Br), prepared anaerobically in perchloric acid at 0.10 M ionic strength, was saturated with alkali-scrubbed nitric oxide. A solution of chromium(II) perchlorate was then slowly added while the solution was efficiently stirred and continuously saturated with NO. After addition of Cr^{2+} was complete, the NO was removed with a vigorous stream of argon. Samples were taken for the analysis of the cobalt(II) produced by the thiocyanate method[57] in 1:1 aqueous acetone. This measurement was made by incorporating an appropriate reagent blank, which was critical given the small concentrations involved, and was based on a molar absorptivity of 1.84×10^3 M^{-1} cm^{-1} at 623 nm. These measurements provided the values of $[Co^{2+}]_\infty$ necessary for the calculation of the data according to eq 8.

Product Analysis. The inorganic products, $Cr(H_2O)_6^{3+}$ and $(H_2O)_5CrNO^{2+}$, were readily recognized by their elution times from a column of Sephadex SP C-25 ion-exchange resin. Their identities were confirmed and yields determined on the basis of their known UV–visible spectra and, in the case of $(H_2O)_5CrNO^{2+}$, analysis for total chromium.

The organic products, with the exception of CH_2O, were identified and determined by gas chromatography. The experiments with $CrCH_2CH_3^{2+}$ and $CrCH(CH_3)_2^{2+}$ used as blanks solutions of the same organochromium complex, which had been allowed to undergo acidolysis to give

$Cr(H_2O)_6^{3+}$ and RH. No sodium nitrite was added to the blanks. The purity of $CrCH_2OCH_3^{2+}$, which undergoes acidolysis very slowly, was checked by gas chromatography of the eluent during purification on the ion-exchange resin. This analysis showed that no methanol (a product of the reaction with HNO_2) was present in the original stock solution of $CrCH_2OCH_3^{2+}$. The compounds sought were compared with the known materials calibrated in concurrent experiments. All of the experiments used a 10% FFAP column.

Registry No. $(H_2O)_5Cr(CH_2OH)^{2+}$, 103533-92-2; $(H_2O)_5Cr(CH_2OCH_3)^{2+}$, 103533-93-3; $(H_2O)_5Cr(CH(CH_3)OCH_2CH_3)^{2+}$, 103562-45-4; $(H_2O)_5Cr(CH_3)^{2+}$, 103533-94-4; $(H_2O)_5Cr(CH_2CH_3)^{2+}$, 103533-95-5; $(H_2O)_5Cr(CH(CH_3)_2)^{2+}$, 103533-96-6; $(H_2O)_5Cr(CH_2C_6H_5)^{2+}$, 103562-46-5; $(H_2O)_5Cr(4\text{-}CH_2pyH)^{3+}$, 103533-97-7; $(H_2O)_5Cr(CH_2CH_2CH_3)^{2+}$, 103533-98-8; $(H_2O)_5Cr(CH_2Cl)^{2+}$, 103533-99-9; $(H_2O)_5Cr(CH_2Br)^{2+}$, 103534-00-5; $(H_2O)_5Cr(CH_2I)^{2+}$, 103534-01-6; $(H_2O)_5Cr(p\text{-}CH_2C_6H_4CH_3)^{2+}$, 103534-02-7; $(H_2O)_5Cr(p\text{-}CH_2C_6H_4CF_3)^{2+}$, 103534-03-8; $(H_2O)_5Cr(p\text{-}CH_2C_6H_4CN)^{2+}$, 103534-04-9; $(NH_3)_5CoBr^{2+}$, 14970-15-1; $(NH_3)_5CoCl^{2+}$, 14970-14-0; $Cr(H_2O)_6^{2+}$, 20574-26-9; O_2, 7782-44-7; NO, 10102-43-9; HNO_2, 7782-77-6.

(57) Kitson, R. F. *Anal. Chem.* **1950**, *22*, 664.

Contribution from the Departments of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, and Rosary College, River Forest, Illinois 60305, and Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Electron-Transfer Reactions of Technetium Complexes. 1. Rate of the Self-Exchange Reaction of the Tc(I)/Tc(II) Couple [Tc(DMPE)₃]⁺/²⁺, Where DMPE = 1,2-Bis(dimethylphosphino)ethane[1]

Mary Noon Doyle,[2] Karen Libson,[2] Mary Woods,[3] James C. Sullivan,[4] and Edward Deutsch*[2]

