against this assignment. First, the best theoretical values for the activation energy for the triplet ethylidene–ethylene transformation are in the order of 40–50 kcal/mol. Theoretically, triplet ethylene generated from aromatic sensitizers (80–85 kcal/mol)[2] would only have 15–20 kcal/mol excess vibrational energy which is insufficient to yield the fast reaction rates observed for the E* = E** process (10^7–10^8 s^{-1}). A simpler interpretation is to assume that E** is singlet ethylene–ethylidene, which above about 80 kcal/mol are in dynamic structural exchange. The measured rates for the E* = E** processes, at least using low-energy sensitizers, are those for intersystem crossing in ethylene, their values being in the order estimated by the trajectory calculations of Warshel and Karplus.[42,43] In this respect, the observed triplet gas-phase photochemistry of ethylene is occurring through a vibrationally hot and equilibrated ground-state species. While it would also be a simplication to assume that direct photolysis generates essentially the same species having considerably more vibrational energy, our computations indicate that there are direct excited-state–product-state exit channels which make the singlet photochemistry conceptually more complicated than either the triplet-sensitized photochemistry or the thermal chemistry.

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[42] Warshel, A.; Karplus, M. *Chem. Phys. Lett.* **1975**, *32*, 11–17.

[43] The excess energy calculations in ref 2a–c are based on estimations of the triplet energy of ethylene about 20 kcal/mol too low, see ref 16 and 18 for more recent values.

Kinetics of Outer-Sphere Electron Transfers between Metal Complexes in Solutions and Polymeric Films on Modified Electrodes

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Abstract: Rotated Pt disk electrodes coated with polymeric films of poly-$Ru(VB)_3^{2+}$ (where VB is 4-vinyl-4′-methyl-2,2′-bipyridine) electrocatalytically mediate oxidations of the complexes $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(4,4'\text{-}bpy)_2]^{2+}$, $[Ru(bpy)_2(py)(CH_3CN)]^{2+}$, $[Ru(bpy)_2(CH_3CN)_2]^{2+}$, and $[Ru(bpy)_2(pyrazine)_2]^{2+}$ and reduction of the complex $[Fe(bpy)_3]^{3+}$, even though these reactions are thermodynamically unfavored with equilibrium constants as small as 5×10^{-6}. Similarly, electrodes coated with poly-$Fe(VB)_3^{2+}$ drive the electron transfer mediated oxidations of $[Fe(bpy)_3]^{2+}$ and $[Fe(VB)_3]^{2+}$ and the reduction of $[Fe(4,4'\text{-}Me_2\text{-}2,2'\text{-}bpy)_3]^{3+}$. The rates $k_{crs}\Gamma$ of these electron-transfer cross-reactions as measured using reciprocal $1/i_{lim}$ vs. $1/\omega^{1/2}$ plots are independent of poly-$Ru(VB)_3^{2+}$ film thickness from $\Gamma_T = 10^{-9}$ to 10^{-8} mol,/cm^2; the electron-exchange reactions involve only the outermost monolayer(s) of poly-$Ru(VB)_3^{2+}$ sites in the film. $k_{crs}\Gamma$ varies systematically with the reaction K_{eq}' (i.e., the difference $\Delta E°$ in formal potentials of catalyst and substrate complexes), $k_{crs}\Gamma$ being least when K_{eq}' is least. A plot of log $k_{crs}\Gamma$ vs. $\Delta E°(1 + \chi\Delta E°)$ is linear with slope predicted by the Marcus relation for electron-transfer cross-reactions. The results demonstrate outer-sphere character for the electron-transfer reaction at the polymer/solution interface.

Electrocatalysis of electrochemical reactions by surfaces to which electron transfer mediator catalysts are attached has been of considerable recent interest.[1,2] Quantitative measurements of the rates of these reactions have started to appear,[1b,e–g,o,p,2] and ideas of how to interpret them in terms of quantity of attached mediator catalyst are emerging.[1b,e,p,3–5] However, the available kinetic data remain quite limited. The reactions catalyzed, with a single exception,[2] have been driven at electrode potentials which are still relatively far from the reversible reaction substrate values. The relationship between reaction substrate structure and catalytic rate has been only briefly explored.[1b] And to date there are no data which examine the relationship between the free energy of the electron transfer mediated reaction and its rate on a modified electrode surface.

