spectrum, providing an exacting test for theoretical vibrational predissociation models.

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## Effect of Charge Transport in Electrode-Confined N, N'-Dialkyl-4,4'-bipyridinium Polymers on the Current–Potential Response for Mediated, Outer-Sphere **Electron-Transfer Reactions**

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Mediated outer-sphere redox processes have been examined at rotating disk  $Pt/[(PQ^{2+/+})_{r}]_{surf}$  electrodes. The  $[(PQ^{2+/+})_{r}]_{surf}$ is a redox polymer anchored to the surface and is formed from N, N'-bis[(trimethoxysilyl)propyl]-4,4'-bipyridinium, I. The polymer coverages for the electrodes selected for study are sufficiently great that Fe(phen)<sub>3</sub><sup>3+/2+</sup>,  $E^{\circ'} = +1.03$  V vs. SCE, shows no electrochemical response near its  $E^{\circ'}$ . The mediated reduction of Fe(phen)<sub>3</sub><sup>3+</sup> and a number of other outer-sphere oxidants is mass-transport limited when the Pt/[(PQ<sup>2+/+</sup>)<sub>n</sub>]<sub>suff</sub> electrode is held ~100 mV more negative than  $E^{\circ'}$ [(PQ<sup>2+/+</sup>)<sub>n</sub>]<sub>suff</sub> = -0.45 V vs. SCE in CH<sub>3</sub>CN/0.1 M [*n*-Bu<sub>1</sub>N]ClO<sub>4</sub>. However, contrary to theoretical expectations based only on the rate constant for reaction of  $Fe(phen)_3^{3+}$  with a surface PQ<sup>+</sup>, the onset of current for the mediated reduction is at the onset for  $[(PQ^{2+})_n]_{surf} \rightarrow [(PQ^+)_n]_{surf}$  reduction; in fact, the mediated reduction current in the onset region is directly proportional to the concentration of PQ<sup>+</sup> in the surface-confined polymer. Data for Pt/ $[(PQ^{2+} \cdot xFe(CN)_6^{3-/4-})_n]_{surf}$  electrodes show directly that charge transport in the polymer can be a limitation to the maximum steady-state mediation current in aqueous electrolyte solution at the coverages of  $[(PQ^{2+/+})_n]_{surf}$  that have been employed. The charge-transport properties of the polymer are concluded to control the current-potential profile, as has been reported previously for other surface-modified electrodes, for the large polymer coverages employed in these studies.

A major topic of current interest is the use of chemically modified electrode surfaces to effect electrocatalytic reactions.<sup>1</sup> Modification of surfaces with designed molecular catalysts could be of use in accelerating the rate of irreversible electrode reactions such as oxygen reduction to water,<sup>2</sup> hydrogen evolution from aqueous solutions at semiconductor surfaces,<sup>3</sup> and metalloprotein redox reactions.<sup>4</sup> Key issues of current study are factors that control the interfacial kinetics of electron transport at polymercoated electrode surfaces.<sup>5</sup> For cases in which multielectron transfers are required, or where the heterogeneous rate values of the particular substrate are anomolously sluggish, it is clear that substantial kinetic improvement should be possible by appropriate electrode modification. However, for reactions of outer-sphere, one-electron-transfer agents whose rate behavior would follow the

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predictions of Marcus' electron-transfer theory,<sup>6</sup> it is not clear if derivatization of the electrode surface will possess any advantages over electrolysis at the naked electrode surface or over electron transfer to the substrate mediated by a dissolved molecular catalyst.

We have investigated in detail the mediated redox reaction of a number of outer-sphere electron-transfer reagents at electrodes modified with the N,N'-dialkyl-4,4'-bipyridinium reagent I.<sup>7</sup> We



use the abbreviation  $[(PQ^{2+/+})_n]_{surf}$  for the surface-confined polymer derived from I. Our interest in mediated outer-sphere processes at electrodes derivatized with I stems from our results that show that the  $[(PQ^{2+/+})_n]_{surf}$  system will catalyze the reduction of horse heart ferricytochrome c at a variety of surfaces.<sup>4a,8</sup> In such systems we are interested in both the maximum rate and potential dependence of the rate, and in this work we show that both can be controlled by the charge-transport properties of the  $[(PQ^{2+/+})_n]_{surf}$  system at coverages of  $[(PQ^{2+/+})_n]_{surf}$  in the vicinity of 10<sup>-8</sup> mol/cm<sup>2</sup>. Similarly, research in this laboratory has established that charge transport through polymer films from an N,N'-dibenzyl-4,4'-bipyridinium reagent can limit the maximum

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rate for a mediated reduction reaction when the coverage is  $>5 \times 10^{-9}$  mol/cm<sup>2,9</sup> However, the data did not allow the demonstration that the current-potential behavior could be limited by the charge-transport rate through the polymer. Consistent with work on other polymer systems,<sup>5e</sup> an important conclusion in this study is that thin polymer coatings with extremely large diffusion coefficients for charge transport would be required to realize the full advantages of outer-sphere electrocatalysis via surface-confined outer-sphere mediators.

#### **Experimental Section**

Rotating Pt disk electrodes were fashioned from 5 mm diameter circles of 0.025 in. thick Pt foil. The Pt disks were sealed onto 6 mm o.d. capillary tubing with conducting Ag epoxy. Electrical contact to the Ag was made with a pool of Hg inside the capillary tubing and on top of the Ag epoxy. Contact to the Hg was made with a Cu wire. The resistance of all electrode assemblies from the Cu contact to the Pt foil was less than 1  $\Omega$ . The Pt foil was insulated from the electrolyte solution with ordinary epoxy, yielding disk electrodes of 5-15-mm<sup>2</sup> exposed area. The rotating disk electrodes were placed vertically and stirred by a variable-speed motor from Polysciences, Inc. Rotation velocity was calibrated with a tachometer, or alternatively, by mounting a slitted piece of cardboard onto the disk shaft and monitoring the time response of a photodiode with an oscilloscope. Plots of the limiting current vs. rotation velocity in  $K_4Fe(CN)_6/2$  M KCl/H<sub>2</sub>O solutions yielded straight lines whose slope was in agreement with the reported diffusion coefficient for  $Fe(CN)_6^{4-}$  (D for  $Fe(CN)_6^{4-}/1$ M KCl is  $6.3 \times 10^{-5} \text{ cm}^2/\text{s}$ ).<sup>10</sup> Similar plots were obtained for all outer-sphere redox reagents used in this study, and each solution was verified to yield linear plots of (rotation velocity) $^{1/2}$  vs. current up to the highest stir rates available. In addition, the heterogeneous rate constant for oxidation of  $Fe(H_2O)_6^{2+}$  in 1 M H<sub>2</sub>SO<sub>4</sub> was determined with these Pt disks, and the value obtained was in agreement with the literature value<sup>11</sup> to within 10%.

Electrode modification was performed by exposing Pt electrodes to solutions of 2 mM I in CH<sub>3</sub>CN for 2–24 h.<sup>7</sup> Before exposure to the derivatizing reagent, Pt electrodes were pretreated electrochemically in 0.5 M H<sub>2</sub>SO<sub>4</sub> in order to introduce Pt–OH functionality, as described earlier.<sup>12</sup> Derivatized electrodes could be stored for extended periods of time under an Ar atmosphere without measurable change in cyclic voltammetry properties in CH<sub>3</sub>CN/electrolyte.

Electrochemical experiments were performed in single-compartment Pyrex cells. Reference electrodes were either an aqueous saturated calomel reference electrode (SCE) or a 0.1 M AgNO<sub>3</sub>/Ag/0.1 M [n-Bu<sub>4</sub>N]ClO<sub>4</sub>/CH<sub>3</sub>CN reference electrode. Potential control was accomplished with a Princeton Applied Research Model 173 potentiostat equipped with a Model 179 digital coulometer and a Model 175 voltage programmer. Current-voltage plots were recorded on a Houston Instruments Model 2000 X-Y recorder.

Solutions were made from either spectroquality  $CH_3CN$  or high-resistivity distilled water. Polarographic-grade  $[n-Bu_4N]ClO_4$ was purchased from Southwestern Analytical Chemicals, Inc., and was dried at 353 K for 24 h and stored in a desiccator until use.

