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An Electrode-Supported Oxidation Catalyst Based on Ruthenium(IV). pH "Encapsulation" in a Polymer Film

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Abstract: The known oxidative catalytic behavior of the ions $(bpy)_2(py)RuO^{2+}$ (bpy is 2,2′-bipyridine; py is pyridine) and $(trpy)(bpy)RuO^{2+}$ (trpy is 2,2′,2″-terpyridine) has been successfully transferred to electrode surfaces. The electrodes were chemically modified by deposition of thin polymeric films containing the $(bpy)_2(H_2O)Ru^{II}$ group bound to poly-4-vinylpyridine. Upon oxidation to Ru^{IV} on the surface, catalytic oxidation currents are observed for the modified electrodes in the presence of 2-propanol, *p*-toluic acid, and the xylenes with an added surfactant. The effective catalytic lifetimes of the films are limited (>30 turnovers per redox site) by a competing reaction within the polymer film which changes the nature of the redox sites. An unusual pH effect has been observed in the polymer films. Below pH 4, potentials measured by cyclic voltammetry for the bound $[(bpy)_2(OH)Ru^{III}(py)-]^{2+}/[(bpy)_2(OH_2)Ru^{II}(py)-]^{2+}$ and $[(bpy)_2(O)Ru^{IV}(py)-]^{2+}/[(bpy)_2(OH)Ru^{III}(py)-]^{2+}$ couples change with pH as expected. Above pH 4, where the unbound pyridyl groups in the polymer become deprotonated, up to pH 9.2 the redox couples no longer respond to pH changes in the bulk solution. The difference in pH behavior between the polymer in solution and on the electrode surface has allowed us to observe the deposition process by cyclic voltammetry. In acid solution, the polymer film is open and large amounts of ferri- or ferrocyanide ions can be incorporated reversibly into the films by ion exchange. Over a longer time period, the cyano ions are permanently bound in the films, apparently by the formation of a cyano-bridged Fe–Ru dimer.

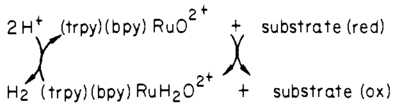
Introduction

One motivation for the development of chemically modified electrodes is the possibility that the desirable properties of a chemical site can be transferred intact to the electrode surface. There are by now a number of elegant examples of this kind based mainly on the reversible electron-transfer properties of an attached redox couple or couples.[1] An especially attractive type of chemical system to consider in attachment studies is based on polypyridine complexes of ruthenium where (1) a relatively high chemical stability is available in a series of oxidation states,[2] (2) there is a well-developed background of synthetic chemistry,[2,3] (3) potentially worthwhile catalytic[4] and excited state[5] properties are known, and (4) successful approaches to electrode attachment have been developed.

The basis for the work reported here is the fact that the Ru(IV) complexes $(bpy)_2(py)RuO^{2+}$ (bpy is 2,2′-bipyridine; py is pyridine) and most notably $(trpy)(bpy)RuO^{2+}$ (trpy is 2,2′,2″-terpyridine) were recently shown to act as oxidants toward a variety of organic substrates including primary and secondary alcohols and aromatic and olefinic hydrocarbons under mild conditions.[4c] It was also shown that the Ru(IV) complexes provide the basis for an electrocatalytic oxidation scheme involving an electrochemical shuttle mechanism in which Ru(IV) is regenerated by oxidation at the electrode.

Given the regenerable redox chemistry in Scheme I, attachment of a $Ru^{IV}{=}O^{2+}/Ru^{II}H_2O^{2+}$ couple holds the promise of creating a catalytic, chemically modified electrode. The approach we have taken to the problem is an initial chemical binding of the Ru site to poly-4-vinylpyridine (P4VP) followed by adsorption of the metallopolymer onto electrode surfaces. The resulting surfaces do show oxidative catalytic behavior and, in addition, a number of unusual pH effects which arise from the nature of the polymeric films have been observed.

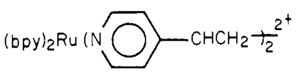
Scheme I



Experimental Section

All reagents and solvents used were reagent or spectral grade and were used without further purification. House-distilled water was further purified by distillation from alkaline $KMnO_4$ in an all glass still. The complexes $Ru(bpy)_2CO_3{\cdot}2H_2O$[7] and $[(bpy)_2(py)Ru^{II}H_2O](ClO_4)_2{\cdot}H_2O$[2a] were prepared according to the literature. Poly-4-vinylpyridine (P4VP) prepared by using AIBN as the radical initiator had a M_r of 3700 as determined by vapor-phase osmometry.[8]

Aquobis(2,2′-bipyridine)(poly-4-vinylpyridine)ruthenium(II), $[(bpy)_2(H_2O)Ru(P4VP)_n{}^{2+}]$. The metallopolymer was prepared by two different procedures which gave identical results. The first was based on the initial observations of Clear et al.,[9] who first prepared the doubly bound complex



which upon irradiation cleanly undergoes photosubstitution to give the bound aquo complex. In retrospect, the photochemical reaction is expected given the known photochemical properties of $Ru(bpy)_2(py)_2{}^{2+}$.[3]