We describe here electron exchanges between metal complexes and modified electrodes where the electrocatalyzed reaction is thermodynamically unfavorable,[7] including one where the reaction equilibrium constant K_{eq}' is as small as 5×10^{-6}. The reactions are electron-exchange cross-reactions between dissolved ruthenium

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[3] (a) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1978**, *93*, 163. (b) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Saveant, J. M. *Ibid.* **1980**, *114*, 159.

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[6] Anson, F. C. *J. Phys. Chem.* **1980**, *84*, 3336.

[7] The sole previous example[2] of (nonphotolytic) thermodynamically unfavorable electrocatalysis had a K_{eq}' of only 0.2.

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Table I. Electron-Transfer Cross-Reaction Rates and Potentials

reaction	$E_{sub}{}^{\circ\prime}$, vs. SSCE	ΔE°	$K_{eq}{}'$	$k_{crs}\Gamma$,[a] cm/s	no. of expts	$E_{1/2}$(rxn)[e]
			Ru[b]			
2	$+1.24_5$	0.11	1.37×10^{-2}	$8.6 \pm 3.0 \times 10^{-2}$	13	+1.25
3	+1.30	0.16_5	1.6×10^{-3}	1.4×10^{-2}	1	$+1.28_5$
4	$+1.32_5$	0.19	6.0×10^{-4}	$3.0 \pm 0.4 \times 10^{-2}$	2	+1.31
5	+1.41	0.27_5	2.2×10^{-5}	$1.7 \pm 0.4 \times 10^{-3}$	2	+1.35
6	+1.45	0.31_5	4.6×10^{-6}	$9.5 \pm 2.9 \times 10^{-4}$	6	+1.35
13	$+1.05_5$	0.08[d]	4.6×10^{-2}	0.12 ± 0.05	3	$+1.05_5$
			Fe[c]			
8	$+0.91_8$	-0.00_4	1.2	3×10^{-1}	1	+0.92
7	+1.05	0.12_8	7.2×10^{-3}	$1.6 \pm 0.2 \times 10^{-2}$	3	+1.02
9	$+0.89_5$	0.02_7[d]	0.35	$1.1 \pm 0.2 \times 10^{-1}$	3	$+0.89_5$

[a] From intercepts of plots like Figure 2C and eq 12. [b] $E_{cat}{}^{\circ\prime} = +1.13_5$ V vs. SSCE. [c] $E_{cat}{}^{\circ\prime} = +0.92_2$ V. [d] Sign reversed since reactions 9 and 13 are reductions. [e] Half-wave potential at $\omega = 8100$ rpm.

and iron bipyridine complexes as reaction substrates and Pt disk electrodes coated with polymeric films of poly-$Ru(VB)_3^{2+}$ and poly-$Fe(VB)_3^{2+}$ where VB ≡ 4-vinyl-4′-methyl-2,2′-bipyridine, respectively, as the mediator catalyst electrodes. The polymeric films can be rapidly driven between the $Ru^{III/II}$ and $Fe^{III/II}$ states,[1d,8] i.e., the electrode reaction

$$\text{Pt/poly-Ru(VB)}_3^{2+} - e \rightarrow \text{Pt/poly-Ru(VB)}_3^{3+} \tag{1}$$

is quite rapid. The continuously regenerated, poly-$Ru(VB)_3^{3+}$ oxidizing state of the modified electrode surfaces was used to drive the reactions

$$\text{Pt/poly-Ru(VB)}_3^{3+} + \text{Ru(bpy)}_3^{2+} \xrightarrow{k_{crs}} \text{Ru(bpy)}_3^{3+} + \text{Pt/poly-Ru(VB)}_3^{2+} \tag{2}$$

$$\text{Pt/poly-Ru(VB)}_3^{3+} + \text{Ru(bpy)}_2(4,4'\text{-bpy})_2^{2+} \rightarrow \text{Ru(bpy)}_2(4,4'\text{-bpy})_2^{3+} + \text{Pt/poly-Ru(VB)}_3^{2+} \tag{3}$$

$$\text{Pt/poly-Ru(VB)}_3^{3+} + \text{Ru(bpy)}_2(\text{py})(\text{CH}_3\text{CN})^{2+} \rightarrow \text{Ru(bpy)}_2(\text{py})(\text{CH}_3\text{CN})^{3+} + \text{Pt/poly-Ru(VB)}_3^{2+} \tag{4}$$

$$\text{Pt/poly-Ru(VB)}_3^{3+} + \text{Ru(bpy)}_2(\text{CH}_3\text{CN})_2^{2+} \rightarrow \text{Ru(bpy)}_2(\text{CH}_3\text{CN})_2^{3+} + \text{Pt/poly-Ru(VB)}_3^{2+} \tag{5}$$

$$\text{Pt/poly-Ru(VB)}_3^{3+} + \text{Ru(bpy)}_2(\text{pyr})_2^{2+} \rightarrow \text{Ru(bpy)}_2(\text{pyr})_2^{3+} + \text{Pt/poly-Ru(VB)}_3^{2+} \tag{6}$$

