culated from the equilibrium constant for the zinc citrate complex, was used in eq 22.

These results indicate that solvent extraction of metals using phenanthroline and related neutral chelating agents involve, first, the formation of a 1:1 complex in the aqueous phase. The location of further complex formation must depend on a balance between the equilibrium extractability of the 1:1 complex (which, in turn, depends on the lipophilicity of the ligand as well as the suitability of the counterion:e.g., CNS^-, ClO_4^-, NO_3^-, and I^- give more extractable ion pairs than do Cl^- of SO_4^{2-}) and the rates of formation of the higher complexes in the aqueous phase. Although the higher metal–phen complexes are unarguably more extractable than the 1:1 complex, the most dramatic increase in facilitating metal ion transfer occurs during the formation of the latter. It is not unreasonable to suppose that even with those chelating extractants yielding neutral chelates, β-diketones, 8-quinolinols, dithizones, etc., the cationic intermediate complexes can form an extractable ion pair when a suitable counterion is present. In such instances, suitable anions may enhance the rate of extraction.[14]

This work demonstrates the usefulness of current scan polarography at the ascending water electrode in characterizing transfer processes of interest in solvent extraction systems. Further work with other metal extraction systems is under way in our laboratory.

Acknowledgment. The project was supported by a grant from the National Science Foundation.

Appendix

If the limiting current of the current scan polarogram is completely determined by the mass-transfer process of the diffusing species from the bulk liquid phase to the electrode interface, the diffusion-controlled limiting current, i, can be formulated in the manner of the classical Ilkovič equation used for the analysis of polarograms at the dropping mercury electrode. The volume (V, cm^3) of one drop of the AWE is expressed in terms of the mean flow rate of the aqueous solution and the drop time as

$$V = mt = 4\pi r_o^3/3 \tag{A-1}$$

Assuming that the AWE is an ideal sphere at any time, the surface area, A, of the AWE can be given as

$$A = 4\pi r_o^2 - A_s = 4\pi(3mt/4\pi)^{3/2} - \pi r^2 \tag{A-2}$$

where A_s is the area shielded by the appreciably large inner diamter of the Teflon capillary and r_o and r are the radii of the AWE and the inner radius of the capillary, respectively. With use of the Cottrell relation as $i_\alpha = nFAD^{1/2}C/\pi^{1/2}t^{1/2}$, the diffusion current at the AWE can be expressed by

$$(3/7)^{1/2}i = nFD^{1/2}C\pi^{-1/2}t^{-1/2}\{4\pi(3mt/4\pi)^{2/3} - \pi r^2\} = (2.64 \times 10^5)nD^{1/2}Ct^{1/6}m^{2/3} - (1.71 \times 10^5)nD^{1/2}Ct^{-1/2}r^2 \tag{A-3}$$

which includes the correction term for the stretching effect of the AWE, i.e. $^7/_3$. The first term on the right hand side of eq A-3 has the conventional form, which is identical with the classical Ilkovič equation, and the second term is negligible if r is much smaller than r_o. From this equation, the diffusion coefficient of phen in the DCE phase can be calculated to be 9.6×10^{-6} cm^2 s^{-1} as shown from the diffusion-controlled current in Figure 1, curve 1.

Registry No. Cd, 7440-43-9; Zn, 7440-66-6; Co, 7440-48-4; Ni, 7440-02-0; phen, 66-71-7.

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Electrochemical Behavior of $Ru(trpy)(bpy)(OH_2)^{3+}$ in Aqueous Solution and When Incorporated in Nafion Coatings

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The rate at which the Ru(III) complex is electrooxidized is controlled by the kinetics of a chemical step that precedes the electrode reaction. Three candidate reactions for the chemical step were examined. Both disproportionation and deprotonation of the Ru(III) complex could be ruled out as the limiting reactions. Instead, it is proposed that the oxidation rate is limited by the rate of pH-dependent ligand-exchange reactions in which a ruthenium–nitrogen bond is broken. Graphite electrodes coated with Nafion incorporate the Ru(II) complex and exhibit high catalytic activity toward the electrooxidation of benzyl alcohol. Unfortunately the incorporated catalyst is converted into an inactive form after about 150 turnovers.

Meyer and co-workers have demonstrated in recent studies that polypyridyl complexes of ruthenium that contain at least one aquo ligand can be oxidized to the corresponding oxo complexes of Ru(IV).[1,2] These oxo complexes were shown to oxidize a variety of normally unreactive organic substrates, and under some conditions the reaction could be made catalytic.[3-5] Attempts to employ the ruthenium complexes as catalysts for the electrooxidation of organic substrates have also been reported.[4,6] The electrochemical oxidation of the ruthenium(II) complexes proceeds in two one-electron steps, the first of which is simple and fully reversible.[1] However, the second oxidation step, in which the Ru(III) complex is oxidized to the Ru(IV)–oxo complex, yields notably smaller currents than the step that precedes it.[1] This phenomenon has been attributed to a slow disproportionation of the Ru(III) complex that was presumed to be the nonelectrochemical mechanism by which the Ru(IV) complex was formed.[1]

We became interested in these complexes as possible candidates for incorporation in Nafion coatings on electrode surfaces where they could serve as redox catalysts for elec-

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[1] Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601; *Inorg. Chem.* **1981**, *20*, 436.

[2] (a) Thompson, M. S. Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC, 1981. (b) Takeuchi, K. J.; Samuels, G. J.; Gersten, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1407.

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trooxidations of organic substrates dissolved in solution. A similar approach in which the ruthenium catalyst was bound coordinatively to a poly(vinylpyridine) coating has been reported,[6] but it suffered from the apparent degradation of the bound catalyst because of the parallel oxidation of the poly(vinylpyridine) coating to which it was bound. We reasoned that such degradative side reactions might be avoided with perfluorinated Nafion coatings while the rate-limiting, presumably second-order, disproportionation reaction might be enhanced by the very high reactant concentrations that can be obtained by electrostatic binding within polyelectrolyte coatings.[7] The experiments described in this report were initiated to test these ideas with one of the complexes studied by Meyer and co-workers:[2a,3,4] $Ru(trpy)(bpy)(OH_2)^{2+}$ (trpy = 2,2′,2″-terpyridine; bpy = 2,2′-bipyridine). Our initial examination of the electrochemical responses exhibited by this complex at uncoated electrodes produced qualitative agreement with the previous brief report,[1] but the results were not consistent with a slow disproportionation reaction's limiting the magnitude of the current corresponding to the oxidation of the Ru(III) to the Ru(IV) complex. A more detailed study of the electrochemical behavior of the complex was therefore undertaken to try to identify the reaction that delays the electrooxidation of the Ru(III) complex. It was also of interest to establish the optimal experimental conditions for enhancing the rate at which the Ru(III) complex could be electrooxidized to the catalytically active Ru(IV) oxidation state.