In the second procedure an aqueous solution of the diaquo complex, $(bpy)_2Ru(H_2O)_2{}^{2+}$,[10] was prepared by dissolving the carbonato complex, $(bpy)_2RuCO_3{\cdot}2H_2O$ (0.045 g), in 2 mL of 0.1 M H_2SO_4. The pH of the solution was brought to 10–11 with 1 M NaOH which converts the diaquo complex into $(bpy)_2(H_2O)RuOH^+$. The basic aqueous solution was added to 50 mL of methanol containing 0.50 g of P4VP, which gave a stoichiometric mixture of 5.2/1 pyridine sites/Ru. The methanol–H_2O solution was heated at reflux for 48 h and acidified (H_2SO_4) to yield the

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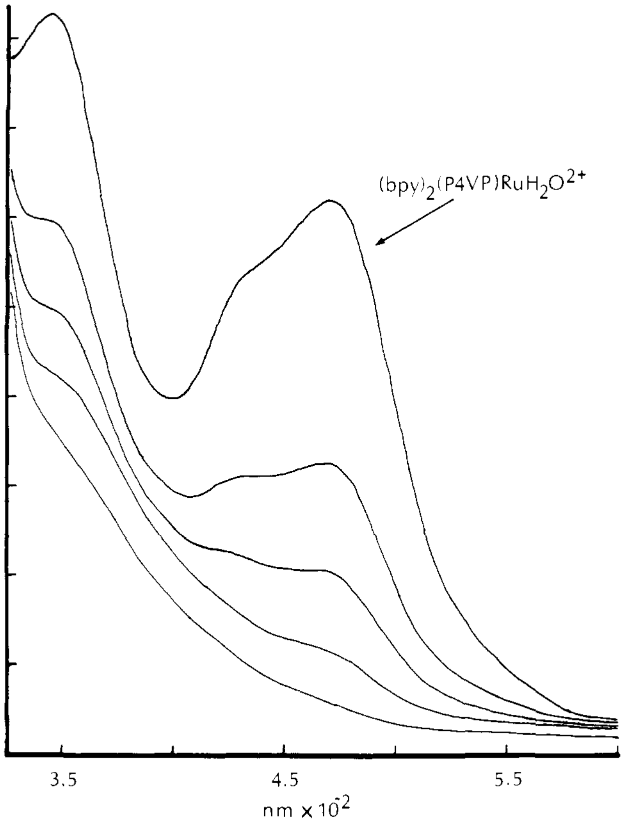

Figure 1. Electronic spectra of solutions containing $(bpy)_2(H_2O)Ru((py)CHCH_2-)^{2+}$ following the addition of increasing amounts of Ce(IV).

aquo complex. The addition of 1 M $HClO_4$ resulted in the precipitation of a nearly insoluble product. Addition of CF_3SO_3H gave a red oil which was soluble in methanol and water in the absence of excess CF_3SO_3H. No attempt was made to vary the ruthenium to pyridine ratio in the experiments described here although it is clear that such variations can be made.[8] Four different preparations of the metallopolymer were used in the experiments described, and there were no apparent differences in the properties of the samples obtained.

Measurements. Electronic spectra were recorded on either a Varian 634S or a Bausch and Lomb 219 UV spectrophotometer. Solution pH measurements were made by using a Radiometer PHM62 pH meter.

Most of the electrochemical experiments were carried out by using glassy carbon disk or reticulated vitreous carbon electrodes although both gold and platinum disk electrodes give similar results. All potentials are vs. the saturated sodium calomel electrode at 25 ± 2 °C and are uncorrected for junction potential effects. The electrochemical measurements were made by standard three-electrode methods using a PAR Model 175 Universal potential programmer, Model 176 current to voltage converter, and Model 173 potentiostat/galvanostat. Potentials given are half-wave potentials measured by cyclic voltammetry.

The films on the various electrode surfaces were deposited by partial evaporation of dilute ($<1 \times 10^{-4}$ M based on ruthenium) methanol solutions of the metallopolymer followed by a distilled water rinse. The film thickness was controlled by evaporation time. Effective film thicknesses were estimated by integrating areas under voltammetric waves assuming a diameter of 20 Å per metallopolymer redox unit (1 Ru complex/5.2 pyridyl groups). Typically, coverages between ~1 and 40 layers were obtained.

Catalytic oxidations were carried out by using standard three-compartment cells with working volumes of 10–15 mL. The coated electrode was potentiostated 100 mV past the Ru(III)/Ru(IV) couple, and after the normal background current level had been reached (~30 s), the substrate was added to the stirred electrolyte. The total number of equivalents of electrons transferred per equivalent of surface bound complex in the catalysis studies was determined by measuring the total area under current vs. time curves after the addition of substrate. Blanks were performed in an identical manner except that uncoated electrodes were used. Because of small amounts of residual currents in the blanks, background corrections were necessary for sodium *p*-toluate and mixed xylenes as substrates. In the catalytic studies the supporting electrolyte used was either 0.2 M $NaH_2PO_4/Na_2HPO_4/Na_2SO_4$ or 0.2 M NaH_2PO_4/Na_2HPO_4. 2-Propanol was added as the neat liquid (0.10-mL aliquots), *p*-toluic acid was added as a 0.1 M solution of the sodium salt, and the oxidation was carried out under neutral or slightly basic conditions. The xylenes were added as the neat liquid and solvolyzed by the addition of sodium dodecylsulfate (0.02 M).