For the poly-$Fe(VB)_3^{2+}$ coated electrodes, the similarly electrocatalyzed reactions are

$$\text{Pt/poly-Fe(VB)}_3^{3+} + \text{Fe(bpy)}_3^{2+} \xrightarrow{k_{crs}} \text{Fe(bpy)}_3^{3+} + \text{Pt/poly-Fe(VB)}_3^{2+} \tag{7}$$

$$\text{Pt/poly-Fe(VB)}_3^{3+} + \text{Fe(VB)}_3^{2+} \rightarrow \text{Fe(VB)}_3^{3+} + \text{Pt/poly-Fe(VB)}_3^{2+} \tag{8}$$

and

$$\text{Pt/poly-Fe(VB)}_3^{2+} + \text{Fe(Me}_2\text{B)}_3^{3+} \xrightarrow{k_{crs}} \text{Fe(Me}_2\text{B)}_3^{2+} + \text{Pt/poly-Fe(VB)}_3^{3+} \tag{9}$$

where Me_2B ≡ 4,4′-dimethyl-2,2′-bipyridine. Although the reactions have equilibrium constants which range from 1 to 5×10^{-6} (Table I), they yield measurable waves in rotated disk voltammetry, by which the product $k_{crs}\Gamma$ of the electron transfer cross-reaction rate (k_{crs}) and the quantity (Γ) of catalyst sites in the film which participate in the reaction were measured.

In the electrochemical sense, oxidizing $Ru(bpy)_2(pyr)_2^{2+}$ by generating poly-$Ru(VB)_3^{3+}$ (reaction 6) is thermodynamically unfavorable; a more positive electrode potential is required to oxidize $Ru(bpy)_2(pyr)_2^{2+}$ (at a naked electrode) than is required to drive reaction 1. Mediation of such nonspontaneous reactions is however theoretically anticipated[6] if the substrate and catalyst electron-transfer couples possess sufficiently fast electron self-exchange rates $k_{ex(cat.)}$ and $k_{ex(sub)}$. The bipyridine complexes used in the above reactions have these favorable kinetic properties.[9]

The rates $k_{crs}\Gamma$ of reactions 2–9 vary systematically with the difference in formal potentials of substrate and catalyst, $E_{sub}{}^{0\prime} - E_{cat.}{}^{0\prime} = \Delta E^\circ$ (i.e., $K_{eq}{}'$) in a manner quantitatively consistent with the relation[10]

$$k_{crs} = [k_{ex(cat.)}k_{ex(sub)}K_{eq}{}'f]^{1/2} \tag{10a}$$

where

$$\log f = [\log K_{eq}{}']^2/4 \log [k_{ex(cat.)}k_{ex(sub)}/Z^2] \tag{10b}$$

and $k_{ex(cat.)}$ and $k_{ex(sub)}$ are the self-exchange rates ($M^{-1}\ s^{-1}$) for the mediator catalyst and dissolved substrate complexes, respectively, and Z is the collision frequency ($10^{11}\ M^{-1}\ s^{-1}$). These results show for the first time that a Marcus electron-transfer relationship can represent rates of reactions at modified electrode surfaces.