Experimental Section

Materials. $[Ru(trpy)(bpy)(OH_2)](ClO_4)_2$ was prepared as described by Thompson.[2a] Solutions of the corresponding Ru(III) and Ru(IV) complexes in acidic media were prepared immediately prior to use by bulk electrolysis of $Ru(trpy)(bpy)(OH_2)^{2+}$ at a platinum-gauze electrode. All other chemicals were reagent grade and were used as received. Buffer solutions were 0.025 M. Solutions were prepared from laboratory deionized water that was passed through a purification train (Barnstead Nanopure). Prepurified argon was used to deaerate solutions. Electrodes were prepared from pyrolytic graphite (Union Carbide Co.) that was mounted to expose the base or the edges of the graphite planes as previously described.[7] Rotating disk electrodes were constructed from edge-plane graphite rods by sealing them to a stainless-steel shaft with heat-shrinkable polyolefin tubing (Alpha Wire Co.). The electrode areas were 0.17 or 0.34 cm^2. A 5 wt % solution of Nafion (equiv wt 1100) was obtained from C and G Processing Co. (Rockland, DE). A 0.5 wt % stock solution was prepared by diluting the original solution with isopropyl alcohol. Coatings were prepared by transferring 10 μL of the stock solution to a 0.34-cm^2 edge-plane graphite electrode surface and allowing the solvent to evaporate. The ruthenium complexes were incorporated in the coatings by soaking the coated electrode in dilute solutions (~1 mM) of the complex for 10–15 min.

Apparatus and Techniques. Cyclic voltammetry and rotating disk voltammetry were conducted with apparatus and procedures previously described.[8,9] Potentials were measured and are reported with respect to a sodium chloride saturated calomel electrode (SSCE). Experiments were conducted at the ambient laboratory temperature, 22 ± 2 °C. Spectra were recorded with a Hewlett-Packard Model 8450A spectrophotometer.

Results and Discussion

Cyclic Voltammetry of $Ru(trpy)(bpy)(OH_2)^{2+}$. The cyclic voltammetry of $Ru(trpy)(bpy)(OH_2)^{2+}$ resembles that reported for the analogous complex $Ru(bpy)_2(py)(OH_2)^{2+}$ (py = pyridine).[1] Between pH 2 and 11 two reversible voltammetric

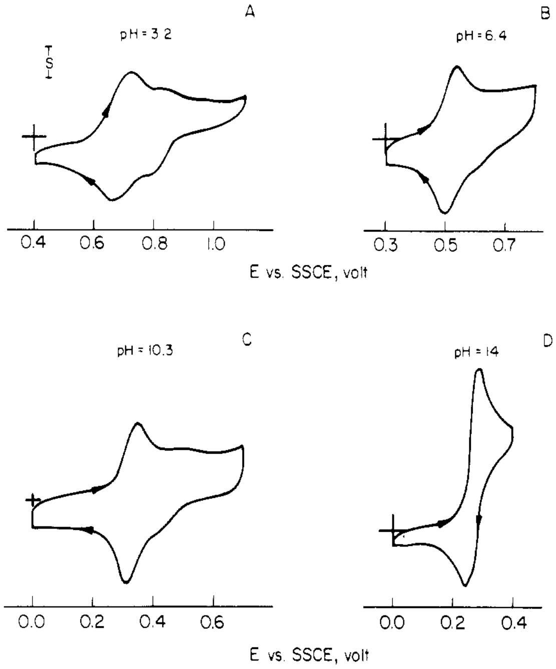

Figure 1. Steady-state cyclic voltammograms for solutions of $Ru(trpy)(bpy)(OH_2)^{2+}$ recorded at a basal-plane graphite electrode as a function of pH. Supporting electrolyte: sodium nitrate buffered with (A) phthalate, (B) phosphate, (C) carbonate, and (D) sodium hydroxide. Ionic strength: maintained at 1.0 M ($NaNO_3$). Sweep rate: 100 mV s^{-1}. Concentration of complex: (A, B, C) 0.58 mM, S = 25 μA; (D) 0.2 mM, S = 5 μA.

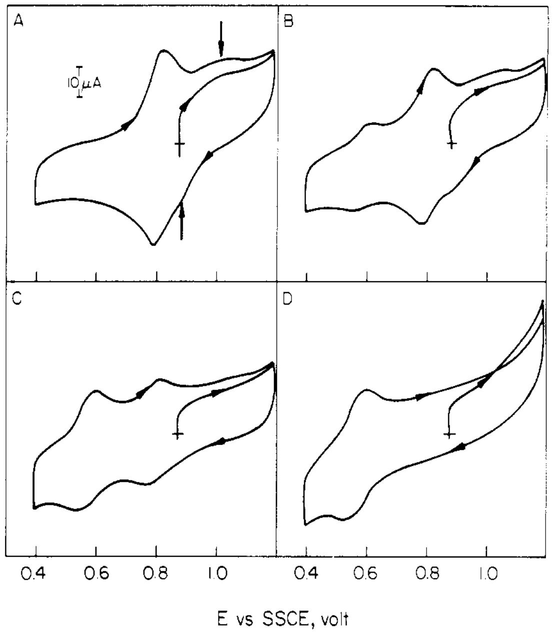

Figure 2. Cyclic voltammograms for 0.28 mM $Ru(trpy)(bpy)(OH_2)^{3+}$ at an edge-plane graphite electrode. Supporting electrolyte: (A) 0.95 M CF_3SO_3Na + 0.05 M CF_3SO_3H; (B, C, D) as in (A) except 0.088, 0.156, and 0.75 M $NaHSO_4$, respectively (successively substituted for the CF_3SO_3Na with ionic strength maintained at 1.0 M). Scan rate: 100 mV s^{-1}.

peaks are observed with significantly smaller peak currents for the Ru(III)/Ru(IV) couple that appears at the more positive potentials (Figure 1A). The response for the latter couple becomes quite indistinct at intermediate pH values (Figure 1B,C). The separation between the peak potentials decreases as the pH increases until, at pH values above 12, a single, reversible two-electron response is obtained.[1,2a] Understanding the chemistry responsible for the striking in-

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[8] Oyama, N.; Anson, F. C. *Anal. Chem.* **1980**, *52*, 1192. Shigehara, K.; Oyama, N.; Anson, F. C. *Inorg. Chem.* **1981**, *20*, 518.

