. Also shown in Table II are $E°'$ values for the $[Tc(depe)_2Cl_2]^{+/0/-}$ couples; the chloro and bromo complexes exhibit similar electrochemical behavior, although for the chloro complex both Tc(III)/Tc(II) and Tc(II)/Tc(I) couples are less reversible than the corresponding couples of the bromo analogue.

(iv) Comparisons of $[TcD_2X_2]^+$ Complexes. The $E°'$ values of the Tc(III)/Tc(II) and Tc(II)/Tc(I) processes represented by eq 1 and 2 for the $[TcD_2X_2]^+$ complexes depend markedly on the nature of D and X. The $[Tc(dmpe)_2X_2]^+$ complexes are more easily reduced by ca. 25 mV than are the corresponding $[Tc(depe)_2X_2]^+$ complexes, and the $[TcD_2Br_2]^+$ complexes are more easily reduced by ca. 125 mV than are the corresponding $[TcD_2Cl_2]^+$ complexes. These trends have been interpreted in terms of π-back-bonding interactions of d electrons in the Tc(III) or Tc(II) centers with appropriate orbitals on the phosphorus and halogen ligands.[16] The stability of electrogenerated species and the reversibility of each process also depend on the nature of D and X. The Tc(III)/Tc(II) couples are more reversible than are the corresponding Tc(II)/Tc(I) couples, the bromo complexes exhibit more reversible couples than do the corresponding chloro complexes, and the dmpe complexes exhibit more reversible couples than do the depe complexes. The technetium(II) complexes $[TcD_2X_2]^0$ are sufficiently stable (independent of D and X) to study by spectroeletrochemistry with the OTTLE at room temperature, but the technetium(I) complexes $[TcD_2X_2]^-$ are too unstable for the spectropotentiostatic experiments. The cyclic voltammetric experiments show that the $[Tc^ID_2Br_2]^-$ complexes are more stable than are the corresponding $[Tc^ID_2Cl_2]^-$ complexes and the $[Tc^I(depe)_2X_2]^-$ complexes are much less stable than are the $[Tc^I(dmpe)_2X_2]^-$ complexes. These effects can also be interpreted in terms of the relative abilities of the ligands to donate and accept charge from the technetium(I) center; the anionic Tc(I) d^6 center is stabilized by the bromide ligand, which is a better π acid than chloride, and by dmpe, which is a poorer σ donor than is depe.

Table IV. Formal Redox Potentials and *n* Values for the $[TcD_3]^{2+/+}$ Couples in 0.5 M TEAP as a Function of Solvent[a]

couple	solvent	$E°'$, V (n)
$[Tc(dmpe)_3]^{2+/+}$	DMF	$+0.422^{b,c}$ $(0.91)^{b,c}$
	acetonitrile	$+0.351^d$
	propylene carbonate	$+0.329^b$ $(0.99)^b$
$[Tc(depe)_3]^{2+/+}$	DMF	$+0.276^d$
	acetonitrile	$+0.175^d$
	propylene carbonate	$+0.166^d$

[a] $E°'$ is vs. Ag/AgCl. [b] From a Nernst plot using the spectropotentiostatic method on an OTTLE. [c] The Tc(II) complex decomposes slowly during the measurement. [d] $E°' = (E_{p,a} + E_{p,c})/2$ from cyclic voltammetry on a PDE.

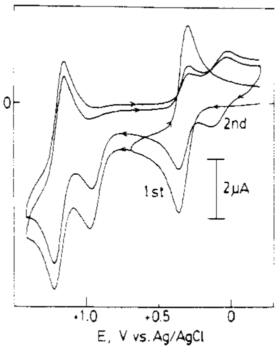

Figure 9. Cyclic voltammogram of 1.53 mM $[Tc(dmpe)_3]^+$ in 0.5 M TEAP/propylene carbonate at a PDE, with scan rate 100 mV/s.