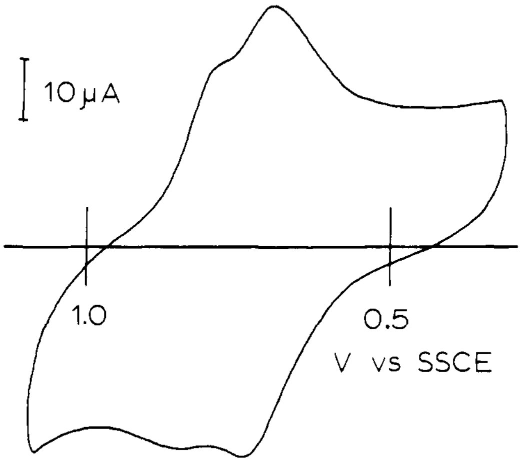

Figure 2. Cyclic voltammogram of a film (~15 layers) of $(bpy)_2(H_2O)Ru((py)CHCH_2-)_{5.2}{}^{2+}$ on a glassy carbon button electrode (pH 2, electrolyte Na_2SO_4/H_2SO_4 (I = 0.2 M) at 20 mV/s).

Results and Discussion

Characterization of the Ru Sites in the Metallopolymer and of the Polymeric Films. The properties of the ruthenium sites when bound to poly-4-vinylpyridine mimic those of the monomeric complex $(bpy)_2(py)RuH_2O^{2+}$. UV–visible spectral properties (λ_{max} = 472 nm and 344 nm in H_2O compared to 470 nm and 335 nm for the monomer)[11] are nearly the same, and chemical (Ce^{IV}) (Figure 1) or electrochemical oxidation of the metallopolymer results in spectral changes nearly identical with those observed during oxidation of the monomer.

$$(bpy)_2(py)Ru^{II}H_2O^{2+} \xrightarrow[-H^+]{-e^-} (bpy)_2(py)RuOH^{2+} \xrightarrow[-H^+]{-e^-} (bpy)_2(py)Ru^{IV}{=}O^{2+}$$

Except for the unusual effects noted below, redox potentials for the Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II} couples in the metallopolymer as either a film on the electrode or free in solution are the same (within ~5 mV) as for the related monomer couples (eq 1, 2)

$$(bpy)_2(py)Ru^{III}OH^{2+} + H^+ + e^- \rightarrow (bpy)_2(py)Ru^{II}OH_2{}^{2+} \quad (1)$$

$$(bpy)_2(py)Ru^{IV}O^{2+} + H^+ + e^- \rightarrow (bpy)_2(py)Ru^{III}OH^{2+} \quad (2)$$

as measured by cyclic voltammetry (Figure 2). In addition, at pH <4, $E_{1/2}$ values for the metallopolymer couples decrease ~59 mV per pH unit as predicted by eq 1 and 2. As shown in Figure 2 there is a noticeable difference in peak currents between the $Ru^{IV}{=}O^{2+}/Ru^{III}OH^{2+}$ and $Ru^{III}OH^{2+}/Ru^{II}H_2O^{2+}$ couples. The same effects have been observed for the analogous couples in homogeneous solution. Its origin appears to be related to a mechanistic difficulty arising from a required proton loss from $(bpy)_2(py)RuOH^{2+}$ when it is oxidized to $(bpy)_2(py)RuO^{2+}$.[11] The effect is a kinetic one[12] since the results of coulometry experiments show that each of the couples involves a reversible one-electron transfer. The cyclic voltammograms showed a decrease in wave separation with decreasing scan rate (Figure 3) with no obvious dependence on film thicknesses for the range of thickness used here, suggesting that there are kinetic restrictions to electron transfer between the film and the electrode.

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[11] Moyer, B. A. Ph.D. Thesis, University of North Carolina, Chapel Hill, N.C., 1979. Moyer, B. A.; Meyer, T. J. *Inorg. Chem.*, in press.

[12] There is a dramatic isotope effect, k_{H_2O}/k_{D_2O} = 16.1, for the comproportionation reaction between $(bpy)_2(py)Ru^{II}H_2O^{2+}$ and $(bpy)_2(py)Ru^{IV}{=}O^{2+}$. The large value strongly suggests the importance of proton coupling to the electron-transfer process. Binstead, Robert, submitted.

[13] Lane, R. F.; Hubbard, A. T. *J. Phys. Chem.* **1973**, *77*, 1401.

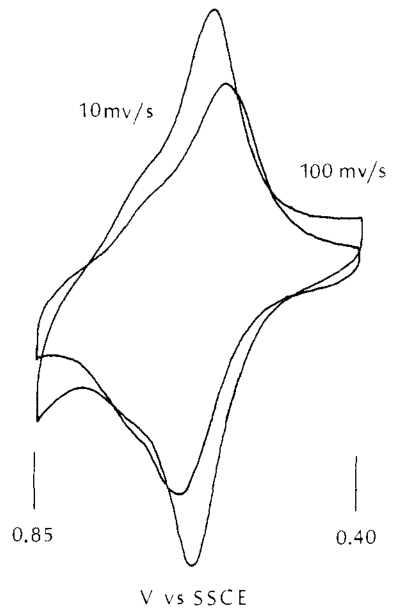

Figure 3. Scan rate dependence of the Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples in cyclic voltammograms of a film (~40 layers) at pH 7.4 on a glassy carbon electrode.