The rate of the self-exchange electron-transfer reaction between [Tc(DMPE)₃]⁺ and [Tc(DMPE)₃]²⁺ has been determined by two independent applications of the Marcus theory. (1) The rates and equilibrium constants governing the cross-reactions between [Tc(DMPE)₃]⁺/²⁺ and [(NH₃)₅RuL]²⁺/³⁺ (L = isonicotinamide, pyridine, 4-picoline) were measured in aqueous LiCl/HCl solutions. The known self-exchange rate of [(NH₃)₅Ru(py)]²⁺/³⁺ was then used within the Marcus cross relationship to calculate three values of k_{ex} for [Tc(DMPE)₃]⁺/²⁺. These values fall within the range $(0.8–4.0) \times 10^6$ M^{-1} s^{-1} (25 °C, $\mu = 0.10$ M). Estimated activation parameters for this reaction are $\Delta H_{ex}{}^* = 7 \pm 3$ kcal/mol and $\Delta S_{ex}{}^* = -8 \pm 4$ eu. (2) Available bond length data show that, because of extensive π-back-bonding from Tc to P, the Tc–P bond *expands* by about 0.068 Å upon oxidation of the technetium center. This information, combined with estimates for the radius of the complex (4.8 Å) and for the force constant of the Tc–P bond $(1.64 \times 10^5$ dyn/cm$)$, can be used within the Marcus formalism to calculate k_{ex}. The resulting calculated value is 3×10^6 M^{-1} s^{-1} (25 °C), in excellent agreement with the median value determined kinetically. This agreement between kinetically and structurally determined values of k_{ex} demonstrates that the self-exchange reaction of the extensively π-back-bonded [Tc(DMPE)₃]⁺/²⁺ system is adequately described within the Marcus formalism. Moreover, the value of k_{ex} for this d^6/d^5 couple is in good agreement with the value of k_{ex} $(2.2 \times 10^6$ M^{-1} s^{-1}; 25 °C, $\mu = 0.10$ M$)$ observed for [(NH₃)₄Ru(bpy)]²⁺/³⁺, a predominantly σ-bonded d^6/d^5 couple of similar radius (4.4 Å). Thus, the success of the Marcus formalism does not depend on the intimate nature of metal–ligand bonding within the complex, and it appears that it is the overall size of low-spin d^6/d^5 couples that is the predominant factor in determining the self-exchange rate.

Introduction

For many years the study of outer-sphere electron-transfer reactions and the concomitant determination of self-exchange rates have been a major focus of the field of inorganic kinetics and mechanism. Much of this research has been aimed at testing the theories of adiabatic electron transfer that were developed by Marcus[5,6] and Hush[7,8] and that have been promulgated by Su-

tin.[9–12] In early studies most of the experimentally accessible redox couples suitable for evaluating outer-sphere self-exchange rates were either (a) first-row transition metals containing six identical, "hard", O- or N-donating ligands or (b) tris(bipyridine) and tris(phenanthroline) complexes of Fe, Ru, Os, and some other metals. In the late 1960s Taube and co-workers introduced the ammine Ru(III)/Ru(II) complexes, which greatly expanded the number and type of suitable redox couples.[13] These systems are characterized by transfer of a t_{2g} electron (as opposed to the e_g

(1) Abstracted in part from: Noon, M. Ph.D. Thesis, University of Cincinnati, 1984.
(2) University of Cincinnati.
(3) Rosary College.
(4) Argonne National Laboratory.
(5) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
(6) Marcus, R. A.; Siders, P. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982; Chapter 10.
(7) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557.

(8) Hush, N. S. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982; Chapter 13.
(9) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.
(10) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.
(11) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3530.
(12) Herbert, J. W.; Macartney, D. H. *Inorg. Chem.* **1985**, *24*, 4398.
(13) Taube, H. *Science (Washington, D.C.)* **1984**, *226*, 1028.

electron transferred in Cr(III)/Cr(II) or Co(III)/Co(II) couples) and selective π-back-bonding from Ru(II) to the unique ligand in a pentaammine coordination sphere (e.g., pyridine in $[(NH_3)_5Ru(py)]^{2+}$) rather than the extensive delocalized π-back-bonding in the $[(bpy)_3Ru]^{2+}$ and $[(phen)_3Ru]^{2+}$ systems.

The recent development of low-valent technetium complexes for use in nuclear medicine[14,15] has lead to new classes of 1-equiv redox couples that are suitable for the mechanistic investigation of outer-sphere electron-transfer reactions. These complexes generally contain technetium stabilized in oxidation states I, II, or III by π-acid ligands such as phosphines,[16-18] arsines,[19,20] or isonitriles.[21] They are substitution-inert and form electrochemically reversible redox couples, the potentials of which are strongly dependent on the nature of the coordinated ligands. In addition, many of these technetium complexes have been structurally characterized and therefore provide an opportunity to assess whether or not the Marcus–Hush formalism can accommodate bond length changes dominated by π-back-bonding to a single donor atom (such as the P or As atom of tertiary phosphines or arsines).

For this initial study we have chosen the archetypal technetium(I) complex $[Tc(DMPE)_3]^+$, where DMPE represents 1,2-bis(dimethylphosphino)ethane.[17] This low-spin, d^6 complex, can be viewed as a second-row analogue of the classical first-row, low-spin, d^6 complex $[Co(en)_3]^{3+}$. $[Tc(DMPE)_3]^+$ exhibits an electrochemically reversible Tc(I)/Tc(II) couple with an accessible E^0 value (0.29 V vs. NHE), and bond length data are available for both the Tc(I) and Tc(II) complexes. In addition, the d^5 Tc(II) complex is purple while the d^6 Tc(I) complex is colorless, making it convenient to monitor the kinetics of interconversion of these species by conventional spectrophotometric techniques.[17,23]

In this work the self-exchange rate of the $[Tc(DMPE)_3]^{+/2+}$ couple is determined by using the Marcus–Hush formalism to treat both kinetic and structural data. Since both the Tc(I) and Tc(II) complexes are soluble in water (as well as in a variety of polar organic solvents) and are stable in both acidic and alkaline media, the $[Tc(DMPE)_3]^{+/2+}$ couple should prove useful in kinetically characterizing other redox systems. There are not many currently available 1-equiv redox couples that exhibit the convenient solubility and stability characteristics of $[Tc(DMPE)_3]^{+/2+}$.

