bond does not dissociate on the NMR time scale. Thus, the monomeric and dimeric forms are not in rapid equilibrium and the 50:50 methanol-d_4/dichloromethane-d_2 solution contains either the dimeric or the monomeric form. Isolation of one form or the other from various solutions presumably depends upon the nature of the anion used in the crystallization procedure. The stability of $[Cu(dmpe)_2]_2(BF_4)_2$ indicates that Cu(I)-protected phosphines might be useful starting materials for the preparation of phosphine-based technetium-99m radiopharmaceuticals.

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Registry No. $[Cu(CH_3CN)_4]BF_4$, 15418-29-8; $[Cu(dmpe)_2]_2(BF_4)_2$, 136736-94-2; ^{63}Cu, 14191-84-5.

Supplementary Material Available: Tables of hydrogen atom positional parameters, bond lengths and angles, anisotropic thermal parameters, and crystal data and data collection and refinement parameters (7 pages); a listing of calculated and observed structure factors (35 pages). Ordering information is given on any current masthead page.

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Electron-Transfer Reactions of Technetium and Rhenium Complexes. 3.[1] Pulse Radiolysis Studies on *trans*-$[M^{III}X_2(DMPE)_2]^+$ and $[M^I(DMPE)_3]^+$ Complexes in Aqueous and Aqueous Surfactant Media, Where M = Tc or Re, X = Cl or Br, and DMPE = 1,2-Bis(dimethylphosphino)ethane

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Pulse radiolytic techniques have been employed to study the rate of reactions of the strong reductant e_{aq}^- and the strong oxidant Cl_2^- with lipophilic, cationic Tc and Re complexes in aqueous and aqueous surfactant media. In aqueous media the reactions of the M(III) complexes *trans*-$[Re^{III}Cl_2(DMPE)_2]^+$, *trans*-$[Re^{III}Br_2(DMPE)_2]^+$, and *trans*-$[Tc^{III}Cl_2(DMPE)_2]^+$ have been studied with both reagents, while the reaction of the M(I) complexes $[Re^I(DMPE)_3]^+$ and $[Tc^I(DMPE)_3]^+$ have been studied with Cl_2^-. Oxidation of the M(I) complexes cleanly yields the corresponding $[M^{II}(DMPE)_3]^+$ species by an outer-sphere mechanism, whereas oxidation of the M(III) complexes appears to proceed by more complicated pathways, which could involve both outer-sphere electron transfer as well as oxidative addition. All reactions proceed at, or near, the diffusion-controlled limit. The positively charged surfactant CTAB (hexadecyltrimethylammonium bromide) and the uncharged surfactant Triton X-100 (α-[p-(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxypolyoxyethylene(9.5)) have little or no effect on the rates of any of the reactions studied. However, micelles formed from the negatively charged surfactant SDS (sodium dodecyl sulfate) exert a dramatic effect on reaction rates by effectively sequestering the cationic complexes and rendering them relatively unavailable for reaction with the anionic reagents e_{aq}^- and Cl_2^-. While the anionic reagents can penetrate the SDS micelles, the cationic complexes do not appear to be released from the micelle during the lifetime of the anionic radicals (ca. 10^2 μs). These results have implications for the use of surfactants in electrochemical studies, as well as for the pharmacokinetics of cationic complexes of interest to nuclear medicine.

Introduction

During the past 5 years detailed biological studies have demonstrated that in vivo redox reactions can dramatically affect the biodistributions of technetium-99m and rhenium-186 radiopharmaceuticals.[3-11] While in some cases the in vivo oxidation or reduction of a radiopharmaceutical adversely affects its biodistribution,[5,6,8,10] in other situations in vivo redox reactivity can be advantageous.[7,11] In either case the rational design of radiopharmaceuticals requires fundamental knowledge of the thermodynamic and kinetic factors which underlie the in vivo redox reactivity of technetium and rhenium complexes. Such knowledge is often difficult to obtain because the complexes of interest to nuclear medicine are generally very lipophilic and thus have very low water solubilities.[12,13] Studies in organic solvents can provide some useful, comparative data, but in general the results of such nonaqueous studies are not directly relevant to the biological milieu. To circumvent this difficulty aqueous surfactant solutions have been utilized to investigate the electrochemistry of lipophilic technetium and rhenium complexes of relevance to nuclear medicine.[14,15] These studies demonstrated that the observed redox potentials, i.e., the *thermodynamic* factors underlying redox reactivity, are sensitive to various properties of both the complexes and the surfactants. In this paper these initial studies are extended with the aim of determining whether or not these properties of

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(1) Part 2: Libson, K.; Woods, M.; Sullivan, J. C.; Watkins, J. W., II; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 999.