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equality of the two sets of peak currents in voltammograms such as those in Figure 1 was a major goal of this investigation.

Anation of Ru(trpy)(bpy)$(OH_2)^{3+}$. Although cyclic voltammograms recorded in solutions of Ru(trpy)(bpy)$(OH_2)^{2+}$ are insensitive to the composition of the supporting electrolyte employed (at fixed pH), solutions of the corresponding Ru(III) complex are affected by the nature of the anions present. In Figure 2 is shown the effect of successive additions of bisulfate anion to a solution of Ru(trpy)(bpy)$(OH_2)^{3+}$ in a noncoordinating trifluoromethanesulfonic acid supporting electrolyte at pH 1.3. (The pK_a of the coordinated aquo ligand in the complex is between 1 and 2.[10] In the absence of HSO_4^- (Figure 2A), waves for the Ru(III)/Ru(IV) couple are barely discernible (they are identified by the arrows in Figure 2A) compared with the prominent response from the Ru(II)/Ru(III) couple. Addition of HSO_4^- (Figure 2B–D) causes a new couple to appear at a potential less positive than that of the original Ru(II)/Ru(III) couple. The new couple grows at the expense of the original couple until, in Figure 2D, only the new couple remains. Concurrent with the changes in the voltammetric responses, the visible absorption spectrum of the solution changes. The weak absorption maximum at 640 nm exhibited by Ru(trpy)(bpy)$(OH_2)^{3+}$ broadens and decreases in intensity. This pattern points to anation of Ru(trpy)(bpy)$(OH_2)^{3+}$ by HSO_4^- or SO_4^{2-}. The anated Ru(II) complex that is produced at the electrode surface by reduction of the corresponding Ru(III) complex is long-lived enough to produce an oxidation peak in the cyclic voltammograms recorded at a scan rate of 100 mV s^{-1}. However, with lower scan rates or in controlled-potential reductions the complex (presumably Ru(trpy)(bpy)(SO_4)) decomposes to the corresponding aquo complex. The apparent instability of the electrogenerated sulfato complex of Ru(II) is in accord with the lack of detectable anation when bisulfate anion was added to solutions of Ru(trpy)(bpy)$(OH_2)^{2+}$.

Behavior similar to that in Figure 2 was also encountered in the presence of hydrogen phthalate anion but not with nitrate or trifluoromethanesulfonate. Therefore, supporting electrolytes composed of the latter anions were employed to conduct rotating disk voltammetric experiments.

Rotating Disk Voltammetry. Solutions of Ru(trpy)(bpy)$(OH)^{2+}$ prepared by electrolytic oxidation of Ru(trpy)(bpy)$(OH_2)^{2+}$ underwent slow decomposition ($t_{1/2} \sim$ 24 h) to an unknown product. In addition, the proximity of the Ru(III)/Ru(IV) wave to the solvent limit and its small magnitude at most pH values introduced a significant error in measuring the limiting plateau currents. To avoid this complication, experiments with the rotating disk electrode were carried out with solutions of the Ru(II) complex even though our primary interest was in oxidation of the Ru(III) to the Ru(IV) complex.

Figure 3 contains two sets of current–potential curves for the oxidation of Ru(trpy)(bpy)$(OH_2)^{2+}$ at a rotating graphite-disk electrode in an acidic and in a basic supporting electrolyte. As expected on the basis of the pH dependences of the formal potentials of the Ru(II)/Ru(III) and the Ru(III)/Ru(IV) couples reported by Moyer and Meyer,[1] the two steps in the current–potential curves are more separated in the acidic than in the basic solution. Indeed, in the latter case, the two steps are merged together at the higher rotation rates because the height of the first wave increases more rapidly than the second. At pH values and rotation rates where the two steps were well separated, Levich plots[11] of the current on the plateau of the first wave vs. $\omega^{1/2}$ (ω is the electrode rotation rate) were linear and corresponded to a diffusion coefficient for the Ru(II) complex of 4.0×10^{-6} cm^2 s^{-1}. A typical example for a 1 M CF_3SO_3H solution is shown in Figure 4A.

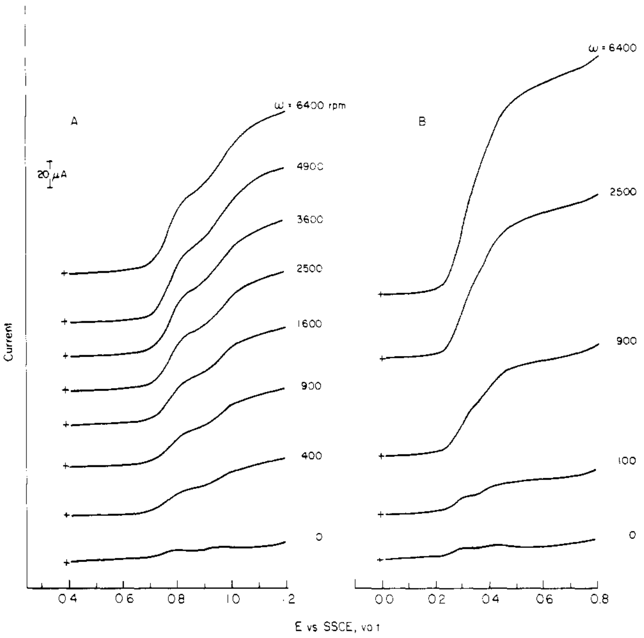

Figure 3. Current–potential curves for the oxidation of Ru(trpy)(bpy)$(OH_2)^{2+}$ at a rotating graphite-disk electrode: (A) supporting electrolyte 1.0 M CF_3SO_3Na + 0.01 M CF_3SO_3H, complex concentration 0.29 mM; (B) supporting electrolyte 1.0 M $NaNO_3$ adjusted to pH 10.85 (NaOH), complex concentration 0.31 mM. Scan rate: 5 mV s^{-1}. Electrode rotation rates are indicated for each curve.