Experimental Section

Caution! 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 and inadvertent ingestion or inhalation of this isotope.

Materials. All common laboratory chemicals were reagent grade and were used as received unless otherwise noted. Pyridine, 4-picoline, and isonicotinamide were obtained from Mallinckrodt, Eastman, and Sigma,

(14) Deutsch, E.; Libson, K.; Jurisson, S.; Lindoy, L. F. *Prog. Inorg. Chem.* **1983**, *30*, 75.
(15) Deutsch, E.; Libson, K. *Comments Inorg. Chem.* **1984**, *3*, 83.
(16) Libson, K.; Barnett, B. L.; Deutsch, E. *Inorg. Chem.* **1983**, *22*, 1695.
(17) Vanderheyden, J.-L.; Ketring, A. R.; Libson, K.; Heeg, M. J.; Roecker, L.; Motz, P.; Whittle R.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 3184.
(18) Jurisson, S. S.; Dancey, K.; McPartlin, M.; Tasker, P. A.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 4743.
(19) Elder, R. C.; Whittle, R.; Glavan, K. A.; Johnson, J. F.; Deutsch, E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1662.
(20) Glavan, K. A.; Whittle, R.; Johnson, J. F.; Elder, R. C.; Deutsch, E. *J. Am. Chem. Soc.* **1980**, *102*, 2103.
(21) Abrams, M. J.; Davison, A.; Jones, A. G.; Costello, C. E.; Pang, H. *Inorg. Chem.* **1983**, *22*, 2798.
(22) Hurst, R. W.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1981**, *20*, 3298.
(23) Ichimura, A.; Heineman, W. R.; Vanderheyden, J.-L.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 1272.
(24) Ichimura, A.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 2134.

Table I. Spectrophotometric and Electrochemical Parameters Characteristic of Selected Technetium and Ruthenium Complexes

complex[c]	λ_{max} $(\epsilon)^b$	$E_{1/2}$ vs. NHE,[a] V
$[Tc(DMPE)_3]^+$	253 (13 100), 224 (11 700)	0.290
$[Tc(DMPE)_3]^{2+}$	571 (1080), 478 (300), 366 (365), 240 (6000)	
$[A_5Ru(isn)]^{2+}$	484 (11 600)	0.384
$[A_5Ru(isn)]^{3+}$	276 (5900)	
$[A_5Ru(py)]^{2+}$	407 (7250), 245 (5000)	0.308
$[A_5Ru(py)]^{3+}$	261 (4600), 225 (4700), 248 (4700)	
$[A_5Ru(pic)]^{2+}$	398 (8700), 242 (4900)	0.266
$[A_5Ru(pic)]^{3+}$	252 (7100)	

$^a E_{1/2}$ determined by cyclic voltammetry in 0.1 M LiCl. $^b \lambda_{max}$ in nm; ϵ in M^{-1} cm^{-1}. ^{c} A = NH$_3$; isn = isonicotinamide; py = pyridine; pic = 4-picoline; DMPE = 1,2-bis(dimethylphosphine)ethane.

respectively. Hexaammineruthenium(III) chloride, $[(NH_3)_6Ru]Cl_3$, was provided by Matthey Bishop. Lithium hydroxide and "Ultrex" Li_2CO_3 were obtained from Baker. Lithium trifluoromethanesulfonate and LiCl were prepared by neutralization of an aqueous solution of LiOH with the corresponding acid. The $LiCF_3SO_3$ solution was evaporated to near dryness to yield a precipitate that was recrystallized from hot methanol and then dried in a vacuum desiccator.

Synthesis of Complexes. Tris(1,2-bis(dimethylphosphino)ethane)-technetium(I) trifluoromethanesulfonate, $[Tc(DMPE)_3]CF_3SO_3$ was prepared according to a published procedure.[17] The pentaammine-ruthenium(III) complexes, $[(NH_3)_5RuL]X_3$, with L = isonicotinamide, pyridine, or 4-picoline, and X = ClO_4 or CF_3SO_3, were prepared by slight modifications of published procedures.[25] Approximately 0.5 g of finely ground $[(NH_3)_5Ru(H_2O)](CF_3SO_3)_3$, prepared from $Ru(NH_3)_6Cl_3$ as described previously,[26] was reduced with Zn/Hg under argon in 5–10 mL of water. The solution was transferred in the dark to an argon-flushed flask containing stoichiometric amounts of ligand. After the mixture was stirred in the dark for 45 min, it was made slightly acidic with CF_3SO_3H and 0.05 g of $Na_2S_2O_8$ was added, effecting a color change from dark orange-red to light yellow. A saturated solution of $LiCF_3SO_3$ or $NaClO_4$ was added to induce precipitation of the desired complex, which was then recrystallized from a 0.01 M solution of the corresponding acid. Table 1 lists the spectrophotometric and electrochemical parameters that characterize the complexes employed in this study.