Because of the short-chain nature of the polymer, the metallopolymer prepared from it is partly soluble in acidic aqueous solutions and consequently electrode films are slowly leached off in acidic solution when H_2SO_4 is used as the acid. The electrode stripping process continues until a film thickness of ~3 layers is reached at which point the loss of polymer is slowed considerably. When $HClO_4$ is used as the acid, the dissolution of the film is significantly slower, apparently due to the insolubility of the protonated metallopolymer in perchlorate media. Specific anion effects are also clearly observed in cyclic voltammograms of the metallopolymer films which are sufficiently thick (~10 layers) to give well-defined waves. At the same pH and anion concentrations, peak currents, i_p, are larger and noticeably more symmetric wave shapes are obtained in sulfate compared to perchlorate media. The differences noted are reversible by ion exchange. Similar effects have been observed by Oyama and Anson for redox processes on electrodes coated by high molecular weight poly-4-vinylpyridine,[14] and their existence illustrates the importance of anionic properties (hydration effects, mobility, specific interactions) in the charge-transfer process.

Although clear similarities in chemical and physical properties exist between the ruthenium sites in the metallopolymers and in related monomers, a series of properties do exist which are attributable to the distinct character of the metallopolymer when it is cast as a film on an electrode surface.

pH Effects. (1) "pH Encapsulation" within the Polymer Film. In films of the metallopolymer on electrodes the proton dependencies predicted by eq 1 and 2 are observed in acidic solutions. However, if the pH of the external solution is increased into the range pH ≥4–9.2, the waves for the Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples become a single broad, but noticeably asymmetric wave ($E_{1/2} \approx 0.63$ V) *whose potential is no longer dependent on pH.* The pH dependences of the potentials for the monomer and polymer film Ru(III)/Ru(II) couples are shown in Figure 4.

The loss of dependence on external pH is observed for both thick and thin films and is reversible. When the external solution is acidified, the expected pH dependence returns but at a finite rate. When the pH of the external solution was changed abruptly from pH 8.7 to pH ~1 by the addition of H_2SO_4, assuming efficient mixing, the characteristic pH independent wave at ~0.63 V is observed initially but within 3 cyclic scans (at a scan rate of 100 mV/s from 0.4 to 0.95 V), the Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples once again reflect the pH of the external solution.

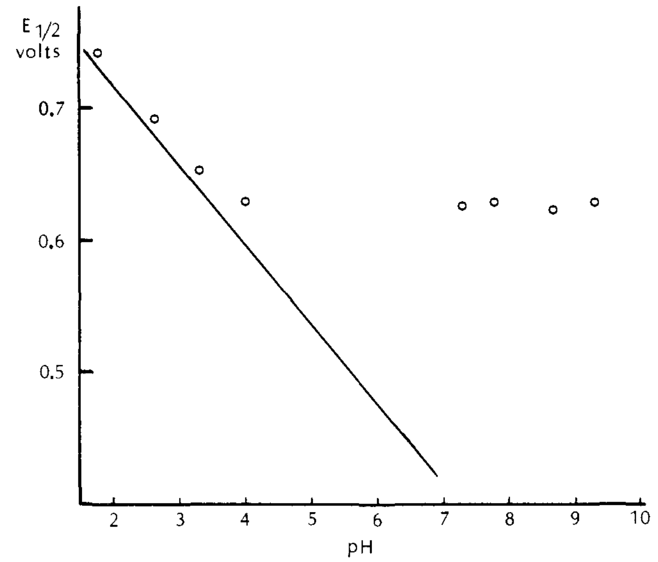

Figure 4. The pH dependence of the film Ru(III)/Ru(II) couple (o) compared to the pH dependence (—) of the monomeric Ru(III)/Ru(II) couple.

The probable origin for the remarkable pH behavior in the films is protonation and deprotonation of the free pyridyl groups in the polymer.[16] From the electrochemical results, protonation gives a surface that is open to the external solution and the external solution dictates the pH properties at the redox sites. Deprotonation leads to the exclusion of the solution or at least of the buffer component of the external solution. The deprotonation effect may come from a structural change induced by the loss of hydration or is perhaps merely a consequence of the change in the dielectric properties of the film. In either case the pH properties within the film are no longer dictated by the pH of the external solution but rather by the microstructure within the film and largely by the internal pyridyl groups ($pK_a = 5.25$ in pyridine). The effect of the pH-induced transition is to block acid–base communication between the film and the external solution. The transition leads to a pH "encapsulation" within the film at pH ≥4.[16] In this sense the potentials for the Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II} couples attached to the polymer act as internal pH indicators for the acid–base environment within the film.

(2) Observation of Film Deposition. Film-Induced Charge-Transfer Blocking. The difference in pH dependence between the homogeneous and film redox couples allows the growth of the film on the electrode surface to be followed by cyclic voltammetry. As shown in Figure 5, the first few scans in an aqueous solution containing metallopolymer at ~2 mM (based on Ru) at pH 7.9 show a well-defined wave at $E_{1/2} = 0.44$ V for the Ru(III)/Ru(II) metallopolymer couple in solution. Under these conditions it is possible to observe the growth of the film on the surface since at this pH the potentials for the solution and film redox couples are well separated because of the pH encapsulation effect. With increasing scan times the peak current for the broad wave at 0.63 V characteristic of the film couples at pH ≳4 grows showing that the metallopolymer is being deposited on the electrode surface. At the end of the scan period shown in Figure 5 the estimated surface coverage was 2–3 layers.