Tris(1,2-bis(dialkylphosphino)ethane)technetium(I) Complexes. The newly synthesized[35] cationic technetium(I) complexes $[Tc(dmpe)_3]^+$ and $[Tc(depe)_3]^+$ exhibit reversible oxidation to Tc(II) in nonaqueous media. The formal redox potentials governing this process in several solvents are shown in Table IV. Propylene carbonate is the preferred solvent for these studies, primarily because of the stability of the Tc(II) $[Tc(dmpe)_3]^{2+}$ electrogenerated complex in this solvent. This work has emphasized the electrochemistry of the $[Tc(dmpe)_3]^+$ complex because of the potential applications of the ^{99m}Tc analogue to nuclear medicine.[35,39] Also, the solubility of the one-electron oxidation product of the depe complex, $[Tc(depe)_3]^{2+}$, is too low to allow this system to be characterized spectroelectrochemically.

(i) Electrochemistry of $[Tc(dmpe)_3]^+$. Figure 9 shows a cyclic voltammogram of $[Tc(dmpe)_3]^+$ in 0.5 M TEAP/propylene carbonate, wherein three oxidation peaks are observed. A positive potential scan from -0.2 V with a scan rate of 100 mV/s gives an oxidation peak with $E_{p,a} = +0.300$ V on the reverse negative potential scan initiated at +0.7 V. From the spectropotentiostatic results (vide infra) and the

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(38) Sahari, S.; Weaver, M.-J. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *122*, 155.

(39) (a) Vanderheyden, J.-L.; Deutsch, E.; Libson, K.; Ketring, A. R. *J. Nucl. Med.* **1983**, *24*, P9. (b) Ketring, A. R.; Deutsch, E.; Libson, K.; Vanderheyden, J.-L.; Sodd, V. J.; Nishiyama, H.; Lukes, S. *Ibid.* **1983**, *24*, P9.

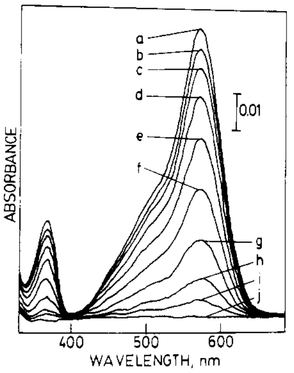

Figure 10. Spectra recorded during an OTTLE spectropotentiostatic experiment on 3.21 mM $[Tc(dmpe)_3]^+$ in 0.5 M TEAP/propylene carbonate. Applied potentials in V vs. Ag/AgCl are as follows: (a) +0.600; (b) +0.400; (c) +0.380; (d) +0.360; (e) +0.340; (f) +0.320; (g) +0.300; (h) +0.280; (i) +0.260; (j) +0.100.

observation that (a) the anodic peak current is proportional to the square root of the scan rate, (b) the ratio of cathodic to anodic peak currents is unity, and (c) the peak separation is 60 mV at a scan rate of 100 mV/s, this couple is assigned as the Tc(I)/Tc(II) oxidation:

$$[Tc^I(dmpe)_3]^+ \rightleftarrows [Tc^{II}(dmpe)_3]^{2+} + e^- \qquad (3)$$

The reversible couple represented by eq 3 is also observed in DMF and acetonitrile; electrochemical data obtained in these solvents are shown in Table IV. The solvent dependence of the Tc(II)/Tc(I) $E^{\circ\prime}$ values is similar to the solvent dependence of the ferrocenium/ferrocene $E^{\circ\prime}$ values (Table I), values in propylene carbonate and acetonitrile being similar to each other and more negative than the value in DMF. This ordering (DMF > propylene carbonate $\cong$ acetonitrile) follows the basicity of these solvents; more basic solvents presumably stabilize the dipositively charged Tc(II) complex relative to the monopositively charged Tc(I) complex. Thin-layer cyclic voltammetry in the OTTLE in propylene carbonate also shows a reversible couple centered at +0.388 V. Spectra recorded for this Tc(I)/Tc(II) couple during a spectropotentiostatic experiment are shown in Figure 10. The purple solution of the electroxidized Tc(II) complex exhibits maxima at 572 and 368 nm and a shoulder at 512 nm, in good agreement with values obtained in acetonitrile with use of chemically prepared samples (vide infra). Repetitive cycles between Tc(I) and Tc(II) oxidation states yield 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 10 (at 572, 512, and 368 nm) yield $E^{\circ\prime}$ = +0.329 V and n = 0.99.