Results and Discussion

In investigations of redox species in contact with poly-$Ru(VB)_3^{2+}$ films on Pt electrodes, where the redox species can be dissolved in a solution[1d,8,11] or present in a secondary redox polymer film,[1d,8] we have established that bulky and/or positively charged redox species do not readily penetrate poly-$Ru(VB)_3^{2+}$ films which are thicker than ca. 10^{-9} mol/cm^2 of electroactive ruthenium sites (ca. 10–12 monolayers). For example, in tests with Pt/poly-$Ru(VB)_3^{2+}$ electrodes prepared during this study, oxidation of acetonitrile solutions of $[Ru(bpy)_2(py)Cl]^+$ is completely suppressed at its normal potential ($E^{0\prime} = +0.76$ V vs. SSCE). Oxidation currents for the bulky but uncharged complex $[Ru(bpy)_2Cl_2]$ at its normal potential are only a few (ca. 3%) of those at naked Pt; from the membrane-limited data we estimate[11] the product of the diffusion and partition coefficients of $[Ru(bpy)_2Cl_2]$ in the poly-$Ru(VB)_3^{2+}$ film as $D_{S,pol}P \sim 10^{-9}$ cm^2/s. $D_{S,pol}P$ for $[Ru(bpy)_2(py)Cl]^+$ and that for the similarly bulky and also dipositive complexes in reactions 2–9 must in comparison be $<10^{-10}$ cm^2/s, i.e., these complexes penetrate the poly-$Ru(VB)_3^{2+}$ film little if at all. Measurement of $k_{crs}\Gamma$ for reactions 2–9 is greatly simplified by this suppression of direct electron transfers between the Pt electrode and the dissolved substrate complexes, since measured currents then solely reflect the rate of the electron transfer mediation process itself.

At potentials more positive than the normal $E^{\circ\prime}$ of $[Ru(bpy)_2Cl_2]$ and $[Ru(bpy)_2(py)Cl]^+$, oxidation waves for these complexes can be observed on rotated disk Pt/poly-$Ru(VB)_3^{2+}$ electrodes via mediation reactions as

$$\text{Pt/poly-Ru(VB)}_3^{3+} + \text{Ru(bpy)}_2\text{Cl}_2 \xrightarrow{k_{crs}} \text{Pt/poly-Ru(VB)}_3^{2+} + \text{Ru(bpy)}_2\text{Cl}_2^{+} \tag{11}$$

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(8) (a) Denisevich, P.; Willman, K. W.; Murray, R. W. *J. Am. Chem. Soc.*, in press; (b) Denisevich, P.; Abruña, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W., submitted.

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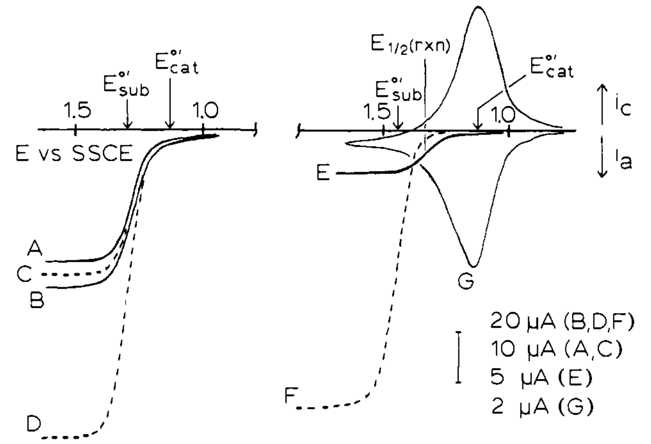

Figure 1. Rotated Pt/poly-Ru(VB)$_3^{2+}$ (—) and naked Pt (- - -) disk voltammetry. Curves A, C: 0.54 mM [Ru(bpy)$_2$(4,4′-bpy)$_2$]$^{2+}$ at (—) $\Gamma_T = 2 \times 10^{-9}$ mol/cm^2 of Pt/poly-Ru(VB)$_3^{2+}$ and (- - -) naked Pt at 400 rpm. Curves B, D: same except 8100 rpm. Curves E, F: 0.46 mM [Ru(bpy)$_2$(pyr)$_2$]$^{2+}$ at (—) 8×10^{-9} mol/cm^2 of Pt/poly-Ru(VB)$_3^{2+}$ and (- - -) naked Pt at 8100 rpm. Curve G: cyclic voltammetry of $\Gamma_T = 4 \times 10^{-9}$ mol/cm^2 of Pt/poly-Ru(VB)$_3^{2+}$ at 20 mV/s. All in 0.1 M Et$_4$NClO$_4$/acetonitrile and with 0.13 cm^2 electrode area.

Limiting currents for these electron transfer mediated waves (to be described elsewhere[11]) are proportional to $\omega^{1/2}$ which means that the electron-transfer rate in reaction 11 is faster than mass transfer of [Ru(bpy)$_2$Cl$_2$] to the polymer film surface, even at the highest electrode rotation rates.[12] We have consequently been unable to measure k_{crs} for reactions like reaction 11.