(2) On leave from The University of the Orange Free State, Bloemfontein 9300, Republic of South Africa.

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complexes and surfactants might similarly affect the *kinetic* factors which underlie the redox reactivity of lipophilic technetium and rhenium complexes in aqueous surfactant media.

Experimental Section

General Considerations. Unless otherwise specified, all references to technetium in this paper are to the isotope ^{99}Tc. No other technetium isotope was used in this work. Technetium-99 emits a low energy (0.292 MeV) β-particle with a half-life of 2.12×10^5 years. When this isotope 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 standard radiation safety procedures must be used at all times to prevent contamination.

The ligand abbreviation DMPE refers to 1,2-bis(dimethylphosphino)ethane.

Materials. Unless otherwise noted, all chemicals were of reagent grade quality. The surfactants SDS (sodium dodecyl sulfate), CTAB (hexadecyltrimethylammonium bromide) and Triton X-100 (α-[p-(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxypolyoxyethylene(9.5)) were obtained from commerical suppliers[14-16] and were used without further purification. All solutions were prepared in triply distilled water and were deaerated using the syringe technique.[16] Frothing of the surfactant solutions during deaeration and subsequent manipulation caused mechanical difficulties, which in turn led to relatively low precision in the final rate parameters.

The following salts were prepared as described in the literature and were available from previous studies:[14,15] *trans*-$[\mathrm{ReCl_2(DMPE)_2}]\mathrm{F_3CSO_3}$,[5] *trans*-$[\mathrm{ReBr_2(DMPE)_2}]\mathrm{F_3CSO_3}$,[5] *trans*-$[\mathrm{TcCl_2(DMPE)_2}]\mathrm{Cl}$,[17] and $[\mathrm{Tc(DMPE)_3}]\mathrm{Cl}$.[18] The $[\mathrm{Re(DMPE)_3}]\mathrm{Cl}$ salt was prepared by the route previously described[6] for the hexafluorophosphate and trifluoromethanesulfonate salts except that (i) $[\mathrm{ReCl_2(DMPE)_2}]\mathrm{Cl}$ was used as starting material, (ii) the desired chloride salt was precipitated from the reaction mixture by the addition of HCl and diethyl ether, and (iii) the final product was purified by successive crystallizations from mixtures of acetone and diethyl ether.

Pulse Radiolysis. All experiments were conducted in optical quartz cells of either 1.00- or 2.00-cm path length. Absorption spectra of transient species were obtained by the streak camera technique[19-21] after irradiation with single 1-μs pulses of 20-MeV electrons generated by the Argonne linear accelerator. Kinetic measurements were obtained by conventional photomultiplier techniques[22] after irradiation with 2-4-ns pulses of 20-MeV electrons (for $\mathrm{Cl_2^-}$ oxidation of $[\mathrm{Re^I(DMPE)_3}]^+$, 20-ns pulses were used). The kinetic data were collected and analyzed as described previously.[16,23]

Reactions of the hydrated electron (e_{aq}^-, $E° = -2.9$ V) were conducted in argon-saturated solutions which contained 0.1 M *tert*-butyl alcohol to scavenge hydroxy radicals and were monitored at 600 nm where none of the other species investigated exhibit any significant absorbance. Control experiments in which the reaction of e_{aq}^- with *trans*-$[\mathrm{Re^{III}Br_2(DMPE)_2}]^+$ was monitored at 460 nm (the wavelength of maximum absorbance of the Re(III) species) yielded the same values of k_{obs} as those in which the reaction was monitored at 600 nm. Reactions of the $\mathrm{Cl_2^-}$ radical ($E° = 2.1$ V) were conducted in solutions which contained 0.1 M NaCl at pH 3 (maintained with HCl) to convert OH$^\bullet$ into $\mathrm{Cl_2^-}$, and which were also saturated with $\mathrm{N_2O}$ to convert e_{aq}^- to OH$^\bullet$; under these conditions, both the OH$^\bullet$ and the e_{aq}^- are converted to $\mathrm{Cl_2^-}$ at diffusion-controlled rates.