The cyclic voltammogram of Figure 9 also shows two additional oxidation peaks at +0.978 and +1.222 V, respectively. Upon a reverse scan initiated at +1.4 V three reduction peaks are observed; one is the rereduction peak of the third oxidation process, one is the rereduction peak converting $[Tc(dmpe)_3]^{2+}$ to $[Tc(dmpe)_3]^+$, and the third is a new cathodic peak with $E_{p,c}$ = +0.033 V. No peak corresponding to the rereduction of the second oxidation process appears. Successive second and further scans show that (a) the peak heights of the new redox couple centered at +0.083 V increase and (b) the peaks of the $[Tc(dmpe)_3]^{2+/+}$ couple and those of the second oxidation peak decrease while (c) the peaks of the third redox couple do not change with increasing numbers of scans. Thin-layer cyclic voltammetry also illustrates the irreversibility of the second oxidation process; a reverse scan yields no distinct reduction peak in the potential range from +1.3 to −0.2 V. Spectra recorded in the OTTLE 5 min after potential application at +1.05 V and then at +1.25 V show absorption maxima at 350 and 385 nm, respectively. The number of electrons transferred in each oxidation process, determined by thin-layer coulometry on the OTTLE, is found to be 0.995 for the first oxidation process (i.e. that expressed by eq 3) and 0.970 for the second oxidation process. The number of electrons was not determined, however, for the third oxidation process because of the overlap of the large background current for gold at this potential; however, comparison of the peak heights in Figure 9 indicates that this may also be a one-electron process. Although this third electrode reaction is complicated and not completely understood, its origins can be viewed as follows. The one-electron oxidation product of $[Tc(dmpe)_3]^+$ according to eq 3, i.e., $[Tcdmpe)_3]^{2+}$, undergoes a further one-electron oxidation to $[Tc(dmpe)_3]^{3+}$, which in turn decomposes to an electroactive technetium complex with $E^{\circ\prime}$ = +0.083 V. Further chemical characterization of the coulometric products of each electron-transfer step will be necessary to elucidate the details of this electrochemical process. This chemical investigation will be the subject of a future publication.

(ii) Comparison of $[TcD_3]^{2+/+}$ Couples. When the dmpe ligand is replaced by depe, the $E^{\circ\prime}$ for the Tc(II)/Tc(I) couple shifts to a more negative value by 164 mV, indicating that $[Tc(depe)_3]^+$ is considerably more easily oxidized than is $[Tc(dmpe)_3]^+$. This is again understood in light of the fact that depe is a better σ donor than dmpe (vide supra) and thus better stabilizes the more positively charged Tc(II) oxidation state. The difference in $E^{\circ\prime}$ values between the $[Tc(dmpe)_3]^{2+/+}$ and $[Tc(depe)_3]^{2+/+}$ couples is reflected in the preparative chemistry of these systems. The $E^{\circ\prime}$ value for the $[Tc(dmpe)_3]^{2+/+}$ couple appears to be close to that governing reduction of molecular oxygen, and thus both the Tc(I) and the Tc(II) forms are stable in air and can be prepared in macroscopic amounts. Contrariwise, the Tc(I) depe analogue, $[Tc(depe)_3]^+$, is too strong a reductant to be prepared in the presence of air and must be synthesized and stored under anaerobic conditions. As expected, the Tc(II) complex $[Tc(depe)_3]^{2+}$ is stable in air and can be readily prepared in large quantities.