As shown in Figure 5, concurrent with the growth of the surface wave is the loss in peak current for the solution redox couple. The time-dependent behavior in Figure 5 shows that oxidation of the metallopolymer in solution is inhibited by formation of the film

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[17] Nishikawa, H.; Tsuchida, E. *Makromol. Chem.* **1976**, *177*, 2295. A related observation may be the fact that maximum loading of $Cu(aq)^{2+}$ onto P4VP in solution occurs at pHs ≳4.

[18] Keene, F. R.; Young, R. C.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2468.

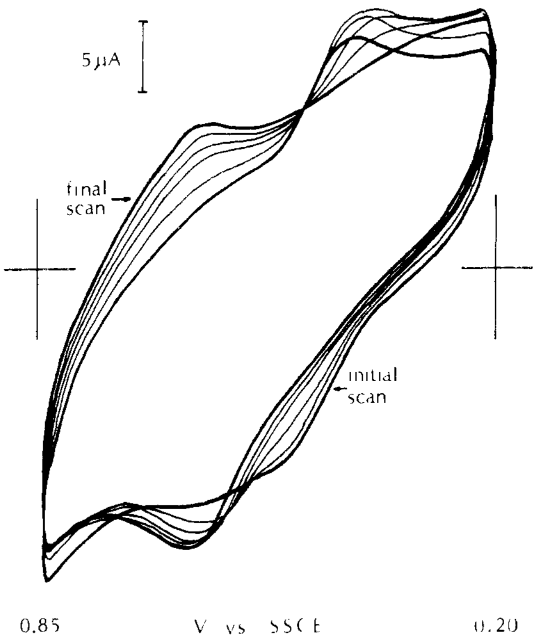

Figure 5. Successive cyclic voltammograms (100 mV/s, 0.2-0.85 V, 0.2 M Na_2SO_4/phosphate buffer) of metallopolymer film deposition onto a glassy carbon electrode from the ~2 mM metallopolymer solution at pH 7.9. The arrows on the figure indicate wave maxima where the peak currents either increase or decrease with time.

on the electrode. Presumably the current for the solution couple falls as the "pinholes" and open spaces on the electrode surface are filled by the growing film. There is an apparent lack of permeability of the polymer through the film. If electron transfer from the external polymer to the electrode does occur, it would have to be mediated by the Ru couples in the film. Although we have no evidence for it, this process could be severely impeded kinetically because rate studies on related couples show the importance of coupled proton-electron-transfer, one-electron-transfer reactions. Inhibition to one-electron transfer, however, is irrelevant to the catalytic oxidation to be described later since mechanistically they appear to involve multiple-electron, hydride ion-transfer steps.

(3) Ion Exchange of Ferri- or Ferrocyanide Ions. An additional pH-related effect is observed for the films when ferro- or ferricyanide ions as the potassium salts are added (~1-10 mM) to the electrolyte solution. At pH 7.4 a quasi-reversible wave centered at ~0.20 V is observed for the $Fe(CN)_6^{3-/4-}$ couple on an uncoated electrode. The wave disappears when the electrode is carefully coated with the metallopolymer (~10 layers) and placed in the same ferri- or ferrocyanide solution. Upon acidification to pH ~2 with H_2SO_4 and protonation of the pyridyl sites, the film opens to the external solution. A wave is now observed for the $Fe(CN)_6^{3-/4-}$ couple, shifted to ~0.37 V and having a dramatically increased peak current. A closely related observation has been made by Oyama and Anson,[14] who observed blockage of the $Fe(CN)_6^{3-/4-}$ couple by relatively thick films of high M_r poly-4-vinylpyridine ($M_r = 7.4 \times 10^5$) which opens to the solution upon acidification.

The results of two experiments show that the $Fe(CN)_6^{4-}$ ion is held in the film, presumably by electrostatic binding. If an electrode which has been exposed to $Fe(CN)_6^{4-}$ is placed in a solution free of added $Fe(CN)_6^{4-}$, the $Fe(CN)_6^{3-/4-}$ wave is still observed but the peak current slowly decreases with time, indicating slow loss of $Fe(CN)_6^{4-}$ ion from the film.[19] The second experiment involves the scan rate dependence of the wave. When the scan rate is decreased from 100 to 20 mV/s, the potential separation between the oxidative and reductive peak currents (ΔE_p) falls from ~100 to ~40 mV (Figure 6). The fact that ΔE_p falls significantly below the value, 59 mV, expected for a diffusion-controlled couple is striking since it suggests that the couple is held within the film. It also suggests that the mechanism of charge transfer is not totally diffusional in character and that the charge-transfer properties of the $Fe(CN)_6^{3-/4-}$ couple in the film resemble those normally associated with surface-bound redox sites.