Equipment. Visible–UV spectra were recorded on either a Cary 210 or a Perkin-Elmer 330 spectrophotometer.

All cyclic voltammetry was conducted with a Bioanalytical Systems CV-1A or CV-1B sweep generator and potentiostat, coupled with a Keithley Model 178 digital multimeter and a Houston Instruments Model 100 X-Y recorder. A standard three-electrode electrochemical cell, containing a platinum working electrode, a Ag/AgCl (3 M NaCl) reference electrode, and either a platinum- or silver-wire auxiliary electrode, was used for cyclic voltammetric experiments. All solutions were deoxygenated with argon and contained 0.1 M LiCl as the supporting electrolyte.

The kinetic experiments were conducted on a modified Durrum D-110 stopped-flow spectrophotometer. The photomultiplier tube of this instrument is mounted in contact with the cuvette, and the stopped-flow system (syringes, mixing chambers, cuvette, etc.) is thermostated to $\pm$ 0.1 °C. In this arrangement the photomultiplier tube is also brought to a temperature similar to that at which the stopped-flow system is equilibrated. This leads to higher than normal noise levels at temperatures over 25 °C and lower than normal noise levels at temperatures under 25 °C. No experiments were conducted at temperatures greater than 35 °C because of excessive instrument noise in this temperature range. Data acquisition during the stopped-flow experiment is accomplished with a Digital Equipment Corp. (DEC) Model 1123 minicomputer. The voltage signals from the stopped-flow detector (which correspond to absorbances) are conditioned and converted to digital signals by the following procedure. The voltage signals, which range from 0 to 10 V, are passed through a programmable gain amplifier, which lowers the impedence of the signals and allows the appropriate magnification factor to be applied. The voltage signals are then digitized by an ADAC 1023AD analogue to digital converter that is triggered by time-based pulses from a Data Translation DT2769. A DEC NT100 terminal equipped with a VT640 Digital Engineering retrographic card is used to

(25) Gaunder, R. G.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2627.
(26) Lavallee, D. K.; Lavallee, C.; Sullivan, J. C.; Deutsch, E. *Inorg. Chem.* **1973**, *12*, 570.

set up the experimental conditions and check the data for flaws before they are stored. The program written for the DEC 1123 system collects 2048 data points (conversions); 2000 of these points are spaced evenly during the preset sweep time, and the remaining 48 data points are collected after 5 sweep times have elapsed to provide an estimate of infinite time absorbance. The data are then transferred to a VAX 11/780 (VMS v3.5) computer for nonlinear least-squares analysis.

Procedures. The equilibrium constant governing the reaction of $[Tc(DMPE)_3]^+$ and $[(NH_3)_5RuL]^{3+}$ was determined spectrophotometrically in 0.1 M LiCl (0.001 M HCl) by monitoring the characteristic visible absorption of the Ru(II) product. Degassed (with platinum syringe needles only) solutions of known concentrations of the reactants were rapidly combined in a spectrophotometer cell under an inert atmosphere. The first absorbance reading was obtained ca. 1 min after mixing, and then this absorption was monitored for 30 min to ensure that equilibrium was maintained.

All solutions used in the kinetic experiments were freshly prepared each working day because of slow decomposition and aerobic oxidation of the reagents. The concentration of each stock solution was determined spectrophotometrically and then checked periodically throughout the day. Solutions of ruthenium complexes were kept in the dark as much as possible. Kinetic experiments were conducted in aqueous HCl solutions maintained at ionic strength 0.100 ± 0.001 M with LiCl. When the reaction between $[Tc(DMPE)_3]^+$ and $[(NH_3)_5RuL]^{3+}$ was studied, both reagent solutions were of the same acidity and ionic strength. However, because the Tc(II) complex is relatively unstable in acidic media, when the reaction between $[Tc(DMPE)_3]^{2+}$ and $[(NH_3)_5RuL]^{2+}$ was studied, the Ru(II) reagent solution contained twice the desired final acidity and ionic strength while the Tc(II) solution contained no added acidity or ionic strength. Stock solutions of $[Tc(DMPE)_3]^{2+}$ were prepared by PbO_2 oxidation of aqueous solutions (or suspensions) of the Tc(I) complex followed by removal of the PbO_2 via filtration through a 0.2-μm Acrodisc syringe filter. Stock solutions of $[(NH_3)_5RuL]^{2+}$ were prepared by zinc amalgam reduction of aqueous solutions of the corresponding Ru(III) complex.

Kinetics. Reactions were monitored at the characteristic visible absorption maximum of the Ru(II) complex (Table I). Concentrations of both reagents ranged from 8×10^{-6} to 200×10^{-6} M, while the ratio of [Ru]/[Tc] ranged from 0.10 to 20. At least four replicate data sets (absorbance vs. time) were collected for each reaction investigated (i.e. for each unique combination of Ru and Tc stock solutions). Rate constants derived from replicate data sets were averaged, and the standard deviation from this average was calculated.