Results and Discussion

Background. Electrochemical measurements on the *trans*-$[\mathrm{Tc^{III/II}X_2(DMPE)_2}]^{+/0}$ and $[\mathrm{Tc^{II/I}(DMPE)_3}]^{2+/+}$ couples in aqueous surfactant media demonstrate that the observed redox potentials are a function of (i) the formal charge on the electroactive complex, (ii) the formal charge on the surfactant molecule that forms the micelle, (iii) the lipophilicity of the components of the redox couple, and (iv) the nature of the supporting electrolyte.[14,15] While many of the specific results comprising these generalizations are readily explained, others are not, and the interpretation of these apparently anomalous results may be confounded by sorption of the complexes or surfactants onto the electrode surface. These complications, which are inherent to a *heterogeneous* electrode surface, can be avoided by monitoring electron-transfer reactions in *homogeneous* micellar media, and this field has been recently reviewed.[24] The use of pulse radiolysis to generate reactive intermediates is a natural extension of this homogeneous approach since it avoids the mechanical difficulties of mixing surfactant solutions and allows the systematic investigation of strong reductants and oxidants which bear the same formal charge (here, e_{aq}^- and $\mathrm{Cl_2^-}$).[25]

Table I. Observed Second-Order Rate Constants for the $\mathrm{Cl_2^-}$ Oxidation and e_{aq}^- Reduction of Cationic, Lipophilic Tc and Re Complexes

reaction[a]	k, $\mathrm{M^{-1}\,s^{-1}}$
trans-$[\mathrm{ReCl_2(DMPE)_2}]^+ + e_{aq}^-$ [b]	$4.2\ (2) \times 10^{10}$
trans-$[\mathrm{ReBr_2(DMPE)_2}]^+ + e_{aq}^-$ [b]	$4.1\ (3) \times 10^{10}$
trans-$[\mathrm{TcCl_2(DMPE)_2}]^+ + e_{aq}^-$ [c]	$>1 \times 10^9$
trans-$[\mathrm{ReCl_2(DMPE)_2}]^+ + \mathrm{Cl_2^-}$	$5.3\ (5) \times 10^9$ [d]
trans-$[\mathrm{ReBr_2(DMPE)_2}]^+ + \mathrm{Cl_2^-}$	$8.6\ (7) \times 10^9$ [d]
trans-$[\mathrm{TcCl_2(DMPE)_2}]^+ + \mathrm{Cl_2^-}$ [e]	$9.3\ (2) \times 10^8$
$[\mathrm{Re(DMPE)_3}]^+ + \mathrm{Cl_2^-}$ [d]	4×10^9 [f]
$[\mathrm{Tc(DMPE)_3}]^+ + \mathrm{Cl_2^-}$ [c]	1×10^9 [c]

[a] Reactions of e_{aq}^- monitored by observing disappearance of e_{aq}^- at 600 nm, unless otherwise noted. [b] Reaction conducted in 0.01 M 2-propanol. [c] Rate estimated from streak camera results. [d] Reaction monitored by observing formation of product complex. [e] Reaction monitored by observing disappearance of $\mathrm{Cl_2^-}$. [f] Rate estimated from studies in SDS media.

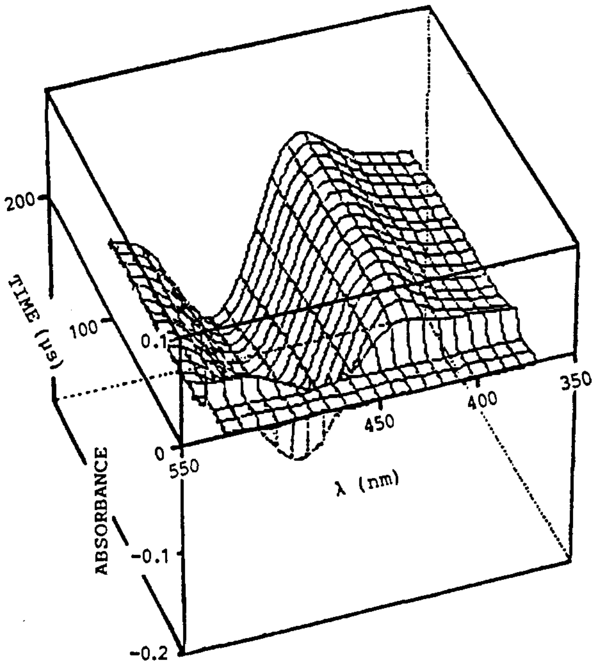

Figure 1. Three-dimensional (absorbance vs time vs wavelength) representation of streak camera results observed for the e_{aq}^- reduction of *trans*-$[\mathrm{Tc^{III}Cl_2(DMPE)_2}]^+$. Conditions: pH ca. 7; [Tc] = 10^{-4} M, [*tert*-butyl alcohol] = 0.1 M.