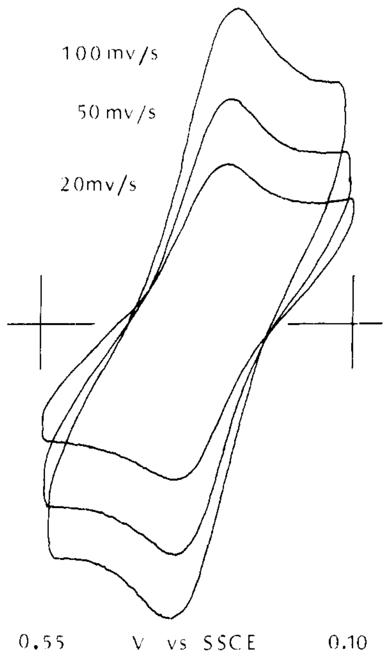

Figure 6. Scan rate dependence (0.1-0.55 V) of the $Fe(CN)_6^{3-/4-}$ couple ion exchanged into the metallopolymer film (pH 1.0, 0.2 M Na_2SO_4/H_2SO_4).

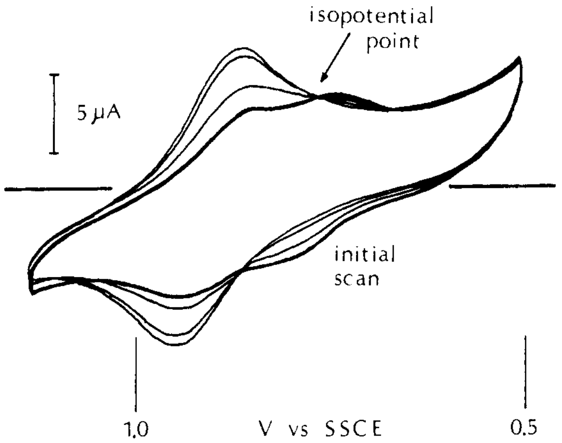

Figure 7. Successive cyclic voltammetric scans (0.5-1.15 V, 100 mV/s) at pH 1.0 (0.2 M Na_2SO_4) on a polymeric film ion exchanged with $Fe(CN)_6^{3-}$. The voltammograms show formation of a new film species, apparently the dimer $[(bpy)_2(py)RuNCFe(CN)_6]^{2-}$. Note that the new species is present during the initial scan.

The effects of variations in anion, ClO_4^- vs. SO_4^{2-}, on the wave shapes for the Ru couples were mentioned earlier. In thicker films ($\gtrsim$10 layers) a related effect is also observed for the $Fe(CN)_6^{3-/4-}$ couple. At the same pH and anion concentration (pH 1, [anion] = 0.25 M) the Ru and $Fe(CN)_6^{3-/4-}$ couples are more nearly reversible and peak currents are higher in SO_4^{2-} media. The observed effects again may be related to the role of anionic mobility in the charge-transfer processes involved or perhaps to a structural effect arising from differences in solvation between the two ions.

Chemical Processes within the Polymeric Films. In addition to the reversible charge-transfer processes which have already been described for the metallopolymer films, we have obtained evidence for additional effects which appear to arise from irreversible chemical reactions which occur in the films.

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[19] (a) Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980**, *127*, 247. (b) Oyama, N.; Anson, F. C. *Anal. Chem.* **1980**, *52*, 1192.

As just described, ferri- or ferrocyanide ions can be reversibly ion exchanged into the metallopolymer film. However, a longer term process also occurs which leads to the permanent binding of the ions in the film as shown by the appearance of a new wave in cyclic voltammograms. The appearance of the new wave is at the expense of the aquo-Ru couples as shown in Figure 7 by the maintenance of isopotential points.[20] Cyclic voltammetry shows that the new electroactive species ($E_{1/2} \approx 0.95$ V) is produced in the metallopolymer film when it is exposed to an acidic aqueous solution of $Fe(CN)_6^{3-}$ (0.01 M) or in a $Fe(CN)_6^{4-}$ film when it is exposed to a ferrocyanide-free electrolyte by repeated cycling through the $Fe(CN)_6^{3-/4-}$ wave. Eventually the only major redox component within the films is the new species.

The chemistry involved in the film appears to follow straightforwardly from related reactions in homogeneous solution where displacement of bound ligands by cyano complexes is known to lead to cyano-bridged dimers.[21]

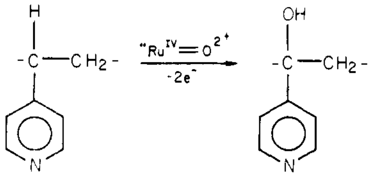
$$(bpy)_2(py)RuH_2O^{2+} + Fe(CN)_6^{3-} \rightarrow [(bpy)_2(py)RuNCFe(CN)_5]^- + H_2O \quad (3)$$

We have attempted to prepare the dimeric analogue of the product of eq 3 by mixing together approximately equimolar solutions (0.007 M) of $(bpy)_2(py)Ru^{II}H_2O^{2+}$ and $Fe(CN)_6^{3-}$ ions. Within a period of several minutes a reddish orange precipitate formed, presumably the potassium salt of the dimer. Unfortunately, the dimer is insufficiently soluble in water to obtain a cyclic voltammogram so that we are unable to make redox potential comparisons with the species in the film.

The apparent substitutional chemistry within the film in eq 3 is worth noting since it may provide an entree into surface-bound analogues of the extensive number of related monomeric bis(bipyridine) complexes which are known.[2-4] The product itself is of interest as a surface-bound mixed-valence dimer and the reaction as an approach to the introduction to multiple redox sites into the polymer film. The ability to undergo substitutional chemistry at the bound water also presages the systematic modification of the redox site by simple chemical reactions.