Data Treatment. The E^0 values listed in Table I show that the cross-reaction

$$Tc(DMPE)_3^+ + (NH_3)_5RuL^{3+} \rightarrow Tc(DMPE)_3^{2+} + (NH_3)_5RuL^{2+}$$
(1)
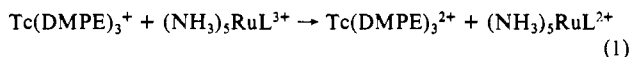
does not have a large driving force, and thus the kinetics of this process involve a second-order approach to equilibrium. The rate law that applies is

$$\frac{d[Tc^{II}]}{dt} = k_f[Tc^I][Ru^{III}] + k_b[Tc^{II}][Ru^{II}]$$

and this general form has been recast in terms of experimental variables by Benson[27] and by us in a previous study.[26] The nonlinear least-squares routine used in our analysis assumes that no products are present initially, that $k_b \neq 0$, and that $[Tc^I]_0 \neq [Ru^{III}]_0$. The only variable parameters in this analysis are k_f, k_b, t_{offset} (a parameter that accounts for the production of some of the products during the 2-ms mixing time of the stopped-flow spectrophotometer[1]), and the initial concentration of the species not in excess. Activation parameters for each reaction were calcualted within the Eyring formalism by a nonlinear least-squares analysis.[28] All quoted errors are standard deviations.

Results

Table I summarizes the relevant spectrophotometric and electrochemical parameters determined for the Ru and Tc complexes employed in this study. The observed absorption maxima and the measured redox potentials agree well with values reported in the literature.[17,29]

Table II lists the equilibrium constants for the three cross-reactions (eq 1) determined at both 25 and 8.0 °C. Each K_{eq} value

(27) Benson, S. W. In *The Foundations of Chemical Kinetics*; McGraw-Hill: New York, NY, 1960; p 29.
(28) Moore, R. H.; Ziegler, R. K. Report No. LA-2367 (plus addenda); Los Alamos Scientific Laboratory: Los Alamos, NM, 1959.

Table II. Equilibrium Constants Governing the Reaction of $[Tc(DMPE)_3]^+$ with $[(NH_3)_5RuL]^{3+}$ Complexes[a]

complex	T, °C	K_{eq}[b]	K_{eq}[c]	K_{eq}[d]
$[A_5Ru(isn)]^{3+}$	25.0	37.7 (4)	26.0 (3)	21.5 (5)
	8.0		25.8 (5)	20.5 (5)
$[A_5Ru(py)]^{3+}$	25.0	2.01 (7)	1.67 (4)	2.11 (3)
	8.0		0.98 (7)	1.0 (2)
$[A_5Ru(pic)]^{3+}$	25.0	0.39 (3)	0.37 (2)	0.39 (5)
	8.0		0.11 (1)	0.16 (1)

[a] Ligand abbreviations are defined in Table I. Standard deviation of last significant digit is given in parentheses. [b] K_{eq} derived from electrochemical measurements. [c] K_{eq} derived from spectrophotometric measurements. [d] K_{eq} derived from kinetic data ($K_{eq} = k_f/k_b$).

was determined from spectrophotometric measurements, redox potentials, and rate data. With the exception of the electrochemically derived value for the isonicotinamide complex, the three independent methods yield values that are in remarkably good agreement with each other.

Table A[34] summarizes the rate constants observed for the Tc(I) + Ru(III) and the Tc(II) + Ru(II) reactions *in the direction that the reaction is written*. Each tabulated value therefore represents a directly observed k_f, i.e. the rate parameter governing the reaction in the forward (as written) direction. It should be noted that the observed k_f for the Tc(II) + Ru(II) reaction is, of course, k_b for the Tc(I) + Ru(III) reaction (where k_b represents the rate parameter governing the reaction in the reverse direction). Nonlinear least-squares analysis of each absorbance vs. time data set yields a value for k_b as well as the value of k_f, but these calculated values of k_b are subject to a variety of errors that render them too inaccurate for our purposes, and they are therefore not tabulated. For all three ruthenium complexes $[(NH_3)_5RuL]^{2+/3+}$ (L = isonicotinamide (isn), pyridine, 4-picoline), the rates were determined as a function of [Ru], [Tc], and temperature. The rate of oxidation of $[Tc(DMPE)_3]^+$ by $[(NH_3)_5Ru(isn)]^{3+}$ was also determined as a function of $[H^+]$ and ionic strength.

Discussion

The stoichiometry of eq 1 is established by the well-known chemistries of these Ru(II)/Ru(III) and Tc(I)/Tc(II) couples[17,29] and the measured equilibrium constants (K_{eq}) governing this reaction (Table II). The fact that three wholly independent methods of determining K_{eq}, with their inherently different sources of error, give equivalent values is very gratifying and provides a sound basis for the kinetic analysis.

Since eq 1 does not involve the gain or loss of protons, it is expected that the rates of the forward and reverse reactions should be independent of $[H^+]$. This expectation is confirmed for the $[Tc(DMPE)_3]^+$ reduction of $[(NH_3)_5Ru(isn)]^{3+}$ (see Table A[34]), the only ruthenium complex investigated that contains a functionality which could conceivably be protonated. The data of Table A[34] also show that the rate of this reaction increases with increasing ionic strength, as expected for electron transfer between two positively charged ions.