Reduction of *trans*-$[\mathrm{M^{III}X_2(DMPE)_2}]^+$ by e_{aq}^- in Water. As expected from the electrochemical reversibility of these M(III/II) couples and the large difference between redox potentials of the reactants, this reaction proceeds at a diffusion-controlled rate for

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Table II. Comparative Literature and Streak Camera UV-Visible Data[a]

complex[c]	$[M^{II}X_2(DMPE)_2]^0$[b]	λ_{iso}	$[M^{III}X_2(DMPE)_2]^+$	λ_{iso}	$[M^{IV}X_2(DMPE)_2]^{2+}$
trans-$[ReCl_2(DMPE)_2]^{0/+/2+}$	345 (2120)	396	411 (2700)	[380]	[282]
	[338]	[403]	[410]		
	383 (3680)[d]		439 (2500)	[473]	[320 sh]
	[383]		[438]		
					[360 sh]
					[506]
					[565]
trans-$[ReBr_2(DMPE)_2]^{0/+}$	343 (1200)[d]	421[d]	466 (2800)		
	[348]	[420]	[465]		
	408 (4300)	...	...		
	[406]				
trans-$[TcCl_2(DMPE)_2]^{0/+}$	414 (600)[d]	434[d]	464[d]		
	[426 (>600)]	[442]	[475]		

complex[c]	$[M^I(DMPE)_3]^+$	λ_{iso}	$[M^{II}(DMPE)_3]^{2+}$[c]
$[Tc(DMPE)_3]^{+/2+}$	226 (11 700)	...	366 (365)[e]
			[365]
	253 (13 100)	[316]	569 (810)[e]
	[260]		
$[Re(DMPE)_3]^{+/2+}$	253 (17 200)[e]	[325]	340 (310)[e]
	[<270]		[342]
			527 (1360)
			[527]

[a] λ_{max} (ϵ). Streak camera data given in square brackets. Literature data taken from refs 1, 6, 14, 15, 17, 18, and 26–28. λ in nm, ϵ in M^{-1} cm^{-1}. [b] Generated by e_{aq}^- reduction. [c] Generated by Cl_2^- oxidation. [d] Literature data obtained in *N*,*N*-dimethylformamide. [e] Literature data obtained in acetonitrile.

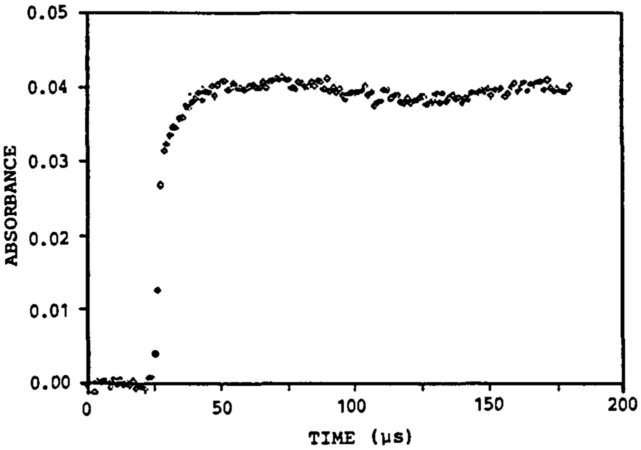

Figure 2. Two-dimensional (absorbance vs time) slice at 426 nm from Figure 1.

Table III. Observed Pseudo-First-Order Rate Constants Governing e_{aq}^- Reduction of *trans*-$[Re^{III}X_2(DMPE)_2]^+$ (X = Cl, Br) Complexes in the Presence of SDS, CTAB, and Triton X-100 Surfactants[a]

	$10^{-5}k_{obs}$, s^{-1}					
	trans-$[ReCl_2(DMPE)_2]^+$			*trans*-$[ReBr_2(DMPE)_2]^+$		
[surfactant], M	SDS	CTAB	Triton X-100	SDS	CTAB	Triton X-100
0	19.1	19.1	19.1	26.2	26.2	26.2
1.9×10^{-5}			18.1			25.3
5.7×10^{-5}			18.9			26.7
1.0×10^{-4}	17.5	18.3	18.4	27.8	28.5	29.9
1.9×10^{-4}			19.6			29.1
3.0×10^{-4}	17.4	18.6		26.1	28.7	
7.0×10^{-4}	12.7	18.2		24.4	28.1	
1.0×10^{-3}	12.7	17.9	19.9	25.2	30.1	33.1
1.9×10^{-3}			20.1			32.0
5.0×10^{-3}	3.8	18.8		3.2	29.8	
1.0×10^{-2}	2.2	20.4	22.0	2.9	31.6	30.0
1.9×10^{-2}		*b*	27.0		*b*	32.5
5.0×10^{-2}	3.0			4.2		
1.0×10^{-1}	3.0			4.2		
1.0×10^{-3}[c]			7.5			7.5
5.0×10^{-3}[c]	4.7	11.5		4.7	11.5	