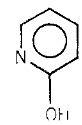
An additional long-term process can also be observed in the films which appears to be associated with an irreversible chemical oxidation by Ru(IV). After the first and every successive scan a wave is observed at ~0.63 V which is independent of pH over the range 0–9.2. The wave continues to grow very slowly, over a period of hours, if the film is potentiostated at a potential past the Ru(IV)/Ru(III) couple or is continuously cycled past the Ru(IV)/Ru(III) couple. The growth of the wave is at the expense of the Ru(III)/Ru(II) and Ru(IV)/Ru(III) couples, and its rate of growth varies from film to film. The appearance of the new couple is clearly dependent on having the redox sites in their oxidized forms since the films are stable indefinitely in the Ru(II) form as shown by occasional cyclic voltammograms taken on films held as Ru(II).

A possible reaction (eq 4) in the polymer film is oxidation of

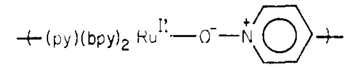


(4)

a C–H bond adjacent to the pyridine ring, since (trpy)(bpy)-$Ru{=}O^{2+}$ is known to oxidize aromatic hydrocarbons catalytically, e.g., toluene to benzoic acid.[4c] However, it is not at all obvious why such chemistry at the polymer skeleton should greatly affect the redox properties at the ruthenium sites. In fact, we have no idea what the nature of the new redox site is or of the chemistry which leads to it. Redox potential comparisons appear to rule out a series of products which might reasonably be expected to occur, including products arising from α-hydroxylation of a pyridine ring to give free or bound α-pyridones,[22]



oxidation to pyridine *N*-oxide,[22]



or oxo-bridge formation, $(bpy)_2(py)RuORu(H_2O)(bpy)_2^{4+}$.[11] The same product appears to be accessible through the monomeric analog since Moyer reports the appearance of a new wave at 0.63 V in solutions containing $(bpy)_2(py)Ru^{II}H_2O^{2+}$ after an extended period of time in 1 M HNO_3.[11]

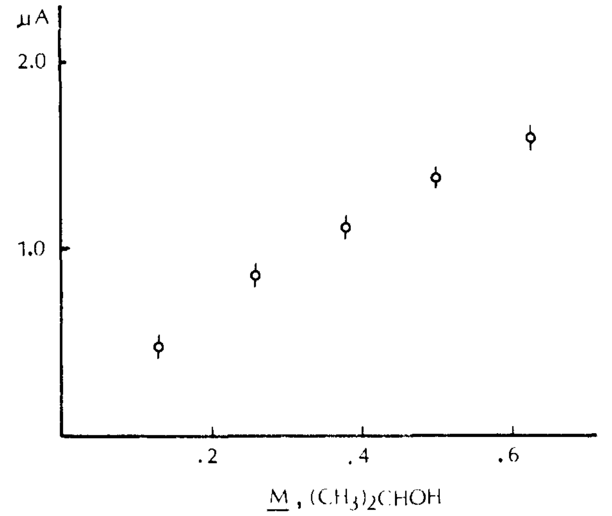


Figure 8. Catalytic steady-state currents as a function of substrate concentration, $[(CH_3)_2CHOH]$, at pH 7.4 for a metallopolymer-coated electrode (~10 layers) potentiostated at 0.85 V vs. SSCE.

Catalytic Oxidations. In a homogeneous electrocatalytic experiment using $(trpy)(bpy)RuO^{2+}$,[4c] it has been shown that the oxidation of 2-propanol to acetone occurs quantitatively (eq 5).

$$(CH_3)_2CHOH \xrightarrow[-2H^+]{-2e^-} (CH_3)_2C{=}O \quad (5)$$

Our initial goal was to develop an oxidatively catalytic electrode based on electrode-bound $Ru^{II}{=}O$ sites. In fact, we have observed catalytic oxidation currents in the presence of 2-propanol, *p*-toluic acid, or the mixed xylenes as substrates all of which had been shown previously to be oxidized catalytically by $(trpy)(bpy)RuO^{2+}$. The oxidation of 2-propanol was examined in the greatest detail.

The majority of the electrocatalytic experiments were carried out by using a glassy carbon electrode of surface area 0.146 cm² which had been coated with varying coverages of the polymer. In a typical experiment with $[(CH_3)_2CHOH] = 0.4$ M and the solution pH > 4, a catalytic current of ~1 μA was observed. The magnitude of the catalytic current was essentially independent of film thickness in the range of 1–20 layers. The lack of a dependence of film coverage suggests that a restricted number

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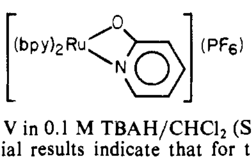
(20) Untereker, D. F.; Bruckenstein, S. *Anal. Chem.* **1972**, *44*, 1009.

(21) Curtis, J. C., work in progress. Roder, P.; Ludi, A.; Chapuis, G.; Schenk, K. J.; Schwarzenback, D.; Hodgson, K. O. *Inorg. Chim. Acta* **1979**, *34*, 113.