The Fe(phen)<sub>3</sub>(PF<sub>6</sub>)<sub>3</sub> was prepared via Cl<sub>2</sub> oxidation of aqueous Fe(phen)<sub>3</sub>Cl<sub>2</sub>·7H<sub>2</sub>O (G. Frederick Smith), followed by addition of NaPF<sub>6</sub> to yield a blue precipitate Fe(phen)<sub>3</sub>(PF<sub>6</sub>)<sub>3</sub>. The Ru-(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> (Alfa), K<sub>4</sub>Fe(CN)<sub>6</sub> (Mallinckrodt), KCl (Baker), and other salts were purchased from commercial sources and used as received. Ferrocene was purchased from Aldrich Chemical Co. and was purified by sublimation. The [Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]PF<sub>6</sub> was prepared by dissolution of ferrocene in concentrated H<sub>2</sub>SO<sub>4</sub>, followed by stirring for 15 min in air. The blue solution was poured

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Figure 1. Calculated current-voltage curves for a derivatized electrode mediating to a solution reagent. The surface-attached material,  $A^+/A$ , is assumed to exhibit Nernstian current-potential behavior over the entire potential range considered. The concentration of solution reagent is 1 mM (this affects only the scale of the ordinate), and the only mechanism for reaction is assumed to be a simple bimolecular interaction between  $A^+/A$  and the solution additive. Bimolecular rate constants considered are as follows:  $10^7$  (1),  $10^8$  (2),  $10^9$  (3),  $10^{10}$  (4), and  $10^{12}$  (5) cm<sup>3</sup>/(mol s). Rotation velocity is assumed to be 225 rad/s. The highest current shown corresponds to the mass-transport limit. Note that the current should reach the mass-transport limit up to 240 mV positive of  $E^{\circ'}$ -( $A^+/A$ ) for the largest values of the bimolecular rate constant.

into water, and NaPF<sub>6</sub> was then added to yield a blue precipitate of  $[Fe(\eta^5-C_5H_5)_2]PF_6$ . The N,N'-bis[3-(trimethoxysilyl)propyl]-4,4'-bipyridinium dibromide was prepared by literature methods.<sup>7</sup> The N,N'-dimethyl-4,4'-bipyridinium (MV<sup>2+</sup>) diiodide was synthesized by refluxing a CH<sub>3</sub>CN solution of CH<sub>3</sub>I and 4,4'-bipyridine for 3 h and was isolated by slow addition of ether. The PF<sub>6</sub><sup>-</sup> salt was obtained by metathesis in aqueous solution. Analogous procedures yielded 1,1'-ethylene-2,2'-bipyridinium (DQ<sup>2+</sup>) and 1,1'-propylene-2,2'-bipyridinium (TQ<sup>2+</sup>) as PF<sub>6</sub><sup>-</sup> salts. The DQ<sup>+</sup>, MV<sup>+</sup>, and TQ<sup>+</sup> were obtained by electrochemical reduction of DQ<sup>2+</sup>, MV<sup>2+</sup>, or TQ<sup>2+</sup> at Pt foil cathodes in a twocompartment electrolysis cell. The Co(bpy)<sub>3</sub><sup>3+</sup>, Fe(\eta<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>, and Fe(\eta<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub><sup>+</sup> are the same reagents used previously.<sup>13</sup> The Cr[S<sub>2</sub>C<sub>2</sub>(CN)<sub>2</sub>]<sub>3</sub><sup>2-</sup> was a gift from Professor A. Davison of Massachusetts Institute of Technology.

# Theoretical Expectations for Mediated Outer-Sphere Redox Processes

We wish to consider the expectations regarding current-potential curves associated with the mediated oxidation or reduction of outer-sphere reagents,  $B^+/B$ , where eq 1 and 2 represent the

reduction rate = 
$$k_{red}[B^+][PQ^+]$$
 (1)

oxidation rate = 
$$k_{ox}[B][PQ^{2+}]$$
 (2)

rate law for the reduction of B<sup>+</sup> and oxidation of B, respectively. We assume that only the outermost portion of the  $[(PQ^{2+/+})_n]_{surf}$  system is accessible. This means that we take  $[PQ^+] = 1 \times 10^{-10}$  mol/cm<sup>2</sup> when  $[(PQ^{2+/+})_n]_{surf}$  is fully reduced, and likewise we take  $[PQ^{2+}] = 1 \times 10^{-10}$  mol/cm<sup>2</sup> when  $[(PQ^{2+/+})_n]_{surf}$  is fully oxidized. Additionally we shall assume that the value of  $[PQ^{2+}]/[PQ^+]$  equals the ratio of oxidized and reduced sites in  $[(PQ^{2+/+})_n]_{surf}$  and that this ratio obeys the Nernst equation, i.e., a 59-mV change in potential from the  $E^{\circ}[(PQ^{2+/+})_n]_{surf}$  gives a 10-fold change in the ratio  $[PQ^{2+}]/PQ^+]$ .

When the reactions represented by eq 3 and 4 have very large

$$[PQ^+] + [B^+] \xrightarrow{\kappa_{red}} [PQ^{2+}] + [B]$$
(3)

$$[PQ^{2+}] + [B] \xrightarrow{k_{ox}} [PQ^+] + [B^+]$$
(4)

equilibrium constants  $(>10^5)$  the back-reactions can be ignored and it is simple to predict the current-voltage curves for the

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mediated reduction or oxidation at a rotating disk electrode as a function of  $k_{red}$  or  $k_{ox}$ , respectively. Figure 1 shows a family of such curves, at a fixed rotation velocity of 225 rad/s, for bimolecular rate constants in the range  $10^7 - 10^{12}$  cm<sup>3</sup>/(mol s)  $(10^4-10^9 \text{ M}^{-1} \text{ s}^{-1})$ . We choose to consider the current-potential curves at a rotating disk electrode because the hydrodynamics are well-defined.<sup>14</sup> For reduction of B<sup>+</sup> according to eq 3, the current-potential dependence is given by eq 5a. Equation 5a is a rearranged form of a more familiar relationship, eq 5b, where the term  $nFAk_{red}[PQ^+][B^+]$  gives the current when the charge-transfer rate is current limiting and there are no diffusion effects and  $0.62nFA[B^+]D^{3/3}\nu^{-1/6}\omega^{1/2}$  gives the mass-transport-limited current.<sup>14,16</sup> The potential dependence comes from the fact that [PQ<sup>+</sup>] varies with potential according to the Nernst equation at a given surface coverage of redox material. The parameters used in generating the curves in Figure 1 are given below eq 5a and 5b:

$$i = nFAD[B^+] \left\{ 1.61D^{1/3}\gamma^{1/6}\omega^{-1/2} + \frac{D}{k_{\rm red}[PQ^+]} \right\}^{-1}$$
(5a)

$$\frac{1}{i} = \frac{1}{nFAk_{\rm red}[\rm PQ^+][\rm B^+]} + \frac{1}{0.62nFA[\rm B^+]D^{2/3}\nu^{-1/6}\omega^{1/2}}$$
(5b)

*n* = number of electrons transferred per molecule = 1.0; *F* = 96490 C/mol of electrons; A = area of electrode (assume 1.0 cm<sup>2</sup>); [B<sup>+</sup>] = bulk concentration of B<sup>+</sup> (assume  $1.0 \times 10^{-6} \text{ mol/cm}^3)$ ;  $\gamma$  = kinematic viscosity (assume  $1.0 \times 10^{-2} \text{ cm}^2/\text{s})$ ;  $\omega$  = rotation velocity (assume 225 rad/s); *D* = diffusion coefficient of B<sup>+</sup> in bulk solution (assume  $1.0 \times 10^{-5} \text{ cm}^2/\text{s})$ ;  $k_{red}$  = rate constant for eq 3; [PQ<sup>+</sup>] = surface concentration accessible,  $0-1.0 \times 10^{-10}$ mol/cm<sup>2</sup> depending on potential. The rate constant  $k_{red}$  has no electrode potential dependence, since it is associated with interaction between two molecular entities.