[a] Conditions: pH ca. 7; [*tert*-butyl alcohol] = 0.1 M; [*trans*-$[ReCl_2(DMPE)_2]^+$] = 4×10^{-4} M; [*trans*-$[ReBr_2(DMPE)_2]^+$] = 5.3×10^{-4} M. Reactions were monitored at 600 nm, but for *trans*-$[ReBr_2(DMPE)_2]^+$ data from control experiments at 460 nm are also included. [b] Higher concentrations of CTAB caused precipitation. [c] [Re] = 0.

all three complexes, *trans*-$[TcCl_2(DMPE)_2]^+$, *trans*-$[ReCl_2(DMPE)_2]^+$, and *trans*-$[ReBr_2(DMPE)_2]^+$ (see Table I). No reaction intermediates are detected. Figure 1 shows a typical three-dimensional (absorbance vs wavelength vs time) streak camera spectrum resulting from these reactions; in this example, the oxidant is *trans*-$[TcCl_2(DMPE)_2]^+$. The absorbance scale represents ($A_t - A_0$) where A_t is the absorbance at time *t* and A_0 is the absorbance before the pulse. Thus, the disappearance of the Tc(III) starting material is manifested as a negative absorption band, while the appearance of the Tc(II) product is manifested as a positive absorption band. Taking into account the effect of the absorption of one component on the observed absorption of the other, the observed maxima of these absorption bands [426 nm for Tc(II) and 475 nm for Tc(III)] are in good agreement with values obtained in nonaqueous media by visible-UV spectroscopy[17] and spectroelectrochemistry[26] [414 nm for Tc(II) and 469 nm for Tc(III)]. In addition, this kinetically based streak camera experiment provides a value for the Tc(III)/Tc(II) isosbestic point (442 nm) which is in good agreement with that (434 nm) derived from the thermodynamically based spectroelectrochemistry experiment.[26] These results demonstrate that the species being monitored in this streak camera experiment are indeed identical to the well-characterized[17,18,26] Tc(III) and Tc(II) complexes *trans*-$[TcCl_2(DMPE)_2]^+$ and *trans*-$[TcCl_2(DMPE)_2]^0$. Equivalent results are obtained for e_{aq}^- reduction of *trans*-$[ReCl_2(DMPE)_2]^+$ and *trans*-$[ReBr_2(DMPE)_2]^+$; spectrophotometric data resulting from all three streak camera studies are summarized in Table II.

Figure 2 shows a two-dimensional (absorbance vs time) slice from Figure 1 at 426 nm, the wavelength of maximum absorption of the Tc(II) product. The lack of decay of the 426 nm absorbance for up to 0.5 ms after generation of Tc(II) indicates that precipitation of the neutral *trans*-$[Tc^{II}Cl_2(DMPE)_2]^0$ product does not occur within this time. Equivalent results are obtained for the neutral *trans*-$[Re^{II}X_2(DMPE)_2]^0$ (X = Cl, Br) products.

Reduction of *trans*-$[Re^{III}X_2(DMPE)_2]^+$ by e_{aq}^- in Aqueous Surfactant Media. Table III presents the rate data observed for X = Cl or Br in the presence of SDS, CTAB, and Triton X-100,

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[26] Ichimura, A.; Heineman, W. R.; Vanderheyden, J.-L.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 1272.

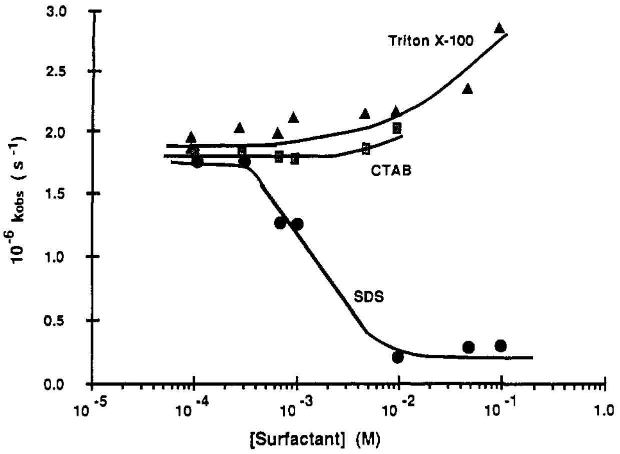

Figure 3. Plots of $10^{-6}k_{obs}$ (s^{-1}) vs log [surfactant] (M) for the e_{aq}^- reduction of *trans*-$[Re^{III}Cl_2(DMPE)_2]^+$ in the presence of either SDS, CTAB, or Triton X-100. Conditions: pH ca. 7; [Re] = 4×10^{-5} M; [*tert*-butyl alcohol] = 0.1 M.