Rate of Self-Exchange of $[Tc(DMPE)_3]^{+/2+}$ from Kinetic Data. A recent modification of the theory underlying the Marcus cross relationships leads to the expression

$$k_{12}^2 = k_{11}k_{22}K_{12}f_{12}W_{12}^2$$
(2)

where k_{12} is the rate of the cross-reaction between reagents 1 and 2, K_{12} is the equilibrium constant governing this reaction, while k_{11} and k_{22} are the self-exchange rates of reagents 1 and 2, respectively, and f_{12} and W_{12} are defined by

$$\ln f_{12} = \frac{[\ln(K_{12}) + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\dfrac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \dfrac{w_{11} + w_{22}}{RT}\right]}$$
(2a)

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT]$$
(2b)

(29) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

Table III. Rate Constants and Activation Parameters Governing Electron-Transfer Reactions of $[Tc(DMPE)_3]^{+/2+}$ with $[(NH_3)_5RuL]^{3+/2+}$ Complexes[a]

L	T, °C	$10^{-5}k_f$, M⁻¹ s⁻¹	$10^{-5}k_b$, M⁻¹ s⁻¹	K_{eq}[b]	ΔH_f^*, kcal/mol	ΔH_b^*, kcal/mol	ΔH°,[c] kcal/mol	ΔH_{ex},[d] kcal/mol	ΔS_f^*, eu	ΔS_b^*, eu	ΔS°,[c] eu	ΔS_{ex}^*,[d] eu
isn	34.0	48.8 (9)	2.7 (2)	18	4.8 (1.5)	5.0 (2)	−0.2	7.4	−12 (5)	−17.4 (7)	5	−8
	25.0	35.7 (6)	1.66 (8)	22								
	8.0	23 (2)	1.12 (1)	21								
	1.0	16.6 (4)	0.88 (14)	19								
py	25.0	5.31 (5)	2.52 (3)	2.1	5.1 (4)	0.08 (2)	5	3.8	−15 (1)	−33 (1)	19	−25
	1.0	2.3 (1)	1.0									
pic	25.0	3.0 (1)	7.6 (1)	0.39	8.5 (1)	2.2 (2)	6.3	9.6	−5 (1)	−24 (1)	19	−5
	1.0	0.79 (4)	5.06 (8)	0.16								

[a] Ligand abbreviations are defined in Table I. Standard deviation of last significant digit given in parentheses. $\mu = 0.10$ M (LiCl). [b] $K_{eq} = k_f/k_b$. [c] $\Delta H^\circ = \Delta H_f^* - \Delta H_b^*$; $\Delta S^\circ = \Delta S_f^* - \Delta S_b^*$. [d] The subscript "ex" refers to the self-exchange reaction of $[Tc(DMPE)_3]^{+/2+}$. Because of the paucity of data and the interdependence of the parameters used in the calculation, a meaningful estimate of the error in these values cannot be readily calculated.

The work terms w_{ij} are defined in the usual way[9-12] (vide infra), and we have taken $A_{11} = A_{22} = 2.8 \times 10^{12}$ M⁻¹ s⁻¹ consistent with previous estimates.[11,12] Thus, eq 2 can be used to calculate the self-exchange rate of the $[Tc(DMPE)_3]^{+/2+}$ couple (k_{22}) from the rate data of Table A,[34] the equilibrium data of Table II, an estimate of the distance separating the two ions in the activated complex (taken as 9.6 Å; vide infra), and the self-exchange rate of the $[(NH_3)_5RuL]^{2+/3+}$ complexes, k_{11}. This latter value has been measured as 4.8×10^5 M⁻¹ s⁻¹ at $\mu = 1.00$ M and has been corrected to 1.1×10^5 M⁻¹ s⁻¹ at $\mu = 0.10$ M (25 °C), for the complex with L = pyridine;[29] the same self-exchange rate is assumed to obtain for the complexes with L = isonicotinamide and 4-picoline. Assuming no error in k_{11}, data for oxidation of the isonicotinamide, pyridine, and 4-picoline complexes lead respectively to the following self-exchange rates for $[Tc-(DMPE)_3]^{+/2+}$: $(4.00 \pm 0.01) \times 10^6$, $(0.84 \pm 0.02) \times 10^6$, and $(1.5 \pm 0.1) \times 10^6$ M⁻¹ s⁻¹ (25 °C, $\mu = 0.10$ M). The agreement among these values is quite satisfactory (the spread being less than a factor of 5) considering that k_{11} is undoubtedly not exactly the same for all three ruthenium complexes and considering that the equilibrium constant for the three reactions varies by about a factor of 70 (Table II).

The temperature dependence of the cross-reactions can be used, within the Marcus formalism,[9-12,29] to obtain estimates of the activation parameters governing the self-exchange reaction of $[Tc(DMPE)_3]^{+/2+}$. Data relevant to this calculation and the results of the calculation are given in Table III. The standard errors of these derived activation parameters cannot be readily estimated due to the interdependence of the parameters used in the calculations, combined with the limited number of data available for the pyridine and picoline systems. Nevertheless, the data in Table III lead to the following estimates of the activation parameters governing the self-exchange of $[Tc(DMPE)_3]^{+/2+}$: $\Delta H_{ex}^* = 7 \pm 3$ kcal/mol; $\Delta S_{ex}^* = -8 \pm 4$ eu. These parameters are consistent with the few relevant literature data available for comparison.[29,30] Thus, the ΔS_{ex}^* value for this $1+/2+$ couple is significantly more positive than values observed for $2+/3+$ couples due to the smaller amount of electrostatic work necessary to achieve the lower charged transition state (e.g. ΔS_{ex}^* for $[(NH_3)_6Ru]^{2+/3+}$ is ca. −27 eu[29]). The estimate of ΔH_{ex}^* for $[Tc(DMPE)_3]^{+/2+}$ is comparable to the estimated $\Delta H_{ex}^* = 4.5$ kcal/mol for $[(NH_3)_6Ru]^{2+/3+}$, another low-spin, d^6/d^5 couple.[29]