In our study the expectations for large values of  $k_{\rm red}$  or  $k_{\rm ox}$  are of most concern. The value of  $10^{12}$  cm<sup>3</sup>/(mol s) represents the approximate maximum rate constant for bimolecular redox reactions in fluid solution. For this rate constant the curves in Figure 1 suggest that a current limited only by mass transport of B<sup>+</sup> up to the electrode can be obtained ~240 mV more positive than  $E^{\circ\prime}[(PQ^{2+/+}_n]_{surf}$  and that the onset of significant current should be seen >400 mV more positive than  $E^{\circ\prime}[(PQ^{2+/+})_n]_{surf}$ . The ability to see large currents for B<sup>+</sup> reduction positive of  $E^{\circ\prime-}[(PQ^{2+/+})_n]_{surf}$  when  $k_{\rm red}$  is large comes about because only a small value of  $[PQ^+]$  is required to accommodate a large current based on the rate law given in eq 1.

As the value of  $k_{\rm red}$  declines to ~10<sup>9</sup> cm<sup>3</sup>/(mol s), the onset of current moves closer to  $E^{\circ/}[(PQ^{2+/+})_n]_{\rm surf}$ , but the limiting current remains nearly mass-transport limited. Further decline in  $k_{\rm red}$  to  $10^7-10^8$  cm<sup>3</sup>/(mol s) results in additional qualitative changes of the current-potential behavior. The limiting current becomes controlled by  $k_{\rm red}$  and by the values of [B<sup>+</sup>] and [PQ<sup>+</sup>]. Finally, for sufficiently low values of  $k_{\rm red}$  (at a given  $\omega$ ), the right-hand term ( $D/k_{\rm red}$ [PQ<sup>+</sup>] of eq 5 dominates the currents. When the right-hand term of eq 5 dominates, the rate of reaction is given by eq 1. This means that all the current-potential curves are the same except the magnitude of the current scales with  $k_{\rm red}$ .

So far we have only considered the situation where  $E^{\circ'}(B^+/B)$ is very different from  $E^{\circ'}[(PQ^{2+/+})_n]_{surf}$  such that there is a large driving force for reaction according to eq 3 or 4. Whenever  $E^{\circ'}(B^+/B)$  is close, within 250 mV, to  $E^{\circ'}[(PQ^{2+/+})_n]_{surf}$ , the combination of eq 3 and 4 must be included in predicting current-potential properties. That is, the back-reaction cannot be ignored. This situation has been treated in detail previously<sup>5</sup> and will not be elaborated here because our main findings relate to the situation where the  $E^{\circ'}(B^+/B)$  is more than 250 mV away



Figure 2. Cyclic voltammetry of  $[(PQ^{2+/+})_n]_{suff}$  ( $\Gamma \approx 10^{-8} \text{ mol/cm}^2$ ): (a) representative electrode in 0.1 M KCl/H<sub>2</sub>O electrolyte; (b) representative electrode in CH<sub>3</sub>CN/0.1 M [*n*-Bu<sub>4</sub>N]ClO<sub>4</sub> (TBAP) electrolyte.

from  $E^{\circ'}[(PQ^{2+/+})_n]_{surf}$  and the curves in Figure 1 could apply.

#### Results

Characterization of  $Pt/[(PQ^{2+/+})_n]_{surf}$  Electrodes in  $CH_3CN/Electrolyte$ . Within the context of the theoretical expectations dealt with above, we wish to show that Pt electrodes derivatized with I behave in a manner consistent with the assumption that  $[PQ^{2+}]/[PQ^{+}]$  varies as predicted by the Nernst equation. First, Figure 2 shows cyclic voltammograms representative of  $Pt/[(PQ^{2+/+})_n]_{surf}$  electrodes used in this study. The presence of surface-confined, electroactive material is evidenced by the large signals attributable to the  $[(PQ^{2+})_n]_{surf} \rightleftharpoons [(PQ^+)_n]_{surf}$ interconversion.7 The full width of the waves at half-height for a number of such electrodes is generally between 90 and 140  $\mathrm{mV}$ and the peak current is directly proportional to sweep rate up to at least 100 mV/s, consistent with expectations for a surfaceconfined, one-electron redox system.<sup>15</sup> Integration of the waves is consistent with coverages in the vicinity of  $10^{-8}$  mol/cm<sup>2</sup>. Second, Figure 3 shows data establishing that the ratio of  $[(PQ^{2+})_n]_{surf}$  to  $[(PQ^+)_n]_{surf}$  obeys the Nernst equation over a significant potential range. The ratio  $[(PQ^{2+})_n]_{surf}/[(PQ^+)_n]_{surf}$ was measured vs. potential by first setting the electrode potential in the vicinity of  $E^{\circ'}[(PQ^{2+/+})_n]_{surf}$  and then scanning the potential to a positive or negative value and integrating the charge passed for complete  $[(PQ^+)_n]_{surf} \rightarrow [(PQ^{2+})_n]_{surf}$  oxidation or  $[(PQ^{2+})_n]_{surf} \rightarrow [(PQ^+)_n]_{surf}$  reduction, respectively. We assume no difference in the  $E^{\circ'}$  for the surface  $PQ^{2+/+}$  centers compared to the bulk redox centers in the surface-confined polymer. The  $E^{\circ'}$ - $[(PQ^{2+/+})_n]_{surf} = -0.45 \text{ V vs. SCE in CH}_3\text{CN/electrolyte.}^7$ 

Derivatized electrodes used in this study have been determined to be uniformly covered with  $[(PQ^{2+/+})_n]_{surf}$  in a manner that precludes the observation of reduction/oxidation of  $Fe(\eta^5-C_5H_5)_2^{+/0}$  or  $Fe(phen)_3^{3+/2+}$  in  $CH_3CN/0.1$  M  $[n-Bu_4N]ClO_4$ . These redox couples have an  $E^{\circ\prime}$  of +0.35 or +1.03 V vs. SCE, respectively. The point is that the coverage of  $[(PQ^{2+/+})_n]_{surf}$  is such that there are no pinholes or channels exposing naked Pt to the solution and that the permeability of these ions through the  $[(PQ^{2+/+})_n]_{surf}$  is insufficient to observe the usual electrochemical response at Pt. Moreover, the selection of such electrodes ensures that only the outermost portion of the polymer is available to a solution reagent and the polymer cannot be viewed as a threedimensional zone of reactivity. An example of the current-potential curve for a Pt/ $[(PQ^{2+/+})_n]_{surf}$  electrode that is blocking to the reduction of Fe(phen)\_3<sup>3+</sup> is shown in Figure 4.

Mediated Reduction Processes at  $Pt/[(PQ^{2+/+})_n]_{surf}$  Electrodes in  $CH_3CN/Electrolyte$ . Figure 4 illustrates the typical current-potential response for a rotating disk  $Pt/[(PQ^{2+/+})_n]_{surf}$ 

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**Figure 3.** (Top) Percent of  $[(PQ^{2+})_n]_{surf}$  reduced to  $[(PQ^{+})_n]_{surf}$  vs. applied potential. The point at which the curve reaches  $\frac{1}{2}$  of its maximum value is the formal potential of the surface-attached material. (Bottom) log  $[(PQ^{2+})_n]_{surf}/[(PQ^{+})]_{surf}$  vs. potential. The linearity of the plot and the slope are a measure of the extent to which the surface-attached material obeys the Nernst distribution.

electrode used in this study for the reduction of Fe(phen)<sub>3</sub><sup>3+</sup> in CH<sub>3</sub>CN/0.1 M [*n*-Bu<sub>4</sub>N]ClO<sub>4</sub>. As noted above, there is no discernible response to the Fe(phen)<sub>3</sub><sup>3+/2+</sup> near the  $E^{\circ'}$ (Fe(phen)<sub>3</sub><sup>3+/2+</sup>) = +1.03 V vs. SCE. Rather, the reduction current onsets near the potential for the reduction of  $[(PQ^{2+})_n]_{surf}$  to  $[(PQ^+)_n]_{surf}$ . In fact, an analysis of the current-potential scan (Figure 5) shows that the current for the reduction of Fe(phen)<sub>3</sub><sup>3+</sup> depends on potential in a manner consistent with changes in the surface concentration of PQ<sup>+</sup> (Figure 3). The point is that the current is found to be proportional to  $[PQ^+]$ , as deduced from the fact that the plot of ln  $(i_L - i)/i$  vs. potential is a straight line with a slope predicted by the Nernst equation. This establishes that the mechanism for Fe(phen)<sub>3</sub><sup>3+</sup> reduction is via interaction with PQ<sup>+</sup>.