while Figure 3 illustrates the data for X = Cl in the presence of the three surfactants. Of the three surfactants, SDS clearly generates the most dramatic effect; increasing SDS concentration systematically reduces the rate of e_{aq}^- reduction of both the *trans*-$[Re^{III}Cl_2(DMPE)_2]^+$ and *trans*-$[Re^{III}Br_2(DMPE)_2]^+$ complexes. The unique behavior of SDS is readily explained on the basis of Coulombic interactions between the negatively charged micelle surface and the positively charged Re(III) complexes. The inflection point of the k_{obs} vs [SDS] plot of Figure 3 corresponds to the cmc of SDS in this medium (ca. 1.5 mM[14,15]), which indicates that the Re(III) complexes effectively partition into the SDS micelles and that once within the micelles they are relatively protected from e_{aq}^- reduction. The observation that a finite limiting rate is observed at high SDS concentrations implies that e_{aq}^- can penetrate the micelle to reduce the Re(III) complex. The limiting rates for e_{aq}^- reduction of both the chloro and bromo complexes are essentially the same (ca. 4×10^5 s^{-1}), and also approximately equal to that observed for the U(VI) cation (ca. 1×10^5 s^{-1})[16] and benzylviologen cation radicals.[27] Since cations of such disparate lipophilicities and reduction potentials exhibit similar limiting rates, it is likely that the limiting rate reflects predominantly the inherent rate at which e_{aq}^- can penetrate the SDS micelle and encounter a cationic complex. This inherent rate should depend largely on the properties of e_{aq}^- and the rate of reorganization of the micellar structure and to a lesser degree on the location of the complex within the micelle.

The positively charged (CTAB) and neutral (Triton X-100) surfactants engender little or no effect on the rate of e_{aq}^- reduction of the Re(III) cations, even though the ranges of surfactant concentrations utilized in this work encompass the cmc values for these surfactants (ca. 0.5 mM for CTAB and ca. 1.0 mM for Triton X-100[14,15]). (The single rate enhancement (ca. 30%) observed for *trans*-$[Re^{III}Cl_2(DMPE)_2]^+$ at the highest Triton X-100 concentration is not observed for the corresponding bromo complex.) This general lack of sensitivity of reaction rate to the presence of CTAB and Triton X-100 micelles is somewhat surprising in light of previous electrochemical studies which showed that these surfactants significantly affect the electrode reductions of *trans*-$[Re^{III}X_2(DMPE)_2]^+$ (X = Cl, Br) complexes.[14,15] In retrosepct, it appears most likely that the electrochemical effects engendered by CTAB and Triton X-100 stem from interactions of these surfactants at the electrode surface and not from partitioning of the cationic Re(III) complexes into the CTAB and Triton X-100 micelles. It is also possible, albeit less likely, that the rate of reaction of the cationic complexes within the CTAB and Triton X-100 micelles is equal to the rate of reaction of these complexes in homogeneous solution.

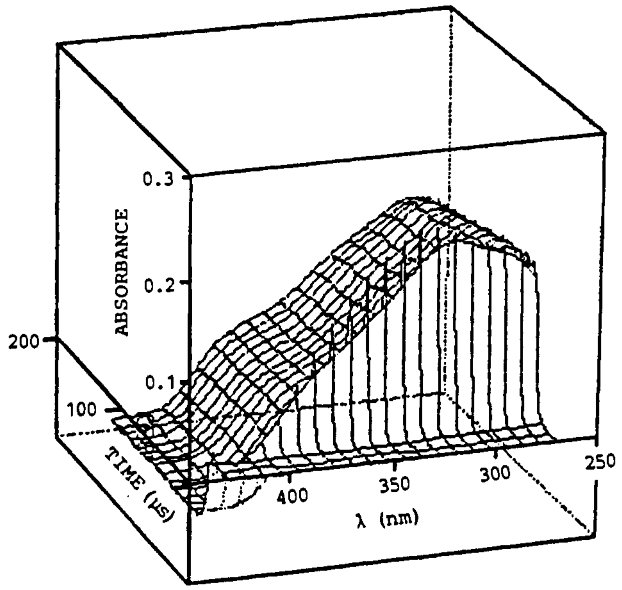

Figure 4. Three-dimensional (absorbance vs time vs wavelength) representation of streak camera results observed for the Cl_2^- oxidation of *trans*-$[Re^{III}Cl_2(DMPE)_2]^+$. Conditions: pH ca. 3; [Re] = 10^{-4} M; [NaCl] = 0.1 M.