(22) For the complex,



$E_{1/2}(Ru^{III}/Ru^{II}) = 0.77$ V in 0.1 M $TBAH/CHCl_2$ (Simmons, Miriam, unpublished results). Initial results indicate that for the complex, $[(bpy)_2(py)Ru^{II}(Opy)]^{2+}$, $E_{1/2} \simeq 1.12$ V under the same conditions (Samuels, G. J., unpublished results).

of the redox sites in the film are accessible as oxidation sites, presumably only those sites on the surface. Considering the pH encapsulation effect described earlier, this conclusion is not unreasonable. It is also known from kinetic and mechanistic studies that there are rather severe microscopic constraints on the oxidation of 2-propanol by (trpy)(bpy)RuO^{2+}.[23] For example, when the rate constants for the oxidation of $(CH_3)_2CHOH$ are compared with those of $(CD_3)_2CDOH$, the kinetic isotope effect is ~18. The microscopic sensitivity of the oxidation mechanism, a lack of permeability of the substrate into the film, and the difference in medium properties between aqueous solution and the interior of the film may all play a role in explaining the observed site selectivity. A small but noticeable (~10%) increase in catalytic current was observed at pH 2 (H_2SO_4) perhaps consistent with an "opening" of the electrode film. However, under these conditions the thicker films are slowly leached from the surface.

As shown in Figure 8, the magnitude of the catalytic currents for the oxidation of 2-propanol increases with increasing 2-propanol concentration. The homogeneous oxidation of 2-propanol by (trpy)(bpy)RuO^{2+} has been found to be first order in both Ru(IV) and alcohol.[23] The beginning of a saturation effect can be observed in Figure 8 at high alcohol concentrations. The saturation effect suggests that if the mechanism remains the same on the film, the composition of the environment around the redox sites may be rich in alcohol compared to the case for bulk solution or perhaps that at high 2-propanol concentrations the rate-limiting step is changing from oxidation of substrate to reoxidation of the redox sites at the surface of the films.

The observed catalytic currents increase with increasing surface area of the electrode. An increase to ~100 μA under conditions identical with those above was observed when films were adsorbed on a medium porosity reticulated vitreous carbon electrode with a 2-cm^3 working volume. At pH >6 the electrode films are apparently stable to dissolution from the electrode surface. A typical half-life of the catalytic current is greater than 30 turnovers on the basis of the total number of ruthenium sites in the film.

The experiments described here are, in the end, limited by the reaction described in the previous section in which the redox sites in the films are converted into an unknown couple having $E_{1/2} \approx 0.63$ V. The ability of the film to catalyze the net electrochemical oxidation of 2-propanol is, however, impressive in some ways. Catalytic experiments with the homogeneous analogue, $(bpy)_2(py)RuO^{2+}$, show that on a per site catalytic turnover basis, the homogeneous system is less stable by a factor of at least 6. In the homogeneous case the decomposition pathway appears to be loss of a pyridyl group and oxo-bridge formation.[11] Although the problem of oxo-bridge formation appears to have been solved in the polymer film, the new pathway described above intervenes to limit the useful catalytic lifetimes of the film.

p-Toluic acid and a mixture of the xylenes, with added surfactant (0.02 M sodium dodecylsulfate), were also investigated as substrates. From the homogeneous electrocatalytic experiments it is known[4c] that with (trpy)(bpy)RuO^{2+} as the oxidant the substrate oxidation reactions are

$$\mathrm{CH_3C_6H_4CO_2^-} \xrightarrow[+2H_2O]{-6e^-,\,-7H^+} \mathrm{C_6H_4(CO_2)_2^{2-}}$$

$$\mathrm{C_6H_4(CH_3)_2} \xrightarrow[+4H_2O]{-12e^-,\,-14H^+} \mathrm{C_6H_4(CO_2)_2^{2-}}$$

The aromatic substrates gave catalytic currents of approximately one-fourth of those observed for 2-propanol at equivalent concentrations, but the reactions were not studied in detail.

Binding the catalyst in the film offers the advantages inherent in the chemically modified surfaces approach: (1) use of relatively small amounts of the catalytic reagent and (2) the conversion of a homogeneous system into a heterogeneous one with the possibilities for flow-through design. In the long run there may be additional advantages associated with substrate concentration effects in the films and with an inhibition of deleterious side reactions which lead to unwanted products or to the decomposition of the catalytic sites themselves. The observation of such a pathway here is discouraging since it limits the effective catalytic lifetimes of the films. However, given our ability to make designed chemical modifications at the redox sites in the film, we regard our initial observations as encouraging toward an ultimate goal of developing a series of chemically modified electrodes which have a high functional group specificity toward oxidation and/or reduction.

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[23] Thompson, M. S.; Meyer, T. J., manuscript in preparation.

Isomers and Isomerization: Elements of Redfield's Combinatorial Theory

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Abstract: Basic principles of Redfield's 1927 enumeration theory are reviewed. The theory is shown to incorporate, supersede, and simplify many of the last decade's developments in molecular combinatorics.

The past decade has witnessed a growing awareness of the applicability of discrete combinatorial structures to the precise formulation and understanding of broad classes of molecular phenomena. The chemically and mathematically classical problem of enumerating distinct isomers of specified composition of a molecular frame and the allied, more contemporary one of enumerating distinct reorganizational processes for those isomers have attracted many theoretical and experimental investigators.[1-8] It appears to have escaped notice that both problems can in large

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