Figure 4. Steady-state current-voltage curve for Pt electrodes in CH<sub>3</sub>CN/0.1 M [*n*-Bu<sub>4</sub>N]ClO<sub>4</sub>. The electrode areas of "naked" Pt and Pt/PQ<sup>2+</sup> electrodes are slightly different (about 7 mm<sup>2</sup>), but they are rotated at the same speed in the solution. Naked Pt shows current for reduction of the 7 mM Fe(phen)<sub>3</sub><sup>2+</sup> at the  $E^{\circ\prime}$  (Fe(phen)<sub>3</sub><sup>3+/2+</sup>); Pt/ [(PQ<sup>2+/+</sup>)<sub>n</sub>]<sub>surf</sub> disks show current only at very negative potentials. For comparison, the cyclic voltammetry (10 mV/s) of the derivatized electrode in a solution without added oxidant is also shown (---).



**Figure 5.** Plot of  $\ln (i - i_L)/i$  for a  $Pt/[(PQ^{2+/+})_n]_{surf}$  electrode mediating the reduction of  $Fe(phen)_3^{3+}$ . The linearity and slope of this plot reflect the extent to which the PQ<sup>+</sup> available for reduction obeys the Nernst distribution. These data are for the electrode in Figure 4.

Reduction of 7 mM Fe(phen)<sub>3</sub><sup>3+</sup> at the rotating disk Pt/ [(PQ<sup>2+/+</sup>)<sub>n</sub>]<sub>surf</sub> has the same limiting current density, within experimental error, as a naked disk in the same solution (Figure 4). Data presented in Figure 6 show that the mediated current for the reduction of Fe(phen)<sub>3</sub><sup>3+</sup> is mass-transport limited for Fe(phen)<sub>3</sub><sup>3+</sup> concentrations of  $\leq 8$  mM for an electrode potential just negative of  $E^{\circ/}[(PQ^{2+/+})_n]_{surf}$ . The data show, as expected, that the mass-transport-limited current is directly proportional to the concentration of the Fe(phen)<sub>3</sub><sup>3+</sup>.

The combination of information included in Figures 4-6 is consistent with the rate law given in eq 6, a specific case of the

rate of Fe(phen)<sub>3</sub><sup>3+</sup> reduction = 
$$k_6$$
[Fe(phen)<sub>3</sub><sup>3+</sup>][PQ<sup>+</sup>] (6)

rate law given in eq 1. Mediated reduction of a series of other outer-sphere oxidants at rotating disk  $Pt/[(PQ^{2+/+})_n]_{surf}$  electrodes has been carried out, and for all of the examples listed in Table I a rate law as in eq 1 is found to apply using the same criteria as for Fe(phen)<sub>3</sub><sup>3+</sup>. It should be emphasized that, for all electrodes selected for study, there is no current for the reduction of Fe-(phen)<sub>3</sub><sup>3+</sup> near the  $E^{\circ\prime}$  for the Fe(phen)<sub>3</sub><sup>3+/2+</sup> system. This ensures that all reduction occurs via the generation of  $[PQ^+]$ . Table I gives the minimum value of  $k_{red}$  for each of the oxidants when the  $[(PQ^{2+/+})_n]_{surf}$  is fully reduced. When the limiting current,  $i_1$ , at a rotating disk electrode is equal to the mass-transport-limited



**Figure 6.** Plot of limiting current,  $i_L$  (at -1.0 V vs. Ag/Ag<sup>+</sup>) for Fe-(phen)<sub>3</sub><sup>3+</sup> reduction at Pt/[(PQ<sup>2+/+</sup>)<sub>n</sub>]<sub>surf</sub> (--) and "naked" Pt (---) electrodes. Solutions are under Ar and contain 0.1 M [*n*-Bu<sub>4</sub>N]ClO<sub>4</sub> in CH<sub>3</sub>CN. These data are for electrodes depicted in Figures 4 and 5.

TABLE I: Outer-Sphere Oxidants Reduced at  $Pt/[(PQ^{2+/+})_n]_{surf}^a$ 

_			
oxidant <sup>b</sup>	$E^{\bullet'}(B^+/B),$ V vs. SCE	$10^{-8}k_{\rm red},^{c}$ cm <sup>3</sup> /(mol s)	
Fe(phen) <sub>3</sub> <sup>3+</sup>	+1.03	>6	
$Fe(\eta^{5}-C_{5}H_{5})_{2}^{+}$	+0.35	>6	
Co(bpy) <sub>3</sub> <sup>3+</sup>	+0.22	>6	
$[Cr(S_2C_2(CN)_2)_3]^{2}$	+0.16	>6	
$Fe(\eta^{5} C_{5} Me_{5})_{2}^{+}$	-0.11	>6	
$\operatorname{Ru}(\operatorname{NH}_3)_6^{3+d}$	$-0.22^{d}$	$>6^d$	
DQ <sup>2+</sup>	-0.37	>6	
MV <sup>2+</sup>	-0.45	>6	

<sup>*a*</sup> All data are for 0.5-10 mM oxidant in CH<sub>3</sub>CN/0.1 M [*n*-Bu<sub>4</sub>N]ClO<sub>4</sub> at 25 °C, unless noted otherwise. <sup>*b*</sup> Abbreviations: phen  $\equiv$  1,10-phenanthroline; bpy  $\equiv$  2,2'-bipyridine; DQ<sup>2+</sup>  $\equiv$  1,1'-ethylene-2,2'-bipyridinium; MV<sup>2+</sup>  $\equiv$  *N*,*N*'-dimethyl-4,4'bipyridinium. <sup>*c*</sup> Minimum reduction rate constant (eq 1) deduced from the strict linearity of the plot of *i*<sub>L</sub> vs.  $\omega^{1/2}$  (cf. Figure 6). The limiting current, *i*<sub>L</sub>, is obtained ~100 mV more negative than  $E^{o'}[(PQ^{2+*})_n]_{surf} = -0.45$  V vs. SCE, except for Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> in H<sub>2</sub>O where *E*<sup>o</sup>. is somewhat more negative. <sup>*d*</sup> Data are for H<sub>2</sub>O/ 1.0 M KCl solvent/electrolyte.

current, a plot of  $i_{\rm L}$  vs.  $\omega^{1/2}$  (cf. Figure 6) is linear. The strict linearity of such plots implies a minimum value of  $k_{\rm red}[\rm PQ^+]$  of >6 × 10<sup>-2</sup> cm/s.<sup>11,16</sup> Assuming that the maximum value of [PQ<sup>+</sup>] = 1 × 10<sup>-10</sup> mol/cm<sup>2</sup> (approximately one monolayer of polymer, the outermost layer of  $[(\rm PQ^{2+/+})_n]_{\rm surf}$ ), the value of  $k_{\rm red}$  must be >6 × 10<sup>8</sup> cm<sup>3</sup>/(mol s). The Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> oxidant has been studied in aqueous KCl (Table I), and the data are consistent with earlier findings previously reported for Pt/[( $\rm PQ^{2+/+})_n$ ]<sub>surf</sub> electrodes.<sup>35,9</sup>

For all the oxidants listed in Table I with the exception of  $DQ^{2+}$ and  $MV^{2+}$  there is a significant driving force for the reaction according to eq 3. For example, the reduction of Fe(phen)<sub>3</sub><sup>3+</sup> by PQ<sup>+</sup> has a driving force of ~1.45 V! The large driving force and the fact that the self-exchange rate of Fe(phen)<sub>3</sub><sup>3+/2+</sup> would be expected to be large<sup>17</sup> both lead to the expectation that  $k_{red}$  would be large within Marcus' theory<sup>6</sup> (ignoring the so-called inverted region). However, for  $DQ^{2+}$  the driving force is small, and for  $MV^{2+}$  there is no driving force. Yet, the mediated reduction of  $DQ^{2+}$  and  $MV^{2+}$  occurs at a mass-transport-limited rate (Figure 7. Surprisingly, these mediated reductions have nearly the same current-potential curves as for the mediated reduction of Fe-



Figure 7. Steady-state current-voltage curves (10 mV/s) for a Pt/ [ $(PQ^{2+/+})_n]_{surf}$  electrode in CH<sub>3</sub>CN/0.1 M [*n*-Bu<sub>4</sub>N]ClO<sub>4</sub>. Cyclic voltammetry of the derivatized electrode at 50 mV/s in solutions with no added electroactive reagents is shown for comparison. Addition of 1 mM MV<sup>2+</sup> and 1 mM MV<sup>+</sup> to the stirred solution produced equal oxidation and reduction currents, while additions of 1 mM DQ<sup>2+</sup> and 1 mM DQ<sup>+</sup> leads to large cathodic currents with negligible anodic currents. A naked Pt electrode of equal area yields large currents for both the DQ<sup>2+/+</sup> and MV<sup>2+/+</sup> solutions. Electrode area is about 5 mm<sup>2</sup>.