Oxidation of [Ru(bpy)$_2$(4,4′-bpy)$_2$]$^{2+}$ at a rotated Pt/poly-Ru(VB)$_3^{2+}$ disk electrode, via reaction 3, occurs more slowly than oxidation of [Ru(bpy)$_2$Cl$_2$], being thermodynamically unfavored ($E_{sub}^{0'} - E_{cat.}^{0'} = +165$ mV), but still rapidly enough to give an electrochemical wave as shown in Figure 1A,B. Whereas limiting currents for direct oxidation of [Ru(bpy)$_2$(4,4′-bpy)$_2$]$^{2+}$ at a naked Pt electrode (Figures 1C,D) are proportional to $\omega^{1/2}$ (Figure 2A), limiting currents for waves like Figure 1A,B respond to ω as in Figure 2B, as expected for control of i_{lim} by the rate of reaction 3. For the case of negligible effects of charge transport in the poly-Ru(VB)$_3^{2+}$ and of [Ru(bpy)$_2$(4,4′-bpy)$_2$]$^{2+}$ permeation into the film (vide infra), the appropriate equation[1b,1e] for analysis of Figure 2B is

$$\frac{1}{i_{lim}} = \frac{1}{nFAk_{crs}\Gamma C_S} + \frac{1}{0.62nFAD_S^{2/3}\nu^{-1/6}\omega^{1/2}C_S} \qquad (12)$$

where k_{crs} is in cm^3/mol·s and Γ is the coverage of poly-Ru(VB)$_3^{2+}$ sites at the polymer–solution interface with which [Ru(bpy)$_2$(4,4′-bpy)$_2$]$^{2+}$ can react. Figure 2C shows that the data fit eq 12, and the intercept of Figure 2C gives $k_{crs}\Gamma = 1.4 \times 10^{-2}$cm/s for reaction 3.

Another example, the mediated oxidation of [Ru(bpy)$_2$(pyr)$_2$]$^{2+}$, reaction 6, where the reaction thermodynamics are even less favorable, is shown in Figure 1E. The limiting current for reaction 6 is essentially independent of electrode rotation rate (Figure 2D); this reaction is so slow that the mass transport rate (right-hand term of eq 12) is negligible. Also, it is evident in Figure 1E that reaction 6 is driven at a potential $E_{1/2(rxn)}$ less positive than that ($E_{sub}^{0'}$) for reversible oxidation of [Ru(bpy)$_2$(pyr)$_2$]$^{2+}$ on a naked Pt electrode (Figure 1F) (e.g., is indeed electrocatalytic) and more positive than that ($E_{cat.}^{0'}$) of the catalyst (Figure 1G). The value of $E_{1/2(rxn)}$ is furthermore dependent on ω in a manner which agrees with predictions of a simple limiting equation[14] for $E_{1/2(rxn)}$; $E_{1/2(rxn)}$ is 50 and 100 mV more negative than $E_{sub}^{0'}$ for [Ru(bpy)$_2$(pyr)$_2$]$^{2+}$ at ω = 400 and 8100 rpm, respectively, whereas the calculated shifts are 49 and 85 mV.

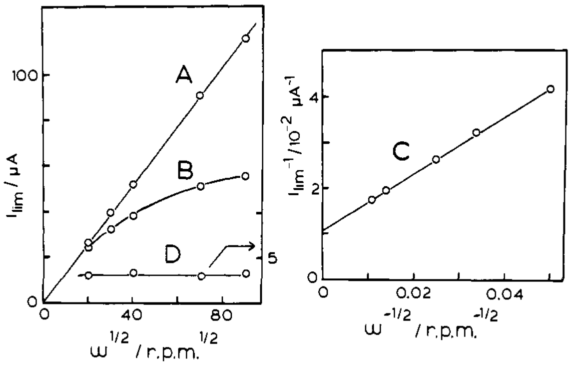

Figure 2. Limiting currents from Figure 1 as a function of electrode rotation rate, ω. Curve A: 0.54 mM [Ru(bpy)$_2$(4,4′-bpy)$_2$]$^{2+}$ at naked Pt (Figure 1C,D); Curves B, C: 0.54 mM [Ru(bpy)$_2$(4,4′-bpy)$_2$]$^{2+}$ at 2×10^{-9} mol/cm^2 of Pt/poly-Ru(VB)$_3^{2+}$ (Figure 1A,B). Curve D: 0.46 mM [Ru(bpy)$_2$(pyr)$_2$]$^{2+}$ at 8×10^{-9} mol/cm^2 of Pt/poly-Ru(VB)$_3^{2+}$ (Figure 1E).