Rate of Self-Exchange of $[Tc(DMPE)_3]^{+/2+}$ from Structural Data. According to Marcus theory,[5,6,29] the rate constant for the self-exchange reaction

$$[Tc^*(DMPE)_3]^+ + [Tc(DMPE)_3]^{2+} \rightarrow$$
$$[Tc^*(DMPE)_3]^{2+} + [Tc(DMPE)_3]^+ \quad (3)$$
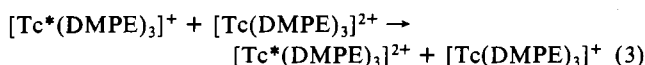
can be predicted from a relation that includes the work required to bring the reactants together, w_r, the activation energies to rearrange the inner, ΔG_{in}^*, and outer, ΔG_{out}^*, coordination spheres

of the reactants, and the collision frequency of neutral molecules in solution, Z.

$$k_{ex} = Z \exp[-(w_r + \Delta G_{in}^* + \Delta G_{out}^*)/RT] \quad (4)$$

$$\Delta G_{in}^* = \frac{6f_1f_2(\Delta a^0)^2}{2(f_1 + f_2)} \quad (5)$$

$$\Delta G_{out}^* = \frac{e^2}{4}\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{n^2} - \frac{1}{D_s}\right) \quad (6)$$

$$w_r = \frac{z_1z_2e^2}{D_sr(1 + \kappa r)} \quad (7)$$

$$\kappa = \left[\frac{8\pi N^2e^2\mu}{1000D_sRT}\right]^{1/2} = \beta\mu^{1/2} \quad (8)$$

The terms used in these expressions are defined as follows: f_1 and f_2 are the force constants for the breathing vibrational modes of the reactant and product; Δa^0 is the difference between the radius of the reactant and that of the product; a_1 and a_2 are the radii of the reactants, estimated as the radius of a sphere of equal volume, $a = 1/2(d_1d_2d_3)^{1/3}$, where d_1, d_2, and d_3 are the dimensions of the complex along the three Cartesian coordinates;[29] r is the separation of the metal centers in the activated complex, assumed to be equal to the sum of a_1 and a_2; D_s and n are the dielectric constant and refractive index of the medium; z is the charge of the reactants; μ is the ionic strength; β is the Debye–Hückel constant (0.329 in water at 25 °C). Z is often taken to be 10^{11} M⁻¹ s⁻¹, but Sutin has shown[29] that better estimates for k_{ex} are obtained if Z is calculated by eq 9, where m_1 and m_2 are the masses

$$Z = \frac{N[8\pi k_BT(m_1 + m_2)/m_1m_2]^{1/2}r^2}{1000} \quad (9)$$

of the reactants, N is Avogadro's number, and k_B is the Boltzmann constant.

For the $[Tc(DMPE)_3]^{+/2+}$ self-exchange reaction, Δa^0 is estimated as 0.068 Å on the basis of EXAFS data for the Tc^I-P bond length (2.40 (1) Å)[17] and X-ray crystallographic data for the $Tc^{II}-P$ bond length of $[Tc(DEPE)_3]^{2+}$ (2.468 (5) Å, where DEPE represents (1,2-bis(diethylphosphino)ethane)).[31] The $Tc^{II}-P$ bond length is expected to be independent of whether the pendant groups on phosphorus are ethyl or methyl. The symmetrical Tc–P stretching frequency of $[Tc(DMPE)_3]^{+/2+}$ is estimated from the known symmetrical Tc–Cl stretching frequency of $[TcCl_6]^{2-}$ (337 cm⁻¹)[32] by correcting the difference in mass between P and Cl. This leads to $f = 2f_1f_2/(f_1 + f_2) = 1.64 \times 10^5$ dyn/cm. Measurements of CPK models yield $r = 2a = 9.6$ Å.

(30) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.

(31) Deutsch, E.; Libson, K.; Bandoli, G.; Mazzi, U., manuscript in preparation.

(32) Baluka, M.; Hanuza, J.; Jezowska-Trzbiatowska, B. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1972**, *20*, 271.

Table IV. Calculation of the Rate Constant Governing the Self-Exchange Reaction of $[Tc(DMPE)_3]^{+/2+}$ [a]

estd params	best estimate of f and r	increase r by 1.0 Å	increase f with intermediate r value
$10^{-5}f$, dyn/cm	1.64	1.64	3.01
r, Å	9.6	10.6	10.0

calcd params	values from various estimates		
ΔG_{in}^{*}, kcal/mol	1.68	1.68	3.00
ΔG_{out}^{*}, kcal/mol	4.69	4.26	4.50
w_r, kcal/mol	0.44	0.38	0.42
$10^{-11}Z$, M^{-1} s^{-1}	2.6	3.2	2.9
$10^{-6}k_{ex}$, M^{-1} s^{-1}	3.0	7.4	0.45

[a] Calculations are conducted with equations given in the text.