**Figure 8.** Cyclic voltammetry (20 mV/s) for Pt/ $[(PQ^{2+/+})_n]_{surf}$  disk in stirred solutions containing CH<sub>3</sub>CN/0.1 M [*n*-Bu<sub>4</sub>N]ClO<sub>4</sub>. Scan in the absence of solution oxidants is shown for comparison (---). Addition of 7.0 mM TQ<sup>2+</sup> leads to stir rate independent currents, while addition of equal concentrations of MV<sup>2+</sup> leads to current which is much larger and linear with increasing  $\omega^{1/2}$ .

 $(phen)_3^{3+}$  (Figure 4) despite the large difference in driving force.

Another intriguing finding (Figure 8) is that the mediated reduction of  $TQ^{2+}$  has a very low value of  $k_{red}$ , despite the fact that  $E^{\circ'}(TQ^{2+/+}) = -0.55$  V vs. SCE is only ~100 mV more negative than  $E^{\circ'}[(PQ^{2+/+})_n]_{surf}$ . The disappointing result is that the  $[(PQ^{2+/+})_n]_{surf}$  cannot rapidly reduce a material that is only modestly more difficult to reduce than  $PQ^{2+}$ . Consistent with this finding is the fact that oxidation of DQ<sup>+</sup> by  $PQ^{2+}$  is also sluggish

<sup>(17)</sup> Sutin, N. In "Inorganic Biochemistry", Eichborn, G. L., Ed.; Elsevier: New York, 1973; Vol. 2, p 611.



**Figure 9.** Cyclic voltammetry (100 mV/s) of a Pt/[(PQ<sup>2+/+</sup>)<sub>n</sub>]<sub>surf</sub> electrode in 0.1 M KCl/H<sub>2</sub>O. The electrode has been dipped into an aqueous solution of 2 mM K<sub>4</sub>Fe(CN)<sub>6</sub> for 5 min, washed with H<sub>2</sub>O, and cycled electrochemically between +0.6 and -0.8 V vs. SCE until the current response has stabilized (about 5 scans). Electrodes not dipped into the Fe(CN)<sub>6</sub><sup>4</sup> solution show negligible current between -0.4 and +0.8 V vs. SCE.

(Figure 7) despite the ~80-mV separation in  $E^{\circ'}(DQ^{2+/+})$  and  $E^{\circ'}[(PQ^{2+/+})_n]_{surf}$ . Under the same conditions, the MV<sup>+</sup> is oxidized by PQ<sup>2+</sup> at a much larger rate.

Mediated Redox Processes at  $Pt/[PQ^{2+} \cdot xFe(CN)_6^{3-/4-}]_{surf}$ Electrodes in  $H_2O/Electrolyte$ . To gain further insight into the factors controlling the mediated redox processes at Pt electrodes derivatized with I, we have carried out studies of mediated redox processes using  $Pt/[(PQ^{2+})_n]_{surf}$  electrodes further modified by the electrostatic binding of either  $Fe(CN)_6^{4-}$  or  $Fe(CN)_6^{3-}$  into the positively charged  $[(PQ^{2+})_n]_{surf}$ . Such binding of large anionic metal complexes is now well established for a variety of situations,<sup>18</sup> including the  $[(PQ^{2+})_n]_{surf}$  system.<sup>19</sup>

Figure 2 includes the cyclic voltammogram for the Pt/  $[(PQ^{2+/+})_n]_{surf}$  in H<sub>2</sub>O/0.1 M KCl. The  $E^{\circ'}$  in this case is somewhate more negative than in CH<sub>3</sub>CN/electrolyte.<sup>7</sup> Figure 9 shows the consequence of binding Fe(CN)<sub>6</sub><sup>4-</sup>: the wave for the  $[(PQ^{2+})_n]_{surf} \rightleftharpoons [(PQ^+)_n]_{surf}$  is broadened and there is a wave at  $\sim +0.2$  V vs. SCE for the electrostatically bound Fe(CN)<sub>6</sub><sup>3-/4-</sup> redox system.<sup>19</sup> The Fe(CN)<sub>6</sub><sup>3-/4-</sup> system is not retained in the polymer indefinitely when the electrode is in H<sub>2</sub>O/0.1 M KCl. However, the Fe(CN)<sub>6</sub><sup>3-/4-</sup> is retained for sufficiently long periods that studies of mediated redox reactions can be undertaken.

Figure 10 shows the current-potential curve for the reduction of 4.0 mM Fe(phen)<sub>3</sub><sup>3+</sup> in 0.1 M H<sub>2</sub>SO<sub>4</sub> at a rotating disk Pt/  $[(PQ^{2+}xFe(CN)_6^{3-/4-})_n]_{surf}$  electrode. The limiting current,  $i_L$ , for the reduction of 4.0 mM Fe(phen)<sub>3</sub><sup>3+</sup> is the mass-transportlimited value for electrode potentials where the Fe(CN)<sub>6</sub><sup>3-/4-</sup> system is fully reduced. However, as when reducing Fe(phen)<sub>3</sub><sup>3+</sup> in CH<sub>3</sub>CN/electrolyte via the PQ<sup>+</sup>, the reduction current does not onset significantly more positive than the current onset for the reduction of the mediator.

The reduction of  $\operatorname{Ru}(NH_3)_6^{3+}$  has already been mentioned (Table I) in connection with the aqueous reaction of PQ<sup>+</sup>. The reduction of  $\operatorname{Ru}(NH_3)_6^{3+}$  has also been carried out at rotating disk Pt/[(PQ<sup>2+</sup>·xFe(CN)\_6^{4-})\_n]\_{surf} electrodes (Figure 11). At Ru(NH<sub>3</sub>)\_6<sup>3+</sup> concentrations below ~6 mM we typically find that the reduction by PQ<sup>+</sup> is mass-transport limited. However, at high concentrations the plot of  $i_L$  vs.  $\omega^{1/2}$  is decidedly nonlinear and it appears that the current is limited by something other than mass transport of the Ru(NH<sub>3</sub>)\_6^{3+}. Data for electrodes derivatized with an N,N'-dibenzyl-4,4'-bipyridinium reagent show that the saturation of the current is due to charge-transport properties of the polymer.<sup>9</sup> In the case studied here, we can also examine the reduction of Fe(CN)\_6^{3-} in the bulk solution via mediation by the







**Figure 11.** Reduction of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> at Pt/[(PQ<sup>2+/+</sup>),<sub>n</sub>]<sub>surf</sub> electrode with Fe(CN)<sub>6</sub><sup>3-/4-</sup> electrostatically bound into the PQ<sup>2+</sup> polymer. The electrolyte is 0.1 M KCl in unbuffered aqueous solution. Addition of 4.0 mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> leads to cathodic current (20 mV/s) due to production of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> by the surface PQ<sup>+</sup>. The bottom figure shows the dependence of current at -0.7 V vs. SCE on  $\omega^{1/2}$  for various concentrations of solution Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>. For low concentrations of solution oxidant, the plot of  $i_L$  vs.  $\omega^{1/2}$  is linear. As the Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> concentration is increased, the current approaches saturation and becomes independent of  $\omega^{1/2}$  and of the Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> concentration.

electrostatically bound  $Fe(CN)_6^{3-/4-}$ . As shown in Figure 12, this mediated reduction of  $Fe(CN)_6^{3-}$  does occur and only below 2

<sup>(18) (</sup>a) Oyama, N.; Anson, F. C. J. Electrochem. Soc. 1980, 127, 247.
(b) Oyama, N.; Sato, K.; Matsuda, K. J. Electroanal. Chem. 1980, 115, 149.
(c) Henning, T. C.; White, H. S.; Bard, A. J. J. Am. Chem. Soc. 1982, 104, 5862.