Electrocatalyzed waves have been observed in a similar manner for the other reactions and $k_{crs}\Gamma$ values determined from linear plots like Figure 2C are given in Table I. $E_{1/2(rxn)}$ is measurably shifted from $E_{sub}^{0'}$ in most cases.

Before discussing the relationship of $k_{crs}\Gamma$ to ΔE^0, the possible importances of electrochemical charge transport, substrate diffusion, and impurity sites in the polymer film should be examined.

The rate of electrochemical charge transport in a poly-Ru(VB)$_3^{2+}$ film (i.e., reaction 1) is of most concern when the mediated reaction rate $k_{crs}\Gamma$ is fast (i.e., reaction 2). The effect would be to lower the apparent mediated rate. A lack of dependence of $k_{crs}\Gamma$ on Ru(bpy)$_3^{2+}$ concentration C_S is one criterion for the absence of such effects.[1b,e,5,6] Table II shows a sample of extensive data[11] on reaction 2 exploring this point, which demonstrate that when $\Gamma_T < 2 \times 10^{-8}$ mol/cm^2 and $C_S < \sim 1$ mM, charge transport rate effects can be ruled out.

Table II also shows that $k_{crs}\Gamma$ does not depend on Γ_T over a tenfold range, for both the fastest (reaction 2) and slowest (reaction 6) reactions in the ruthenium series, as long as $\Gamma_T >$ ca. 10^{-9} mol/cm^2. *Clearly all of the Ru(VB)$_3^{2+}$ sites do not participate in the reaction.* This behavior is similar to that of several other recent examples of electrocatalysis,[1b,e,f,m,p] where $k\Gamma$ was independent of, or less than proportional to Γ_T, and *is theoretically anticipated*[1b,4,5] *when the catalytic film has low permeability to the substrate* and means that only the outermost few (one?) monolayers of catalyst sites actually undergo electron transfers with the substrate.[15] We should note that eq 12 in fact explicitly[1b,4b] applies to nearly zero permeability (recall the preceding discussion of permeability of poly-Ru(VB)$_3^{2+}$ film) of the dissolved complexes into the film. Equation 12 is in this respect believed to be more appropriate[16] in treating the present results than theoretical relations by Saveant, et al.,[5] whose models did not include the limit of zero-partition coefficient in the most closely related case ("SR", eq 26 of ref 5). All experiments leading to $k_{crs}\Gamma$ values in Table I were conducted at low C_S and with $1 \times 10^{-9} < \Gamma_T < 2 \times 10^{-8}$ mol/cm^2. We will, below, estimate Γ in $k_{crs}\Gamma$ as ca. 1×10^{-10} mol/cm^2, an approximate monolayer of poly-Ru(VB)$_3^{2+}$ sites.

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(11) Ikeda, T., unpublished results, University of North Carolina, 1980.

(12) According to the Levich equation, $i_{lim} = 0.62nFA\nu^{-1/6}D_S^{2/3}\omega^{1/2}C_S$, where D_S is diffusion coefficient of the complex and ω is electrode rotation rate in rad/s; a i_{lim} vs. $\omega^{1/2}$ proportionality signifies mass transport control of the current.[13]

(13) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; John Wiley: New York, 1980; p 288.

(14) When $K_{eq}' \ll 1$, it can be shown[11] that $E_{1/2(rxn)} = E_{sub}^{0'} + (RT/nF)$ ln $[i_{lim(k)}/i_{lim(d)}]$ where $i_{lim(k)}$ and $i_{lim(d)}$ are the mediated and naked electrode-limiting currents, respectively, i.e., limiting currents of Figures 1E and 1F, respectively.

(15) This corresponds to Figure 4A of ref 1b.

(16) This assertion is reinforced by calculating the "reaction layer thickness", $(D_{S,pol}/k_1C_p^0)^{1/2}$, which in eq 26 of ref 5 is related to $k_{crs}\Gamma$ in eq 12 by the relation $k_{crs}\Gamma = PD_{S,pol}/(D_{S,pol}/k_1C_p^0)^{1/2}$. For $k_{crs}\Gamma = 0.1$ (reaction 2) and $PD_{S,pol} \cong 10^{-10}$, we obtain a "reaction layer thickness" of 0.1 Å. This number is less than a monomolecular layer dimension and shows that only slight penetration is needed for electron transfer.