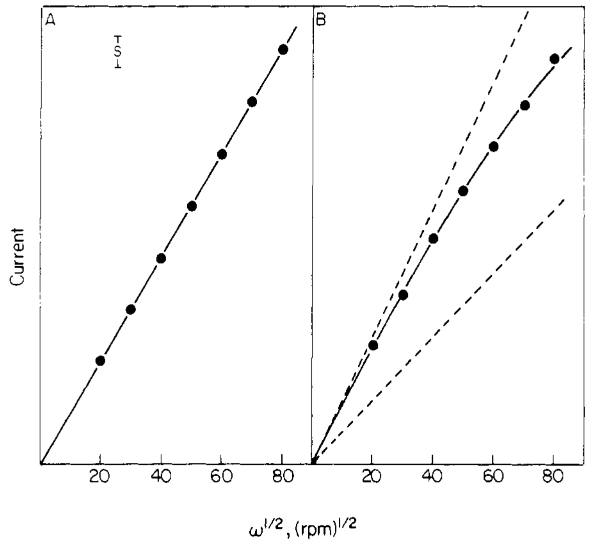

Figure 4. Levich plot of plateau currents for the oxidation of Ru(trpy)(bpy)$(OH_2)^{2+}$ vs. electrode (rotation rate)$^{1/2}$: (A) first oxidation wave, 0.25 mM complex in 1 M CF_3SO_3H, S = 15 μA cm^{-2}; (B) total current on plateau of composite wave, 0.31 mM complex in 1 M $NaNO_3$ at pH 10.85, S = 30 μA cm^{-2}, dashed lines calculated for a one- or two-electron diffusion–convection controlled process.

The total current measured on the second plateau (or the single plateau when only one wave was evident) was significantly smaller than expected for a two-electron oxidation and yielded nonlinear Levich plots (Figure 4B). This behavior signals the presence of a current-limiting chemical step prior to the removal of the electron from Ru^{III}(trpy)(bpy)$(OH)^{2+}$.

Kinetics and Mechanism of the Slow Chemical Step. To establish reaction mechanisms and extract rate constants from rotating disk current data such as those in Figure 4B, it is necessary to compare the measured currents with those calculated for various possible schemes for the overall electrode process. In the case of the closely analogous complex, Ru-

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(10) Meyer, T. J. *J. Electrochem. Soc.*, in press.

(11) Levich, V. G. "Physicochemical Hydrodynamics"; Prentice-Hall, Englewood Cliffs, NJ, 1962; Chapter VI.

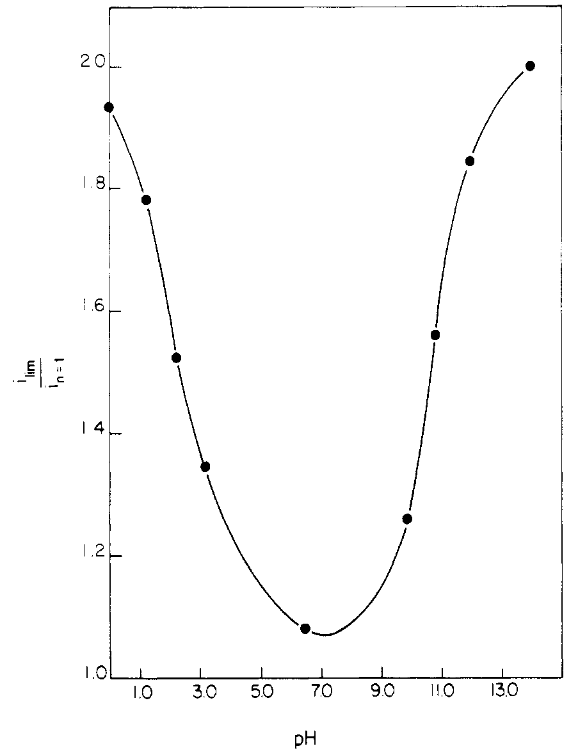

Figure 5. Normalized plateau currents for the oxidation of Ru(trpy)(bpy)$(OH_2)^{2+}$ at a rotating graphite-disk electrode as a function of pH. The ordinate is the ratio of the measured total plateau current to that for the one-electron diffusion–convection controlled oxidation of the same concentration of complex. Rotation rate: 6400 rpm. Ionic strength: 1.0 M.

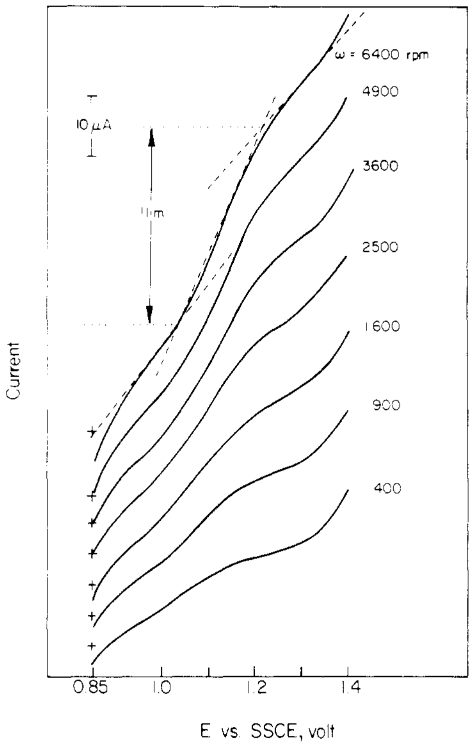

Figure 6. Current–potential curves for the oxidation of 0.32 mM Ru(trpy)(bpy)$(OH)^{2+}$ at a rotating graphite-disk electrode. Supporting electrolyte: 1 M CF_3SO_3Na adjusted to pH 1.9 (CF_3SO_3H). The procedure used to estimate values of i_{lim} is illustrated for the curve at ω = 6400 rpm.