<sup>(19)</sup> Bruce, J. A.; Wrighton, M. S. J. Am. Chem. Soc. 1982, 104, 74.



Figure 12. Top indicates cyclic voltammetry at 100 mV/s for a Pt/ [ $(PQ^{2+/+})_n$ ]<sub>surf</sub> rotating disk electrode with Fe(CN)<sub>6</sub><sup>3-/4-</sup> electrostatically bound into the PQ<sup>2+</sup> polymer (see Figures 9 and 10). This is the same electrode used for the Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> reduction summarized in Figure 11. When 4.0 mM Fe(CN)<sub>6</sub><sup>3-</sup> is added to the stirred solution, cathodic current due to reduction of Fe(CN)<sub>6</sub><sup>3-</sup> is observed. The bottom figure indicates the dependence of current at 0.0 V vs. SCE on  $\omega^{1/2}$  for various concentrations of solution Fe(CN)<sub>6</sub><sup>3-</sup>. For low concentrations of solution oxidant, a plot of  $i_L$  vs.  $\omega^{1/2}$  is linear. As the Fe(CN)<sub>6</sub><sup>3-</sup> concentration is increased, the current approaches saturation and becomes independent of  $\omega^{1/2}$  and of the Fe(CN)<sub>6</sub><sup>3-</sup> concentration.

mM (for the electrode shown) is the reduction current limited by the rate of mass transport of the Fe(CN)<sub>6</sub><sup>3-</sup>. While we have not done a detailed set of measurements as a function of coverage of  $[(PQ^{2+/+})_n]_{surf}$ , we expect that the maximum steady-state current at a given concentration of oxidant will be greater at lower coverages of  $[(PQ^{2+/+})_n]_{surf}$  as demonstrated in the reduction of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> at Pt electrodes derivatized with the N,N'-dibenzyl-4,4'-bipyridinium reagent.<sup>9</sup>

A most important result comes from the comparison of the mediated reduction of  $Fe(CN)_6^{3-}$  by the bound  $Fe(CN)_6^{3-/4-}$ (Figure 12) compared to the mediated oxidation of  $Fe(CN)_{6}^{4-}$ by the bound  $Fe(CN)_6^{3-/4-}$  (Figure 13). The significant difference is that there is qualitatively less mediated oxidation current than reduction current when there is an equal bulk concentration of  $Fe(CN)_6^{4-}$  or  $Fe(CN)_6^{3-}$ . In general, comparing the limiting currents for polymer compensated with  $Fe(CN)_6^{3-/4-}$  is important because these reactions allow study of situations where the composition of the polymer backbone is constant, but what varies is the nature of the charge compensating anionic metal complex that can change the charge-transport properties of the polymer. In the case of  $Fe(CN)_6^{3-/4-}$  mediation detailed analyses must await careful determination of the  $E^{\circ'}$  of polymer-bound  $Fe(CN)_6^{3-/4-}$ compared to  $E^{\circ'}$  of the solution species. The fact that the  $i_{\rm L}$  vs.  $\omega^{1/2}$  plots are nonlinear and tend toward different limiting currents at high redox reagent concentrations is consistent with a role for charge-transport limitations in the polymer.

#### Discussion

A comparison of the theoretical curves in Figure 1 and the current-potential curves for the mediated reduction of Fe(phen)<sub>3</sub><sup>3+</sup> by  $Pt/[(PQ^{2+/+})_n]_{surf}$  (Figure 4) or by  $Pt/[(PQ^{2+}xFe(CN)_6^{4-})_n]_{surf}$  (Figure 10) shows that the simple theoretical expectations are not



**Figure 13.** Oxidation of  $Fe(CN)_6^{4-}$  at a  $Pt/[(PQ^{2+/+})_n]_{surf}$  electrode with  $Fe(CN)_6^{3-/4-}$  electrostatically bound into the  $PQ^{2+}$  polymer. This is the same electrode as in Figures 12 and 11. The electrolyte is 0.1 M KCl in unbuffered aqueous solution. Addition of 4.0 mM  $Fe(CN)_6^{4-}$  leads to anodic current due to production of  $Fe(CN)_6^{3-}$  by the surface  $Fe(CN)_6^{3-/4-}$ . The bottom figure shows the dependence of current at +0.4 V vs. SCE on  $\omega^{1/2}$  for various concentrations of solution  $Fe(CN)_6^{4-}$ . For low concentrations of solution reductant, the plot of i vs.  $\omega^{1/2}$  is linear. As the  $Fe(CN)_6^{4-}$  concentration is increased, the current approaches saturation and becomes independent of  $\omega^{1/2}$  and of the  $Fe(CN)_6^{4-}$  concentration. Note that the magnitude of the current at saturation is significantly below that observed for the reduction of  $Fe(CN)_6^{3-}$  (Figure 12) and  $Ru(NH_3)_6^{3+}$  (Figure 11) at the same surface.

realized. The studies of rotating disk electrodes allow the conclusion that  $k_{\rm red}$  exceeds  $6 \times 10^8$  cm<sup>3</sup>/(mol s) for a number of oxidants (Table I) where the driving force for reduction by PQ<sup>+</sup> is large. The point is that in no case do we observe reduction current significantly positive of  $E^{\circ\prime}[(PQ^{2+/+})_n]_{\rm surf}$ , as would be expected for a  $k_{\rm red}$  exceeding  $6 \times 10^8$  cm<sup>3</sup>/(mol s).

The discrepancy between the experimental data and theoretical expectation is even greater when we use Marcus' theory<sup>6</sup> to estimate the values of  $k_{red}$ . The rate constant,  $k_{A/B}$ , for a bimolecular, outer-sphere redox reaction between a species A<sup>+</sup> and B is given approximately by eq 7, where  $k_{A^+/A}$  and  $k_{B^+/B}$  are the

$$k_{A/B} = \{f(k_{A^+/A})(k_{B^+/B})K_{AB}\}^{1/2}$$
(7)

self-exchange rates for the A<sup>+</sup>/A and B<sup>+</sup>/B couples, respectively, and  $K_{AB}$  is the equilibrium constant for the cross-reaction A<sup>+</sup> + B  $\rightarrow$  B<sup>+</sup> + A. Often f is taken to be approximately unity. For f = 1 application of this relationship to the case of Fe-(phen)<sub>3</sub><sup>3+</sup>/PQ<sup>+</sup> yields a value of  $k_{red}$  for eq 6 for >10<sup>12</sup> cm<sup>3</sup>/(mol s), since the self-exchange rate of Fe(phen)<sub>3</sub><sup>3+</sup> is >10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, the equilibrium constant exceeds 10<sup>24</sup>, and the value of the self-exchange rate for the  $[(PQ^{2+/+})_n]_{surf}$  system has been estimated to be >10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>7</sup> Thus, if the Marcus relationship applies, the value of  $k_{red}$  is the extreme of the situations considered theoretically and plotted in Figure 1. For an equilibrium constant

of  $10^{24}$  the approximation that f = 1 may not be valid. However, measured rate constants  $k_{A/B}$  do not fall off as predicted by Marcus theory where the driving force is great. The so-called "inverted region" has not been observed for reagents in solution and is not expected for solvated surface-confined redox molecules. In any event, we measure a cross rate that exceeds  $6 \times 10^8 \text{ cm}^3/(\text{mol})$ s) for oxidation of surface-bound PQ<sup>+</sup> when  $\Delta G$  is very large.