Table II. Examples of Electron-Transfer Cross-Reaction Rates as a Function of Coverage Γ_T and Substrate Concentration C_S

reaction	Γ_T,[a] mol/cm² × 10^9	C_S, m*M*	$k_{crs}\Gamma$,[b] cm/s
2	1.4	0.08	0.14
		0.25	0.12
		0.53	0.11
		0.91	0.13
	12	0.10	0.10
	16	0.14	0.084
	49	2.4	(0.0078)[c]
6	1.5	0.48	0.0011
	11	0.25	0.00094

[a] Total quantity electroactive centers in Pt/poly-$Ru(VB)_3^{2+}$ film as measured by slow potential scan cyclic voltammetry. [b] Here, Γ is the quantity of poly-$Ru(VB)_3^{2+}$ participating in reactions 2 and 6 and clearly $\Gamma \neq f(\Gamma_T)$. [c] Results for $k_{crs}\Gamma$ are low at large Γ_T and large C_S due to partial rate control by charge transport through the film; such data will be presented and analyzed in more detail elsewhere.[11]

Lastly, cyclic voltammetric waveshapes for poly-$Ru(VB)_3^{2+}$ films (Figure 1G) often suggest the presence of an overlapping, minor (<10%) film component[11] with $E_x^{0\prime} \sim +1.32$ V. In order to show that this more oxidizing component (when present) is not artificially responsible for the observed electrocatalytic effects, $k_{crs}\Gamma$ for reaction 9 and the reaction

$$\text{Pt/poly-Ru(VB)}_3^{2+} + \text{Fe(bpy)}_3^{3+} \xrightarrow{k_{crs}} \text{Pt/poly-Ru(VB)}_3^{3+} + \text{Fe(bpy)}_3^{2+} \quad (13)$$

were measured in the *reduction* direction. The rates of these two reactions, in which the $E_x^{0\prime}$ component should have little role, are both large and quantitatively lie in the same $k_{crs}\Gamma$ vs. ΔE^0 pattern as the other reactions (Table I and Figure 3).

Table I shows that $k_{crs}\Gamma$ for reactions 2–9 and 13 vary systematically with K_{eq}' and ΔE^0 as anticipated from the Marcusian eq 10a and 10b. To compare the Ru and Fe data to these equations, we plotted log $k_{crs}\Gamma$ vs. ΔE^0 to obtain approximately linear plots, from whose intercepts the products $k_{ex(cat.)}k_{ex(sub)}$ were estimated. Assuming $\Gamma = 1 \times 10^{-10}$ mol/cm², this gives $k_{ex(cat.)}k_{ex(sub)} = 6.3 \times 10^{13}$ and 5.0×10^{12} M^{-2} s^{-2} for the Ru and Fe series, respectively. Assuming $k_{ex(cat.)} \approx k_{ex(sub)}$ yields 8×10^6 and 2.2×10^6 M^{-1} s^{-1} for $Ru(bpy)_3^{2+}$ and $Fe(bpy)_3^{2+}$ self-exchange rates in satisfying accord with literature values,[9] 8×10^6 and 4×10^6 M^{-1} s^{-1}, respectively. Taking $Z = 10^{11}$, these values were used to recast eq 10a and 10b into the form

$$\log k_{crs}\Gamma + 7 = (1/2) \log [k_{ex(cat.)}k_{ex(sub)}] - 8.46\Delta E^0(1 + \chi\,\Delta E^0) \quad (14)$$

where $k_{crs}\Gamma$ is in cm/s and k_{ex} in M^{-1} s^{-1}, and $\chi = 0.52$ and 0.46 for the Ru and Fe series, respectively. (Since χ is small, the behavior of eq 14 is not very sensitive to the above assumptions.)

Data plotted as log $k_{crs}\Gamma$ vs. $\Delta E^0(1 + \chi\,\Delta E^0)$ in Figure 3 follow linear relationships for the Ru and Fe series within experimental error. Lines with the theoretical slope −8.46 (eq 14) are superimposed on the data, and the results show that reactions 2–9 quantitatively follow eq 10a and 10b. The result (Δ) for the mixed Ru–Fe reaction (reaction 13) falls in between the Ru and Fe correlations, as expected.