Oxidation of $[M^I(DMPE)_3]^+$ by Cl_2^- in Water. As expected from the electrochemical reversibility of these M(II/I) couples and the large difference between the redox potentials of the reactants, this reaction proceeds at near the diffusion-controlled rate for both $[Tc(DMPE)_3]^+$ and $[Re(DMPE)_3]^+$ (see Table I). The slightly faster reaction of the Re(I) complex ($k_{obs}^{Re}/k_{obs}^{Tc}$ = 4) presumably reflects the difference in the self-exchange rates of the $[M^I(DMPE)_3]^+$ complexes ($k_{ex}^{Re}/k_{ex}^{Tc} = 2.2 \pm 0.9$)[1] as well as an 80-mV difference in the driving force for the reactions.[27] No reaction intermediates are detected. Streak camera experiments summarized in Table II show that the species being monitored are identical to the well-characterized[1,6,15,18,28,29] M(II) and M(I) complexes $[M(DMPE)_3]^{2+/+}$ (M = Tc, Re), establishing that the reaction with Cl_2^- is outer sphere. Both of the M(II) products are relatively stable[1,26] and do not undergo any detectable decomposition during the 150-μs time scale of the streak camera experiment.

Oxidation of *trans*-$[M^{III}X_2(DMPE)_2]^+$ by Cl_2 in Water. Electrochemical experiments[26,28] show that the M(IV/III) couple is accessible, but not electrochemically reversible. Consistent with these observations, the oxidations of *trans*-$[TcCl_2(DMPE)_2]^+$, *trans*-$[ReCl_2(DMPE)_2]^+$, and *trans*-$[ReBr_2(DMPE)_2]^+$ by Cl_2^- proceed at diffusion-controlled rates (Table I) to yield unstable products which detectably decay during the 150-μs time scale of the streak camera experiment. Figure 4 shows a streak camera spectrum resulting from the oxidation of *trans*-$[ReCl_2(DMPE)_2]^+$ by Cl_2^-, while Table II lists the predominant peaks observed in this spectrum. The several absorption peaks appear to decay at different rates, indicating that more than one Re(IV) intermediate is formed. This is not unexpected since Tc and Re complexes are known to undergo both simple electron-transfer reactions and oxidative-addition reactions; for example, the analogous M(III) complexes *trans*-$[MCl_2(diars)_2]^+$ react with molecular chlorine to yield the eight-coordinate M(V) species $[MCl_4(diars)_2]^+$ [M = Tc, Re; diars = *o*-phenylenebis(dimethylarsine)].[30]

Figure 5 shows two absorption vs time slices from the streak camera experiment. Absorption at 340 nm is due primarily to the Cl_2^- radical, with a smaller contribution from Re(IV); thus, this four-component trace corresponds to (1) diffusion-controlled

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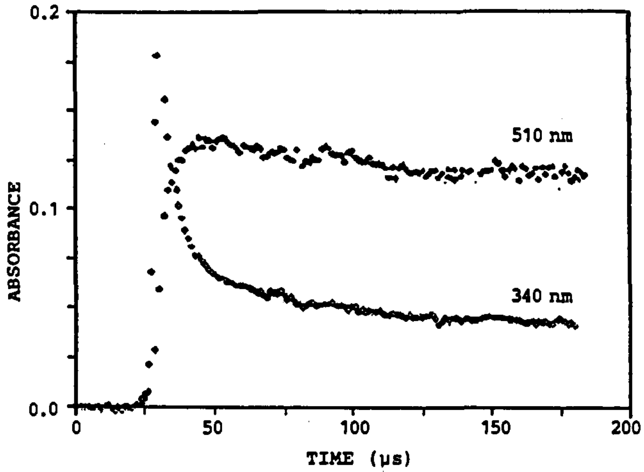

Figure 5. Two-dimensional (absorbance vs time) slices at 340 and 510 nm from Figure 4.

Table IV. Observed Pseudo-First-Order Rate Constants Governing Cl_2^- Oxidation of $[Re^I(DMPE)_3]^+$ in the Presence of SDS[a]

[SDS] M	$10^{-4}k_{obs}$, s^{-1}	[SDS] M	$10^{-4}k_{obs}$, s^{-1}
0	46.0	3×10^{-3}	11.0
1×10^{-4}	34.1	1×10^{-2}	4.4
2×10^{-4}	27.8	3×10^{-2}	7.7
5×10^{-4}	43.0	1×10^{-1}	4.4
1×10^{-3}	24.0	3×10^{-2}[b]	6.0

[a] Conditions: pH ca. 3; [NaCl] = 0.1 M; 340 nm. [b] [Re] = 0.

formation of Cl_2^-, (2) rapid decay of Cl_2^- with concomitant formation of Re(IV), (3) slow decay ($k = 2.7 \times 10^4$ s^{-1}) of a Re(IV) intermediate, which exhibits predominant absorbance at this wavelength, and then finally (4) decay of a second Re(IV) intermediate. Absorption at 510 nm is due only to this second Re(IV) intermediate, and thus this two-component trace corresponds to rapid formation and subsequent slow decay of Re(IV).