Cyclic voltammetry can sometimes be used to evaluate crossreaction rates.<sup>20</sup> For example, consider horse heart ferricytochrome c, cyt  $c_{ox}$ . The reduction does not occur readily at most electrodes and mediators such as  $MV^{2+/+}$  can be useful in effecting the reduction of cyt  $c_{ox}$ .<sup>4,8,21</sup> The  $E^{o'}$  for cyt  $c_{ox}$ /cyt  $c_{red}$  is at 0.02 V vs. SCE<sup>21</sup> whereas that for  $MV^{2+/+}$  is -0.69 V vs. SCE in aqueous electrolytes. The cross-reaction rate constant associated with eq 8 has been determined to be >10<sup>8</sup>  $M^{-1} s^{-1} s^{-2}$  In a cyclic

$$MV^+ + cyt c_{ox} \xrightarrow{k_8} MV^{2+} + cyt c_{red}$$
 (8)

voltammogram the electrochemical response of the  $MV^{2+/+}$  in the absence of cyt  $c_{ox}$  is as expected for a reversible, one-electron redox couple.<sup>20</sup> When cyt  $c_{ox}$  is present, there is the possibility of measuring  $k_8$  because the cyt  $c_{ox}$  does not respond at a Pt electrode and the theory for EC with catalytic regeneration of reactant has been developed.<sup>20</sup> In fact, a prewave, a wave appearing positive of  $E^{\circ'}(MV^{2+/+})$ , is observed when the cyclic voltammogram of 0.2 mM MV<sup>2+</sup> is recorded in the presence of 2-4 mM cyt  $c_{ox}$ ).<sup>23</sup> Such a result is expected for a value of  $k_8$  as large as 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>20</sup> Likewise, the cyclic voltammetry of 1 mM MV<sup>2+</sup> at a graphite electrode in O<sub>2</sub>-saturated aqueous solution also shows a prewave attributable to the reduction of  $O_2$  via rapid reaction with  $MV^{+,23}$ These cyclic voltammetry experiments are the analogue of our rotating disk experiment and are consistent with theoretical considerations upon which the curves in Figure 1 are based. We have carried out cyclic voltammetry of  $Fe(\eta^5-C_5H_5)_2^+$  at a Pt/  $[(PQ^{2+/+})_n]_{surf}$  electrode. There is no prewave observed; i.e., the reduction current peak for  $Fe(\eta^5-C_5H_5)_2^+$  to  $Fe(\eta^5-C_5H_5)_2$  is coincident with the peak for the  $[(PQ^{2+})_n]_{surf} \rightarrow [(PQ^+)_n]_{surf}$  reduction peak. The driving force for the reduction of  $Fe(\eta^5-C_5H_5)_2^+$  $C_5H_5)_2^+$  by PQ<sup>+</sup> is greater than for cyt  $c_{ox}$  and the self-exchange rate of  $Fe(\eta^5-C_5H_5)_2^{+/0}$  (ref 24) is larger than for cyt  $c_{ox}/cyt c_{red}$ . Thus, we would expect a prewave, but, as in the mediated reductions at rotating disk electrodes, the mediated current does not onset significantly positive of  $E^{\circ'}[(PQ^{2+/+})_n]_{surf}$ .

Another troubling feature is that we are unable to rapidly reduce  $TQ^{2+}$  (Figure 8) even though  $E^{\circ}(TQ^{2+/+})$  is only 100 mV more negative than  $E^{\circ'}[(PQ^{2+/+})_n]_{surf}$ . Naked Pt electrodes held ~100 mV more negative than  $E^{\circ'}(TQ^{2+/+})$  do reduce  $TQ^{2+}$  at a mass-transport-limited rate, consistent with the fact that the  $TQ^{2+/+}$  redox couple is well-behaved. Given the similarity of  $TQ^{2+/+}$  and  $MV^{2+/+}$ , we would expect both to have large self-exchange rates (>10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>),<sup>26</sup> and we are thus disappointed to find that the Pt/[(PQ<sup>2+/+</sup>)<sub>n</sub>]<sub>surf</sub> electrodes are apparently incapable of rapidly reducing a species such as TQ<sup>2+</sup> where the driving force is just modestly unfavorable. Similarly, the oxidation of  $DQ^+$  at  $Pt/[(PQ^{2+/+})_n]_{surf}$  is sluggish (Figure 7) where  $E^{\circ'-}$  $(DQ^{2+/+})$  is only 80 mV more positive than  $E^{\circ'}[(PQ^{2+/+})_n]_{surf}$ . Finally, less favorable processes, such as the oxidation of Fe- $(\eta^5-C_5Me_5)_2$ , yield no detectable current, although theory would predict a sizable oxidation rate.

The question is why do the processes mediated by  $[(PQ^{2+/+})_n]_{surf}$ deviate so significantly from the simple theoretical expectations?

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We believe that the logical answer is that the charge-transport properties of the polymer  $[(PQ^{2+/+})_n]_{surf}$  mediator limit the steady-state current that can be achieved in mediated processes. While this may seem obvious, it is not immediately clear why the rate of reduction of  $Fe(phen)_3^{3+}$ , for example, can be mass-transport limited just negative of  $E^{\circ'}[(PQ^{2+/+})_n]_{surf}$  (Figure 4) and yet be polymer charge-transport limited at more positive potentials and lower curent densities. Before we attempt to clarify this issue, we consider the data for mediated processes at the  $Pt/[(PQ^{2+/+} \cdot xFe(CN)_6^{3-/4-})_n]_{surf}$  electrodes.

The use of the  $Pt/[(PQ^{2+/+} \cdot xFe(CN)_6^{3-/4-})_n]_{surf}$  electrodes has provided direct evidence that slow charge-transfer rates at the polymer/liquid interface do not generally account for the discrepancy between the theoretical expectations and the results. For example, the  $Fe(CN)_6^{4-}$  mediated reduction of  $Fe(phen)_3^{3+}$  shows no significant reduction current positive of  $E^{\circ\prime}$  for the bound  $Fe(CN)_6^{3-/4-}$  couple (Figure 10) even though the driving force and self-exchange rates of the redox couple would suggest a large positive shift relative to  $E^{\circ'}$  for the bound  $Fe(CN)_6^{3-/4-}$ . However, similarly prepared polymers show severe limitation to the flow of steady-state mediation current at high current densities. This limitation is not due to low charge-transfer rate constants  $k_{red}$  or  $k_{ox}$ . The possibility that low charge-transfer rates are responsible for the current limitation is ruled out by the fact that the mediated processes are all mass-transport limited at sufficiently low concentrations of the solution reagent where there are low absolute current densities. Therefore, values of  $k_{red}$  or  $k_{ox}$  are >6 × 10<sup>8</sup> cm<sup>3</sup>/(mol s) for the reduction of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, Fe(phen)<sub>3</sub><sup>3+</sup>, and Fe(CN)<sub>6</sub><sup>3-</sup> or oxidation of Fe(CN)<sub>6</sub><sup>4+</sup>, respectively. Thus, the theoretical expectation would be that the reduction of Fe(phen)<sub>3</sub><sup>3+</sup> would obtain several hundred millivolts more positive than  $E^{\circ\prime}$ for the bound  $Fe(CN)_6^{3-/4-}$  mediator. The limitation to current observed at high concentrations of the redox ragents is attributable then to sluggish charge transport in the polymer. This is as previously concluded for the N,N'-dibenzyl-4,4'-bipyridinium-based derivatizing reagent.<sup>9</sup> At the high concentrations of  $Ru(NH_3)_6^{3+}$ , for example, the plot of  $i_{\rm L}$  vs.  $\omega^{1/2}$  is nearly flat at the large values of  $\omega^{1/2}$ , and the  $i_{\rm L}$  at these  $\omega^{1/2}$  values does not increase linearly with increasing  $Ru(NH_3)_6^{3+}$  concentration (Figure 11). Theory is available to treat these results quantitatively,<sup>5c,d</sup> but the qualitative results are the ones of importance in establishing practical limitations for the use of  $[(PQ^{2+/+})_n]_{surf}$  as an electrode-confined mediator system.

We have asserted that the current limitation is due to sluggish charge transport in the polymer. Often it is difficult to separate this problem from an intrinsically slow rate of electron exchange at the polymer/bulk solution interface. Assuming that Marcus' theory (eq 7) can be applied, the self-exchange rate of the  $[(PQ^{2+/+})_n]_{surf}$  system can be estimated from the mediated reduction of  $MV^{2+/+}$ , a system having an approximate self-exchange rate of 10<sup>6</sup> M<sup>-1</sup> s<sup>-1,26</sup> This system is best for estimating the self-exchange rate of the  $[(PQ^{2+/+})_n]_{surf}$  because the driving force is zero, so the equilibrium constant is unity. With the value of  $k_{\rm red} > 6 \times 10^8 \, {\rm cm}^3/({\rm mol \ s})$  (Table I) the self-exchange rate of the  $[(PQ^{2+/+})_n]_{surf}$  is >10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>. This result means that the electron-exchange rate of the PQ<sup>+</sup> with an outer-sphere oxidant cannot be the rate-determining step in the redox reactions studied in our work. This includes the mediated  $TQ^{2+}$  reduction that represents a situation where the reduction by PQ<sup>+</sup> is modestly unfavorable.