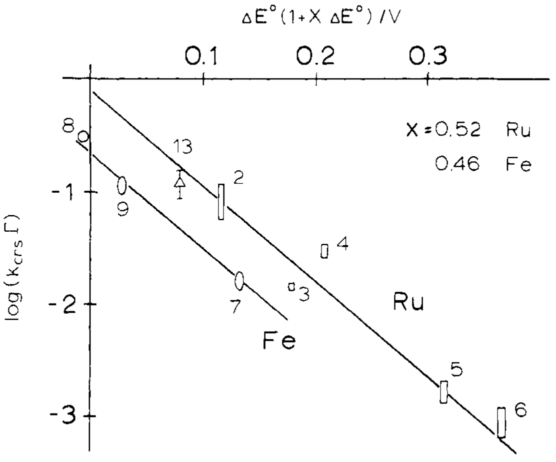

Figure 3. Plot of experimental $k_{crs}\Gamma$ results (□, Δ, and ○) from Table I ($k_{crs}\Gamma$ in cm/s) according to eq 14 where $\chi = 0.52$ for Ru and 0.46 for Fe and (assumed) 0.50 for reaction 13. The lines (—) are drawn with theoretical (8.46) slope. Results are coded according to reaction number (see text) and the error bars represent the range of data.

Figure 3 represents the first successful comparison of electron-transfer kinetics at modified electrodes to Marcus relationships. The results suggest that activation barriers for electron transfers as in reactions 2–9 resemble those for electron transfers between ruthenium and iron bipyridine complexes in homogeneous solutions where outer-sphere reorganizational barriers are important. This is a significant result for polymer film coated modified electrodes, where many alternative energy barriers to electron transfers at/in redox polymer solution interfaces might be imagined. These include penetration of the dissolved complex into the interfacial polymer film in which the Ru or Fe bipyridine catalyst sites are embedded, and the ingress/egress of counterion(s) needed for fixed site electroneutrality in the polymer. Figure 3 indicates that such barriers are not dominant for the reactions examined here, and is further interesting in suggesting that the energetics of solvation of the complexes are not seriously perturbed by the unusual environment of the polymer/solution interface.

Finally, there have been numerous experimental tests of eq 10a and 10b for electron-exchange cross-reactions occurring in homogeneous solution, and of the Marcus relationship[10] between the rate constants for electron self-exchange occurring homogeneously and at an electrode surface. We are unaware, however, of prior quantitative tests of eq 10a and 10b where the electron-transfer cross-reaction occurs *at an interface* (the polymer film–solution interface in the present case) as opposed to reaction in homogeneous solution.[17]

Experimental Section

Chemicals and Coated Electrodes. The complexes $[Ru(VB)_3]^{2+}$,[1d] $[Fe(VB)_3]^{2+}$,[1d] $[Ru(bpy)_3]^{2+}$,[18a] $[Ru(bpy)_2(4,4'\text{-bpy})_2]^{2+}$,[18a] $[Ru(bpy)_2py(CH_3CN)]^{2+}$,[18b] $[Ru(bpy)_2(CH_3CN)_2]^{2+}$,[18b] $[Ru(bpy)_2(pyr)_2]^{2+}$,[18a] $[Fe(bpy)_3]^{2+}$,[18c] and $[Fe(Me_2B)_3]^{2+}$,[18c] and the ligand 4-vinyl-4′-methyl-2,2′-bipyridine[1d] were all prepared by literature methods or were gifts as indicated. Acetonitrile (Burdick and Jackson) was stored over molecular sieves. The supporting electrolyte was 0.1 M Et_4NClO_4 (Eastman) in all cases. Teflon shrouded Pt disk electrodes were coated with films of poly-$Ru(VB)_3^{2+}$ and poly-$Fe(VB)_3^{2+}$ by electrochemical reduction of ca. 0.1 mM solutions of the respective monomers as described elsewhere,[1d,8] Γ_T was controlled by the duration of the reduction process.

Electrochemical. Γ_T of the polymer films was determined by slow potential scan cyclic voltammetry. Electrode potentials are referenced to a NaCl-saturated SCE (SSCE). The electrochemical cell and potentiostat were conventional three-electrode designs. Rotated electrode voltammetry was carried out with a Pine Instruments rotator (Grove City, PA) at room temperature (25 ± 1 °C).

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(17) (a) The so-called Yamaoda mechanism[17b,c] is loosely related to electrocatalysis at redox polymer films, but the cross-reaction occurs remotely from the electrode and no Marcus correlations have been made; (b) Yamaoka, H. *J. Electroanal. Chem.* **1972**, *36*, 457. (c) Ruzic, I.; Smith, D. E.; Feldberg, S. W. *Ibid.* **1974**, *52*, 157.

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