$(bpy)_2(py)(OH_2)^{2+}$, which exhibits similar electrochemical behavior, Moyer and Meyer[1] suggested that the slow chemical step was the disproportionation of the Ru(III) complex to form the Ru(IV) product and regenerate the initial Ru(II) complex, which would thus be the only species oxidized directly at the electrode. The proposed reaction sequence is depicted in Scheme I.

Scheme I

$$\mathrm{Ru(II)} - e^- \rightleftarrows \mathrm{Ru(III)} \qquad (1)$$

$$2\mathrm{Ru(III)} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{Ru(II)} + \mathrm{Ru(IV)} \qquad (2)$$

The values of the two second-order rate constants, k_2 and k_{-2}, would control the magnitude of the plateau current obtained at the rotating disk electrode. The second-order character of reaction 2 prevents a closed-form solution of the combined kinetic–mass transfer problem posed by reactions 1 and 2. However, the problem can be treated by means of digital simulation.[12] The result of such an analysis is a set of calculated plateau currents at each electrode rotation rate that can be compared with the measured currents. To carry out the simulation it is necessary to have values of k_2 and k_{-2} as well as the diffusion coefficients of the reactants. The two rate constants are not known for the Ru(trpy)(bpy)$(OH)^{2+}$ complex, but a value of $k_{-2} = 2 \times 10^5$ M^{-1} s^{-1} has been reported for the closely analogous $Ru(bpy)_2(py)(OH)^{2+}$ complex.[13] Using this value of k_{-2} and the equilibrium constant for reaction 2 evaluated from the difference in the formal potentials of the two reversible waves in Figure 1, log $K_2 = 16.9(\Delta E^f)$, we calculated a value of k_2 of 1.05×10^3 M^{-1} s^{-1}. These two rate constants and the measured diffusion coefficient of 4.0×10^{-6} cm^2 s^{-1} were employed in the digital simulation program to calculate the expected disk current at a rotation rate of 100 rpm. (Higher rotation rates were not employed in the calculation because of the excessive calculation times required with the values of k_2 and k_{-2} involved.) The calculated total plateau current for a 0.33 mM solution of Ru(trpy)(bpy)$(OH_2)^{2+}$ was 12.6 μA cm^{-2} while the measured current was 22.5 μA cm^{-2}. Thus, the magnitude of the rotating disk plateau current appears quantitatively incompatible with disproportionation according to reaction 2 as the current-limiting step.

Additional qualitative evidence pointing to the same conclusion was obtained by measuring the pH dependence of the plateau current. In Figure 5, the ratio of the measured plateau current to the current for the simple one-electron oxidation of the complex is shown as a function of the pH of the solution. The magnitude of the current, which would be controlled by the rate of reaction 2 if Scheme I applied, exhibits a strong dependence on pH throughout the range where the kinetics of reaction 2 have been found to be independent of pH for the analogous $Ru(bpy)_2(py)(OH)^{2+}$ complex.[13]

Experiments were also conducted with the rotating disk electrode in solutions of Ru(trpy)(bpy)$(OH)^{2+}$ prepared by electrolytic oxidation of Ru(trpy)(bpy)$(OH_2)^{2+}$. The single oxidation wave obtained with such solutions was not well formed (Figure 6), which presented some difficulties in measuring the anodic plateau currents, but these were estimated as indicated in Figure 6. The measured currents were much smaller than those obtained on the first plateau for the oxidation of Ru(trpy)(bpy)$(OH_2)^{2+}$ and exhibited a nonlinear dependence on rotation rate. The anodic plateau currents to be expected if reaction 2 preceded reaction 1, instead of following reaction 1 as in Scheme I, were calcualted by means

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[13] Binstead, R. A.; Moyer, B. A.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2897.

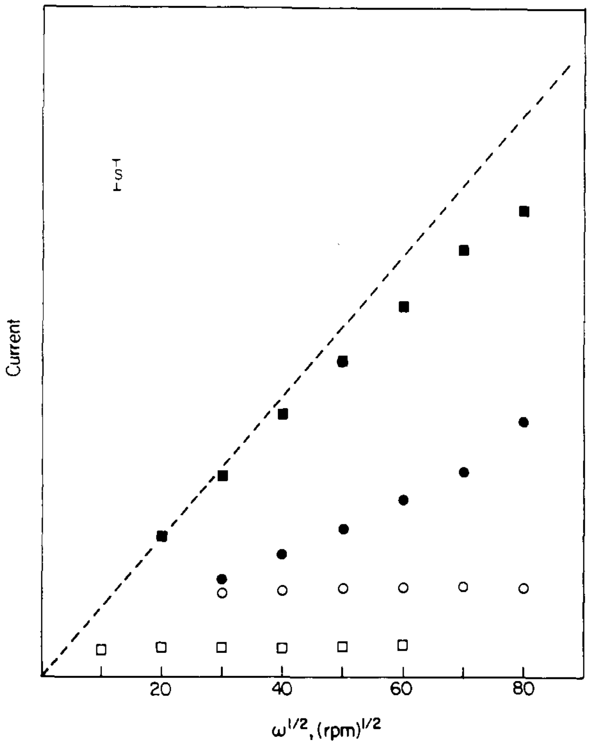

Figure 7. Levich plots for the oxidation of 0.33 mM Ru(trpy)(bpy)(OH)$^{2+}$ at rotating graphite-disk electrodes. Dashed line is that calculated for the diffusion–convection controlled reaction. Closed points indicate experimental plateau currents at pH 1.0 (■) and pH 3.3 (●). Open points indicate plateau currents calculated if reaction 2 (Scheme I) preceded reaction 1: (□) $k_2 = 1.05 \times 10^3$ M^{-1} s^{-1}; (○) $k_2 = 1.05 \times 10^4$ M^{-1} s^{-1}. $k_2/k_{-2} = 5 \times 10^{-3}$. Supporting electrolyte: CF_3SO_3H–CF_3SO_3Na at ionic strength 1 M.

of digital simulation. The simulation proved applicable to a wider range of electrode rotation rates than was true for Scheme I, and some calculated values of plateau currents vs. (rotation rate)$^{1/2}$ are shown in Figure 7. The value of k_2 used in the simulation was the known value for the Ru(bpy)$_2$(py)(OH)$^{2+}$ complex. The equilibrium constant governing reaction 2, $K_2 = 5 \times 10^{-3}$, was obtained from the difference in the formal potentials of the Ru(II)/Ru(III) and Ru(III)/Ru(IV) couples. The calculated currents are much smaller than the observed currents at all rotation rates. Even when k_2 was assumed to be 10 times larger than the known value for Ru(bpy)$_2$(py)(OH)$^{2+}$, the calculated currents (open circles in Figure 7) remained smaller than those observed. Thus, the rate of disproportionation of Ru(trpy)(bpy)(OH)$^{2+}$ appears to be too slow to account for the observed disk currents.