With these values, under the conditions of our experiments, eq 6 and 7 become[29]

$$w_r = \frac{4.24 z_1 z_2}{r(1 + 0.104r)} \quad (10)$$

$$\Delta G_{out}^{*} = \frac{45.0}{r} \quad (11)$$

Table IV shows the results of using these estimated parameters within eq 4–7 to calculate the self-exchange rate of $[Tc(DMPE)_3]^{+/2}$. This calculated value is 3.0×10^6 M^{-1} s^{-1} (25 °C), in excellent agreement with the range of kinetically observed values, $0.8-0.4 \times 10^6$ M^{-1} s^{-1}. Table IV also shows how moderate alterations in the estimated values of r and f can lead to substantial changes in the calculated self-exchange rate. This demonstrates that the calculated value has an inherently large uncertainty, and the excellent agreement with the experimentally determined value is to some extent fortuitous. Nonetheless, even in the worst cases the calculated value of k_{ex} agrees with the measured value to within a factor of 20, clearly demonstrating that the Marcus theory can be successfully applied to the $[Tc(DMPE)_3]^{+/2+}$ couple.

This latter conclusion is of some general interest because of the nature of the Tc–P bonding within $[Tc(DMPE)_3]^{+/2+}$. This bonding is dominated by π interactions, and thus the Tc^{II}–P bond length is actually *longer* than the Tc^I–P bond length. Moreover, it appears that the predominant factor in effecting the self-exchange rate of d^6/d^5 complexes is the radius of the complex, a, which determines the distance of closest approach ($r = 2a$). Thus, Brown and Sutin[29] have shown that for the series of related ru-

thenium complexes $[(NH_3)_6Ru]^{2+/3+}$, $[(NH_3)_5Ru(py)]^{2+/3+}$, $[(NH_3)_4Ru(bpy)]^{2+/3+}$, $[(NH_3)_2Ru(bpy)_2]^{2+/3+}$, and $[Ru(bpy)_3]^{2+/3+}$, log (k_{ex}) is linearly correlated with $1/r$. The log (k_{ex}) $- 1/r$ datum for $[Tc(DMPE)_3]^{+/3+}$ falls only slightly off this correlation; if an r value of 8.8 Å were estimated for $[Tc(DMPE)_3]^{+/2+}$, rather than the value of 9.6 Å used in this work, the $[Tc(DMPE)_3]^{+/2+}$ datum would be coincident with that of $[(NH_3)_4Ru(bpy)]^{2+/3+}$. This small difference in a values (4.4 vs. 4.8 Å) is readily ascribed to experimental uncertainties in determining this parameter.[33] For these low-spin d^6/d^5 Tc(I)/Tc(II) and Ru(II)/Ru(III) couples, Δa^0 is relatively small and thus ΔG_{in}^{*} provides a relatively small contribution to k_{ex} while ΔG_{out}^{*} is the predominant factor in determining the magnitude of k_{ex}. Since ΔG_{out}^{*} depends strongly on a (and therefore r), it is this parameter that is paramount in determining k_{ex} for low-spin d^6/d^5 couples.

Conclusions. The self-exchange reaction of the $[Tc(DMPE)_3]^{+/2+}$ couple is adequately described by the Marcus formalism. Both kinetic and structural analyses lead to a self-exchange rate of ca. 2×10^6 M^{-1} s^{-1} (25 °C, $\mu = 0.10$ M). There are no unusual effects resulting from the extensive metal–ligand π-back-bonding in this complex. Rather, the rate of self-exchange of this Tc(I)/Tc(II) couple is comparable to that of σ-bonded Ru(II)/Ru(III) couples of similar size. The $[Tc(DMPE)_3]^{+/2+}$ couple should be useful in kinetically characterizing other redox systems because of its water solubility, its accessible E^0 value, and its stability over a wide range of pH values.

Registry No. $[Tc(DMPE)_3]^+$, 89378-27-8; $[Tc(DMPE)_3]^{2+}$, 89378-21-2; $[A_5Ru(isn)]^{2+}$, 103258-87-3; $[A_5Ru(isn)]^{3+}$, 103258-88-4; $[A_5Ru(py)]^{2+}$, 21360-09-8; $[A_5Ru(py)]^{3+}$, 33291-25-7; $[A_5Ru(pic)]^{2+}$, 19482-30-5; $[A_5Ru(pic)]^{3+}$, 80584-19-6.

Supplementary Material Available: Table A, containing observed second-order rate parameters as a function of temperature, ionic strength, and [H⁺] (2 pages). Ordering information is given on any current masthead page.

(33) If it is assumed that there is no error in a, the fact that the $[Tc(DMPE)_3]^{+/2+}$ point does not fall on the log (k_{ex}) vs. $1/r$ plot for the ruthenium system would then reflect the larger value of ΔG_{in}^{*} for the DMPE couple (giving rise to a lower rate constant).

(34) Supplementary material.