(iii) Electronic Spectra of $[TcD_3]^{2+/+}$ Complexes. The spectropotentiostatic data illustrated in Figure 10 nicely show that while the Tc(I) complex is colorless, the Tc(II) analogue has three discernible absorption bands in the visible region. Since the extinction coefficients of these bands are all less than 10^3 M^{-1} cm^{-1} for both the $[TcD_3]^{2+}$ complexes (vide infra), these absorptions are assigned as arising from d–d transitions. For a spin-paired d^5 complex, the ground-state configuration is $^2T_{2g}$ and the first excited states are $^2A_{1g}$, $^2T_{1g}$, and then ^2E_g.[40] For $[Tc(dmpe)_3]^{2+}$, reasonable values of the ligand field parameters Dq (2500 cm^{-1}) and B (1000 cm^{-1}) can be derived by assuming that (a) the lowest energy absorptions at 569 and 520 nm arise from the $^2T_{2g} \rightarrow {}^2A_{1g}$, $^2T_{1g}$ transitions, (b) the absorption at 366 nm arises from the $^2T_{2g} \rightarrow {}^2E_{2g}$ transition, and (c) the ratio C/B = 4.4. Essentially the same values of Dq and B are obtained for the $[Tc(depe)_3]^{2+}$ analogue.

The Tc(II) complexes also exhibit charge-transfer absorptions in the ultraviolet region (270 and 239 nm for $[Tc(dmpe)_3]^{2+}$; 270 and 249 nm for $[Tc(depe)_3]^{2+}$). These absorptions are too closely spaced (spacing of 4800 and 3100 cm^{-1} for the dmpe and depe complexes, respectively) to allow them to be assigned as $D \rightarrow e_g$ and $D \rightarrow t_{2g}$ transitions; this assignment would require that the absorptions be separated by $10Dq$, or ca. 25000 cm^{-1}. It is, however, likely that both of these absorptions, and the corresponding 252- and 226-nm bands of the Tc(I) analogue $[Tc(dmpe)_3]^+$, arise from lig-

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[40] Naiman, C. S. *J. Chem. Phys.* **1961**, *35*, 323.

Table V. Comparison of $E^{\circ\prime}$ Values in Aqueous and Nonaqueous Media

	$E^{\circ\prime}$, V vs. NHE		
couple	0.5 M KNO_3/ H_2O^a	0.5 M TEAP/ DMF^b	Δ, V
$[Tc(dmpe)_2Cl_2]^{+/0}$	−0.122	−0.338	0.216
$[Tc(dmpe)_2Br_2]^{+/0}$	−0.016	−0.214	0.198
$[Tc(depe)_2Cl_2]^{+/0}$	−0.023	−0.365	0.342
$[Tc(depe)_2Br_2]^{+/0}$	+0.115	−0.238	0.353
$[Tc(dmpe)_3]^{2+/+}$	+0.290	+0.316	−0.026
$[Tc(depe)_3]^{2+/+}$	*c*	+0.170	

[a] Potential of the Ag/AgCl/NaCl (3 M) electrode taken as +0.201 V vs. NHE. [b] Referred to the ferrocenium/ferrocene couple ($E^{\circ\prime}$ = +0.400 V vs. NHE) as an internal standard. [c] This complex is too insoluble to permit reliable data to be obtained.

and-to-metal charge-transfer transitions.

Comparison of $[TcD_3]^{2+/+}$ and $[TcD_2X_2]^{0/-}$ Couples. The data of Tables II and IV show that, for Tc(II)/Tc(I) couples in DMF, $E^{\circ\prime}$ values for $[TcD_3]^{2+/+}$ are much more positive than $E^{\circ\prime}$ values for $[TcD_2X_2]^{0/-}$. Specifically, when D = dmpe, $E^{\circ\prime}$ for $[TcD_3]^{2+/+}$ is 1.83 V more positive than $E^{\circ\prime}$ for $[TcD_2Cl_2]^{0/-}$ and 1.69 V more positive than $E^{\circ\prime}$ for $[TcD_2Br_2]^{0/-}$; when D = depe, the corresponding differences are 1.72 and 1.57 V. Thus, the replacement of two halide ligands by one bis(phosphine) ligand on going from $[TcD_2X_2]^{0/-}$ to $[TcD_3]^{2+/+}$ dramatically stabilizes spin-paired, d^6 Tc(I) relative to spin-paired, d^5 Tc(II). This is readily understood in terms of the strong π-acid character of the bis(phosphine) ligands, which greatly stabilizes low oxidation states by removing electron density from the metal center.