The measured plateau currents for the oxidation of Ru(trpy)(bpy)(OH)$^{2+}$ also did not respond to changes in the bulk concentration of complex in the ways expected for a second-order process such as reaction 2. For example, increasing the concentration of Ru(trpy)(bpy)(OH)$^{2+}$ from 1.84×10^{-4} to 5.78×10^{-4} M caused the ratio of the plateau current to the concentration of the complex at a rotation rate of 2500 rpm to remain essentially constant while the increase calculated from the digital simulation program was 141%.

The variety of experimental data that were incompatible with a current-limiting disproportionation reaction made it apparent that alternative current-limiting processes needed to be considered. The response of the plateau current to changes in the concentration of the Ru(III) complex pointed to a first-order current-limiting reaction. It therefore seemed reasonable to consider a generalized reaction sequence such as that shown in Scheme II for the case where the solution contains the Ru(II) complex.

Scheme II

$$\mathrm{Ru(II)} - e^- \rightarrow \mathrm{Ru(III)} \tag{3}$$

$$\mathrm{Ru(III)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Ru(III)}^* \tag{4}$$

$$\mathrm{Ru(III)}^* - e^- \rightarrow \mathrm{Ru(IV)} \tag{5}$$

The two anodic electrode reactions, (3) and (5), are written as irreversible steps because the data are obtained on the plateaus of the current–potential curves where the cathodic back-reactions are negligible no matter how intrinsically reversible the electrode reactions may be. Reaction 4 involves the conversion of the apparently unoxidizable Ru(III) complex into the form that can be oxidized, Ru(III)*. As written, Scheme II constitutes a so-called EC$_r$E mechanism[14] involving two electron-transfer steps (E) separated by a reversible chemical step (C$_r$). A theoretical analysis of the expected rotating disk currents as a function of k_f and k_b for the EC$_r$E mechanism is not available. However, as with the disproportionation mechanism of Scheme I, the expected disk currents can be calculated by means of digital simulation. To do so requires values of k_f and k_b so that it is necessary to identify reaction 4 more specifically. In basic supporting electrolytes, a conceivable candidate reaction is reaction 6. So

$$\mathrm{Ru(trpy)(bpy)(OH)^{2+}} + \mathrm{OH^-} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \mathrm{Ru(trpy)(bpy)O^+} + \mathrm{H_2O} \tag{6}$$

long as adequately buffered solutions are employed reaction 6 would behave as a first-order reaction governed by a pseudo-first-order forward rate constant, $k_6[\mathrm{OH^-}]$. We employed a digital simulation program appropriate for the EC$_r$E mechanism to calculate expected disk currents as a function of $k_6[\mathrm{OH^-}] = k_{\mathrm{obsd}}$ and the electrode rotation rate for assumed values of $k_6[\mathrm{OH^-}]/k_{-6} = K_6[\mathrm{OH^-}]$ between 10^{-2} and 10. To simplify the calculations the effect of the comproportionation reaction between the Ru(IV) and Ru(II) complexes within the Levich layer was ignored in the simulation because the concentrations and rotation rates employed were such that the reaction would not have had time to reach equilibrium. The fact that the rate constants obtained showed no dependence on the concentration of the complex is added evidence that the comproportionation reaction could be neglected. The working curves resulting from the simulation are plotted in Figure 8 in the format of $i_{\mathrm{lim}}/i_{n=1}$ vs. a dimensionless kinetic parameter for the various assumed values of $K_6[\mathrm{OH^-}]$. In part A are shown a set of experimental values of $i_{\mathrm{lim}}/i_{n=1}$ measured at pH 10.9. The data appeared to fit the curve for $K_6[\mathrm{OH^-}] = 1$ better than any of the other curves. By using this curve, reasonably constant values of k_{obsd} were obtained with an average of 1.3×10^2 s^{-1}. Since $k_{\mathrm{obsd}} = k_6[\mathrm{OH^-}]$, this value of k_{obsd} at pH 10.9 corresponds to $k_6 = 1.9 \times 10^5$ M^{-1} s^{-1}. To check that this value of k_6 was correct, a second set of measurements were conducted at pH 9.9 where the values of $i_{\mathrm{lim}}/i_{n=1}$ should correspond to the working curve for $K_6[\mathrm{OH^-}] = 10^{-1}$. The experimental points are compared with this working curve in Figure 8B. The large mismatch is evident. A similar disagreement resulted at other pH values. For example, at pH 9.6 the data points could be fit much better to the working curve for $K_6[\mathrm{OH^-}] = 1$ than to that for $K_6[\mathrm{OH^-}] = 10^{-1.3}$ (Figure 8C). However, the resulting value of k_6 (1.3×10^5 M^{-1} s^{-1}) is different from that obtained at pH 10.9. Furthermore, if the points are assumed to fall on the curve for $K_6[\mathrm{OH^-}] = 1$ at pH 9.6, it follows that the acid dissociation constant for Ru(trpy)(bpy)(OH)$^{2+}$, $K_a = K_wK_6$,

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[14] Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980; Chapter 11.