When one concludes that charge transport through the polymer can be the limitation to steady-state current, it becomes apparent that the coverage of the  $[(PQ^{2+/+})_n]_{surf}$  is a factor in the magnitude of the current. Lower coverages should yield higher steady-state currents when the current is limited by the charge transport through the polymer, vide infra. This has been quantitatively verified for mediated reduction using the related N,N'-dibenzyl-4,4'-dipyridinium-based polymer.9 In the present work, we have done the experiments in such a way that the coverage is always high because we have selected electrodes that do not show an electrochemical response to  $Fe(\eta^5-C_5h_5)_5^+$  or  $Fe(phen)_3^{3+}$ at their  $E^{\circ\prime}$  in CH<sub>3</sub>CN/electrolyte solution. This apparently

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We now return to the issue of how it is possible to see a mass-transport-limited reduction  $\sim 100 \text{ mV}$  negative of  $E^{\circ\prime}$  of the mediator, while polymer limitations can exist at potentials just positive of  $E^{\circ'}$ . That is, without charge-transport limitation in the polymer we would have expected a mass-transport-limited reduction of  $Fe(phen)_3^{3+}$  at least 400 mV positive of where it is actually observed in Figure 4. Whenever charge transport through the fully reduced polymer limits the steady-state reduction current, eq 9 gives the steady-state current that can pass through a polymer

$$i = nFAD_{\rm CT}C_{\rm T}/d \tag{9}$$

thickness, d, having a diffusion coefficient for charge transport of  $D_{CT}$ .<sup>5f</sup> In eq 9, *n*, *F*, and *A* (projected area) have their usual meaning;  $C_{\rm T}$  is the concentration of the charge-carrying species in the polymer in  $mol/cm^3$ . When the polymer is not fully reduced the steady-state reduction current is expected to depend linearly on the [PQ<sup>+</sup>] concentration at the electrode/polymer interface.<sup>5f</sup> This gives rise to the potential dependence given in Figure 5, since [PQ<sup>+</sup>] varies according to the Nernst equation. We assume that the oxidants used react so fast that [PQ<sup>+</sup>] is zero at the polymer/electrolyte interface. For the  $[(PQ^{2+/+})_n]_{surf}$  system in  $H_2O$ /electrolyte  $D_{CT}$  has been determined to be no greater than  $\sim 10^{-9} \text{ cm}^2/\text{s}^{.7,9}$  Using this value in eq 9 and the fact that a coverage of  $[(PQ^{2+/+})_n]_{surf}$  of  $10^{-8}$  mol/cm<sup>2</sup> gives a thickness d of  $\sim 3 \times 10^{-6}$  cm<sup>7</sup>, one can predict the value of *i* for a given [PQ<sup>+</sup>] (which will depend on potential, Figure 3). The value of  $C_{\rm T}$  for the  $[(PQ^{2+/+})_n]_{surf}$  system is 3.0  $\times$  10<sup>-3</sup> mol/cm<sup>3.7</sup> These approximate values<sup>7</sup> of d,  $C_{\rm T}$ , and  $D_{\rm CT}$  resolve the discrepancy between the theory (Figure 1) and our findings. For example, at 240 mV positive of  $E^{\circ'}[(\dot{P}Q^{2+/+})_n]_{surf}$  for a coverage of  $10^{-8}$ mol/cm<sup>2</sup>, the value of *i* is calculated to be  $\sim 10 \,\mu\text{A/cm}^2$ , assuming

that the value of [PQ<sup>+</sup>] is as predicted by the Nernst equation. At concentrations of redox reagents in our study of 0.5-10 mM, current densities limited by mass transport exceed 10  $\mu$ A/cm<sup>2</sup> by several orders of magnitude (Figure 1). Thus, in order to see a mass-transport-limited reduction at 240 mV positive of  $E^{\circ'}$ - $[(PQ^{2+/+})_n]_{surf}$ , we must have a large value of  $k_{red}$ , but additionally very low concentrations of oxidant must be employed because  $D_{CT}$ is so small. Preliminary results do show that very low (10  $\mu$ M) concentrations of  $Ru(NH_3)_6^{3+}$  in  $H_2O$  can be reduced positive of  $E^{\circ'}[(PQ^{2+/+})_n]_{surf}$ .

To conclude, we now have a consistent view of the relationship between the rate constants  $k_{red}$  or  $k_{ox}$  governing the mediation step and the charge-transport properties of the  $[(PQ^{2+/+})_n]_{surf}$  mediator system. Large values of  $k_{red}$  or  $k_{ox}$  alone do not guarantee large steady-state currents. Rather, the ratio  $D_{CT}/d$  must also be considered in predicting steady-state current-potential behavior. This is the same conclusion drawn from work with a different impermeable polymer system.<sup>5e</sup> It appears that low  $D_{\rm CT}$  values<sup>5</sup> will severely limit the application of thick polymer mediator systems. Effort should be directed toward studies of thin, impermeable polymers that have large values of  $D_{CT}$  and consist of units having large self-exchange rates, in order to use outer-sphere mediators in high current density applications.

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**Registry No.** I, 74173-49-2; Fe(phen)<sub>3</sub><sup>3+</sup>, 13479-49-7; Fe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub><sup>+</sup>, 12125-80-3; Co(bpy)<sub>3</sub><sup>3+</sup>, 19052-39-2; [Cr(S<sub>2</sub>C<sub>2</sub>(CN)<sub>2</sub>)<sub>3</sub>]<sup>2-</sup>, 47383-09-5; Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub><sup>+</sup>, 54182-41-1; Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, 18943-33-4; Fe(CN)<sub>6</sub><sup>3-</sup>, 13408-62-3; Fe(CN)<sub>6</sub><sup>4-</sup>, 13408-63-4; Pt, 7440-06-4; DQ<sup>2+</sup>, 2764-72-9; MV<sup>2+</sup>, 4685-14-7.

### Recoil Fluorine-18 Chemistry. 14. High-Pressure Investigation of $C_2F_{s}$

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With gas-phase C<sub>2</sub>F<sub>6</sub> nuclear recoil <sup>18</sup>F undergoes F-for-F, F-for-2F, and F-for-CF<sub>3</sub> hot atom elementary reactions with respective primary yields of  $13.8 \pm 0.2\%$ ,  $0.68 \pm 0.03\%$ , and  $1.90 \pm 0.05\%$ . Under collisionless conditions,  $91 \pm 2\%$ ,  $57 \pm 2\%$ , and  $35 \pm 3\%$  of the nascent products from these reactions decompose. At pressures below 1 ktorr,  $22 \pm 2\%$  of the F-for-F product, CF<sub>3</sub>CF<sub>2</sub><sup>18</sup>F, undergoes complete atomization through sequential C-C and C-F bond dissociations. Above 50 ktorr, caging reactions enhance the yields of most of the observed products.

#### Introduction

Nuclear recoil <sup>18</sup>F atoms undergo novel atomic exchange reactions with fluorinated hydrocarbons.<sup>1,2</sup> Based on fast neutron irradiations and the <sup>19</sup>F(n,2n)<sup>18</sup>F nuclear reaction, mechanistic results have been reported from this laboratory for recoil <sup>18</sup>F reacting with CF<sub>4</sub>, c-C<sub>3</sub>F<sub>6</sub>, c-C<sub>4</sub>F<sub>8</sub>, CH<sub>3</sub>CF<sub>3</sub>, and CH<sub>3</sub>CHF<sub>2</sub>.<sup>3-8</sup>

The present experiments with  $C_2F_6$  are compared with a previous study based on the  ${}^{19}F(p,pn){}^{18}F$  nuclear reaction.<sup>9,10</sup> We report primary yields for the F-for-F, F-for-2F, and F-for-CF<sub>3</sub> hot reactions, we describe the decomposition behavior of the nascent products, and we determine the yields of caging reactions at pressures above 50 ktorr.

#### **Experimental Methods and Results**

Because our procedures are described elsewhere, the following account is limited to aspects novel to this work. Freon 116 ( $C_2F_6$ ,

 $\geq$ 99.6%) and ultrahigh-purity Cl<sub>2</sub> ( $\geq$ 99.96%) were obtained from Matheson, and research-grade  $C_6F_6$  ( $\geq 98.0\%$ ) was obtained from

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