Comparison of $E^{\circ\prime}$ Values in Aqueous and Nonaqueous Media. The bis(phosphine) technetium complexes investigated in this work have potential utility in diagnostic nuclear medicine,[22-24] and in this context it is important to understand the chemistry of these species in aqueous, as well as nonaqueous, media. Electron transfer to and from the bis(phosphine) technetium complexes changes their charge type, which perforce alters their biodistributions; it has been suggested[41] that while the cationic technetium(III) complexes $[TcD_2X_2]^+$ can be taken up by the heart, the neutral, more lipophilic technetium(II) analogues preferentially undergo hepatobiliary clearance. It is therefore important to have some gauge as to whether or not technetium complexes of potential use in diagnostic nuclear medicine can undergo electron-transfer reactions under biological conditions. For this reason some preliminary electrochemistry experiments were conducted on $[TcD_2X_2]^+$ and $[TcD_3]^+$ complexes in 0.5 M aqueous KNO_3; it should be noted that these cationic complexes have only low solubility in water and the neutral $[TcD_2X_2]^0$ analogues are essentially insoluble in water.

With use of cyclic voltammetry, $[Tc(dmpe)_3]^+$ exhibits a diffusion-controlled, reversible oxidation wave, but reduction of $[TcD_2X_2]^+$ species leads to deposition of the neutral $[TcD_2X_2]^0$ analogues on the GCE. Normal pulse voltammetry allows investigation of all technetium species, and Table V lists the $E^{\circ\prime}$ values resulting from this technique. Table V also compares these values obtained in aqueous media to those obtained in DMF, assuming that the $E^{\circ\prime}$ value of the internal standard ferrocenium/ferrocene couple is +0.400 V vs. NHE. These comparisons show that the $[Tc(dmpe)_3]^{2+/+}$ couple has essentially the same potential in water as it does in DMF. This encouraging result arises from the fact that both the Tc(I) and the Tc(II) analogues have some slight solubility in both water and DMF, and thus there are no effects due to precipitation or deposition. However, comparisons of the $[TcD_2X_2]^{+/0}$ couples show that the insolubility of the neutral technetium(II) complexes in water seriously affects the data obtained in aqueous media. For the more water-soluble dmpe complexes, the aqueous $E^{\circ\prime}$ values are ca. 0.20 V more positive than the nonaqueous $E^{\circ\prime}$ values, while for the less water-soluble depe complexes the difference is ca. 0.35 V. Thus, precipitation or deposition of the neutral $[TcD_2X_2]^0$ species favors their production in aqueous media, and this large effect must be taken into account when one considers the redox behavior of $[TcD_2X_2]^+$ complexes in biological milieu.

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Registry No. $[Tc(dmpe)_3](PF_6)_2$, 89378-22-3; $[Tc(depe)_3]PF_6$, 89378-24-5; $[Tc(depe)_3](PF_6)_2$, 89378-26-7; $[Tc(dmpe)_3]PF_6$, 89378-28-9; $Tc(dmpe)_2Cl_2^+$, 85552-77-8; $Tc(dmpe)_2Br_2^+$, 85552-79-0; $Tc(depe)_2Cl_2^+$, 85552-83-6; $Tc(depe)_2Br_2^+$, 89378-29-0; $Tc(dmpe)_2Cl_2$, 85552-69-8; $Tc(dmpe)_2Br_2$, 85552-71-2; $Tc(depe)_2Cl_2$, 85552-68-7; $Tc(depe)_2Br_2$, 85552-70-1; $Tc(dmpe)_2Cl_2^-$, 85565-21-5; $Tc(dmpe)_2Br_2^-$, 85552-94-9; $Tc(depe)_2Cl_2^-$, 89378-30-3; $Tc(depe)_2Br_2^-$, 89378-31-4; $Tc(dmpe)_3^{2+}$, 89378-21-2; $Tc(dmpe)_3^+$, 89378-27-8; $Tc(depe)_3^{2+}$, 89378-25-6; $Tc(depe)_3^+$, 89378-23-4; TEAP, 2567-83-1; (TEA)Cl, 56-34-8; (TBA)Br, 1643-19-2; ferrocenium, 12125-80-3; ferrocene, 102-54-5.

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