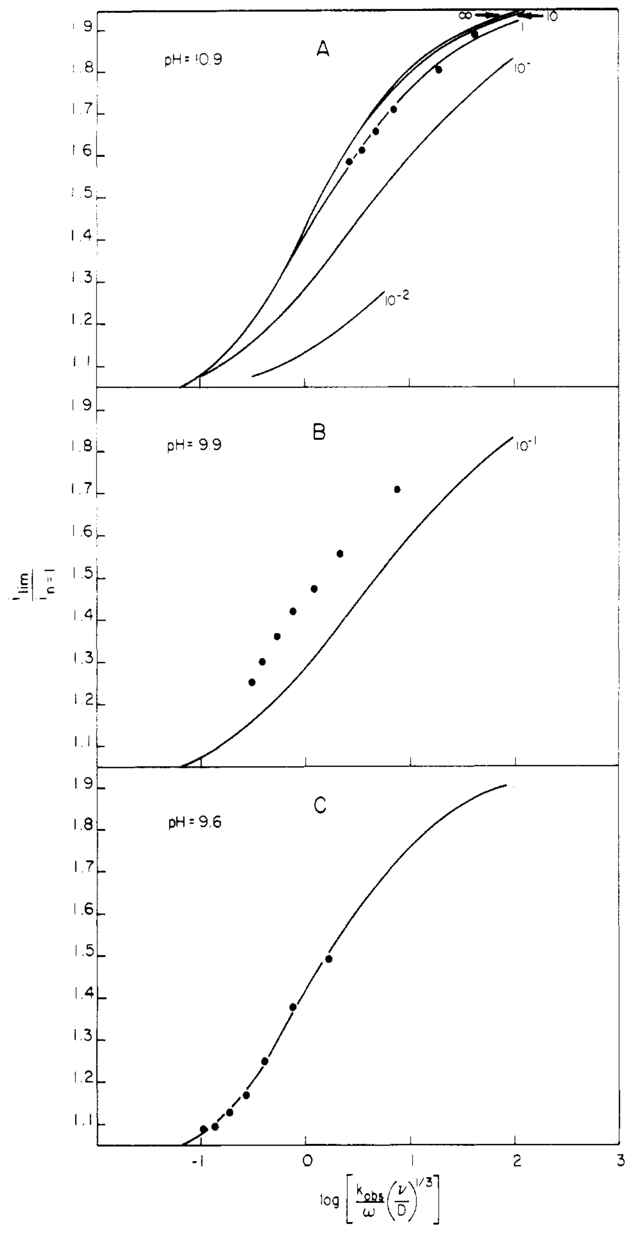

Figure 8. (A) Working curves simulated for Scheme II with reaction 6 as the slow chemical step. The abscissa is a dimensionless parameter composed of $k_{obsd} = k_6[OH^-]$ (reaction 6), ν, the kinematic viscosity of the solution (0.01 cm^2 s^{-1}), ω, the electrode rotation rate, and D, the diffusion coefficient of the complex (4 × 10^{-6} cm^2 s^{-1}). The ordinate is the ratio of the measured plateau current at each rotation rate to the corresponding one-electron Levich current. The number on each curve is the value of $K_6[OH^-]$. The points are experimental values of $i_{lim}/i_{n=1}$ measured at pH 10.9. They were positioned along the abscissa by horizontal transposition to obtain the best fit to the working curves. The best fit resulted with the curve for $K_6[OH^-] = 1$. (B) Comparison of experimental values of $i_{lim}/i_{n=1}$ for the oxidation of Ru(trpy)(bpy)(OH$_2$)$^{2+}$ measured at pH 9.9 with the working curve for $K_6[OH^-] = 10^{-1}$. The value of k_{obsd} used in plotting the points was set equal to 13 s^{-1}, i.e., one-tenth of the value obtained in part A. (C) Experimental values of $i_{lim}/i_{n=1}$ measured at pH 9.6 fitted (by horizontal translation along the abscissa) to the calculated working curve for $K_6[OH^-] = 1$.

must be greater than 10$^{-9.6}$ M. However, Binstead et al.[13] report no evidence for the deprotonation of Ru(trpy)(bpy)(OH)$^{2+}$ up to pH 12. Thus, the behavior shown in Figure 8 seems incompatible with reaction 6 as the current-limiting process.

The experimental data at all pH values could be fit quite well to the simple working curve that corresponds to an EC$_i$E mechanism where reaction 4 in Scheme II is irreversible instead of reversible. In Figure 9 experimental data for two pH values are plotted along with the working curve calculated from the equation of Karp.[15] The average values of k_{obsd} obtained from the working curve and the two sets of data were 92 and 5 s^{-1} at pH 10.9 and 9.6, respectively. The data obtained over the entire range of pH value investigated fit the Karp equation about as well as those shown in Figure 9. Curves calculated from Karp's equation neglect the comproportionation reaction between Ru(II) and Ru(IV). We believe this approximation is warranted for the reason given above.

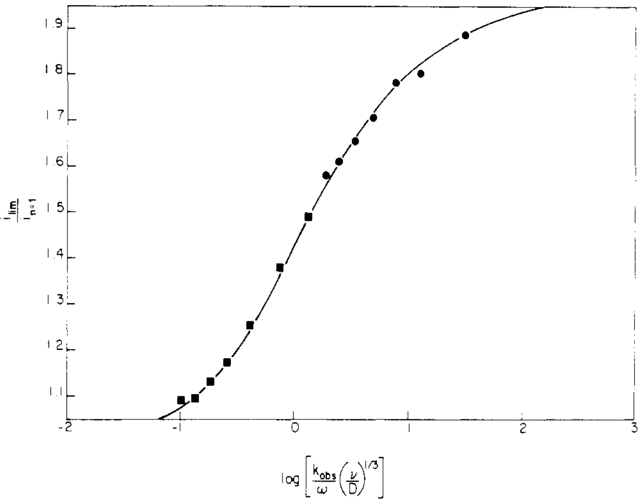

Figure 9. Comparison of experimental values of $i_{lim}/i_{n=1}$ for oxidation of Ru(trpy)(bpy)(OH)$^{2+}$ measured at pH 10.9 and 9.6 with the working curve for the EC$_i$E mechanism according to Karp:[15] (●) pH 10.9; (■) pH 9.6.

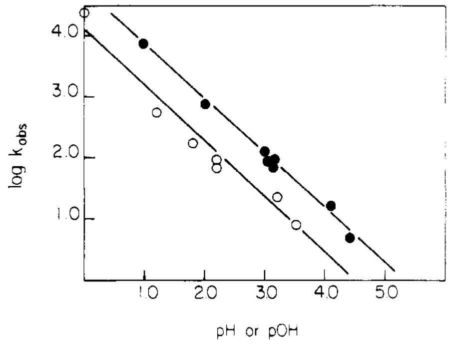

Figure 10. pH dependence of the observed rate constants: (○) acidic solutions, abscissa is pH; (●) basic solutions, abscissa is pOH. The points are experimental. The lines are drawn with unit slope.