Oxidation of $[Re^I(DMPE)_3]^+$ by Cl_2^- in SDS Solutions. The data of Table IV show that k_{obs} is markedly dependent on the concentration of SDS. This dependence is graphically illustrated in Figure 6, and it is seen to be essentially identical to that shown in Figure 1 for the reaction of e_{aq}^- with *trans*-$[Re^{III}Cl_2(DMPE)_2]^+$ in SDS media; thus, these two dependences presumably have a common origin. It appears as though the cationic $[Re(DMPE)_3]^+$ complex efficiently partitions into the negatively charged SDS micelles, and once within the micelles this complex is relatively protected from reaction with Cl_2^-. Again, the observation of a finite limiting rate at high SDS concentration implies that Cl_2^- is capable of penetrating into the micellar region where the Re complex is situated. This limiting rate (ca. 5×10^4 s^{-1}) presumably reflects the rate at which Cl_2^- can penetrate the SDS micelle. The fact that this limiting rate is about 1 order of magnitude smaller than the limiting rate observed for e_{aq}^- penetration of the SDS micelle is not surprising given the greater mobility of e_{aq}^-.

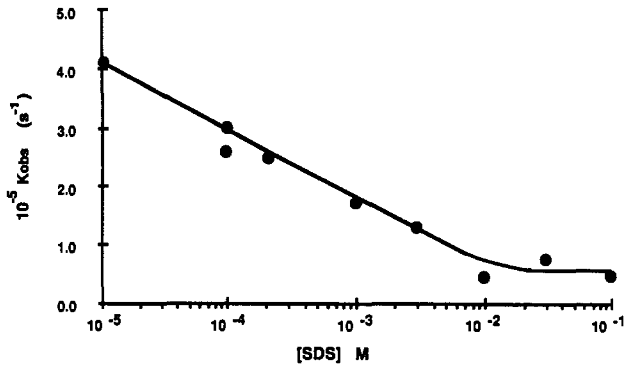

Figure 6. Plot of $10^{-5}k_{obs}$ (s^{-1}) vs log [SDS] (M) for the Cl_2^- oxidation of $[Re^I(DMPE)_3]^+$. Conditions: pH ca. 3; [Re] = 10^{-4} M; [NaCl] = 0.1 M.

Conclusions

The salient conclusion to be reached from this study is that the lipophilic, cationic complexes *trans*-$[M^{III}X_2(DMPE)_2]^+$ and $[M^I(DMPE)_3]^+$ (M = Tc, Re) effectively partition into micelles formed from the anionic surfactant SDS, and once inside the SDS micelles, these complexes are relatively protected from reaction with the highly reactive but negatively charged reagents e_{aq}^- and Cl_2^-. This phenomenon is independent of whether the metal center is being oxidized (by Cl_2^-) or reduced (by e_{aq}^-), and thus appears to be primarily electrostatic in origin. The effective sequestration of lipophilic, cationic complexes within negatively charged surfactant assemblies has direct consequences for the pharmacokinetics of such complexes being investigated for use in nuclear medicine. Cell membranes consist primarily of negatively charged surfactant molecules, and thus the partitioning of cationic, lipophilic complexes into cell membranes can be expected to drastically alter the rates at which these complexes undergo redox reactions (especially with negatively charged reagents).

The results of this study also highlight some of the pitfalls inherent to the use of micelles in electroanalytical chemistry.[31] Interactions of surfactants and lipophilic substrates at the heterogeneous electrode surface, which is inherent to electrochemistry, can confound the interpretation of results. Such interactions have been avoided in these pulse radiolysis studies which utilize homogeneous surfactant media. In these experiments, micelles formed from the cationic and neutral surfactants CTAB and Triton X-100 exert no significant effect on the rate of e_{aq}^- reduction of lipophilic, cationic complexes; this implies that the previously observed[14,15] effects of these surfactants on the analogous electrochemical reductions most likely stem from interactions of the surfactants with the electrode surface. As a consequence, potentials measured in surfactant media must be applied with caution in the prediction of dynamic in vivo behavior.

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