The values of k_{obsd} obtained from working curves such as those in Figure 9 vary with pH. Figure 10 is a logarithmic plot of K_{obsd} vs. pH or pOH. The lines are drawn with unit slope, and the points are experimental. In basic solutions the irreversible current-limiting reaction is evidently first order in hydroxide ion. A possible current-limiting reaction that is compatible with the experimental data is the hydroxide-assisted breaking of one of the ruthenium–terpyridine bonds in Ru(trpy)(bpy)(OH)$^{2+}$.

$$\mathrm{Ru(trpy)(bpy)(OH)^{2+} + OH^- \rightarrow Ru(trpy\text{-}N)(bpy)(OH)_2^{+}} \quad (7)$$

The resulting dihydroxyruthenium(III) complex might be more easily oxidized to the ruthenyl complex because the accompanying loss of H$_2$O would be facilitated. The proposed dihydroxyruthenium(III) complex would have to revert spon-

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(15) Karp, S. *J. Phys. Chem.* **1968**, *72*, 1082.

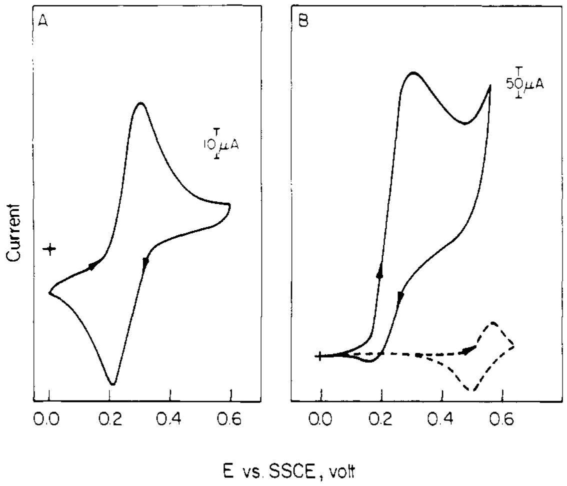

Figure 11. Cyclic voltammograms for 1 × 10^{-8} mol cm^{-2} of Ru(trpy)(bpy)(OH$_2$)$^{2+}$ incorporated in a Nafion coating containing 1.3 × 10^{-7} mol cm^{-2} of sulfonate groups (scan rate 100 mV s^{-1}; basal-plane graphite electrode (0.17 cm^2)): (A) supporting electrolyte 0.1 M CF_3SO_3Na + 0.1 M NaOH (steady-state response); (B) supporting electrolyte plus 0.1 M benzyl alcohol (solid line, first scan; dashed line, response remaining after six complete cycles).

taneously to the more stable complexes from which it is formed, but if this reversion required more time than it took for the complex to diffuse across the Levich layer at the rotating disk electrode (~0.03 s at ω = 2500 rpm), reaction 7 would appear irreversible.

The profile of limiting current (i.e., reaction rate) vs. pH in Figure 5 shows that the rate increases in acidic as well as basic solutions. Attempts to fit the data in acidic electrolytes to a reversible current-limiting reaction (e.g., protonation of Ru(trpy)(bpy)(OH)$^{2+}$) were also unsuccessful. However, the data could be accommodated reasonably well to the working curve for an irreversible reaction (Figure 9). The resulting values of k_{obsd} exhibit a linear dependence on [H$^+$] (Figure 10) so that a reaction such as (8) is suggested where (trpy-NH$^+$) represents a bidentate terpyridine ligand with a proton on the uncoordinated nitrogen atom. Thus, the rotating disk kinetic data in both acidic and basic media lead us to the speculation that the oxidation of Ru(trpy)(bpy)(OH)$^{2+}$ is preceded by a proton or hydroxide ion assisted ligand-exchange reaction.

$$\mathrm{Ru(trpy)(bpy)(OH)^{2+} + H^+ \rightarrow Ru(trpy\text{-}NH^+)(bpy)(OH)(OH_2)^{3+}} \quad (8)$$

Behavior of Ru(trpy)(bpy)(OH$_2$)$^{2+}$ at Nafion-Coated Electrodes. In common with other polypyridine–metal complexes,[7c,16] Ru(trpy)(bpy)(OH$_2$)$^{2+}$ is readily incorporated by coatings of polyanionic Nafion on graphite electrodes. The complex is held quite tenaciously by the coating so that its electrochemical behavior within the coating can be oberved with the coated electrode immersed in pure supporting electrolyte solutions. A cyclic voltammogram for the incorporated complex is shown in Figure 11A. The response resembles that observed at the same pH in homogeneous solution of the complex at a bare graphite electrode. (Significant differences in the voltammetric responses of the incorporated and unincorporated complex appear in neutral and acidic supporting electrolytes, but we focused on alkaline electrolytes in this study.)

Meyer and co-workers have established that in the catalytic oxidation of organic substrates by ruthenium–polypyridine complexes it is the Ru(IV) complex, e.g., Ru(trpy)(bpy)O^{2+}, that is the active catalyst.[3-5] Therefore, to utilize the complex incorporated in Nafion coatings as a catalyst for electrooxidations it is desirable to choose conditions that allow the electrooxidation of Ru(trpy)(bpy)(OH$_2$)$^{2+}$ to Ru(trpy)(bpy)O^{2+} to proceed at a high rate at the least positive potentials. These criteria and the results summarized in Figure 5 point to a supporting electrolyte having pH 12 or higher as optimal.

The Ru(IV) appeared to decompose at a modest rate to unknown products at pH values above 12, but if the electrode potential was maintained at values where the complex remained as Ru(II) until a catalytic oxidation was attempted, pH values as high as 13 proved useful. At pH 10 the electrochemical response obtained from Ru(trpy)(bpy)(OH$_2$)$^{2+}$ within Nafion coatings immersed in the pure supporting electrolyte remained unchanged for several days. At pH 13 the response decreases slowly because of the slow loss of Ru(trpy)(bpy)(OH)$^+$ (the resting form of the catalyst at pH 13) from the Nafion coatings by reverse ion exchange.

The Nafion coatings apparently provide a more stable polymeric environment for binding the oxidized complexes to electrode surfaces than the poly(vinylpyridine) coatings that were previously employed for this purpose.[6] Changes in the cyclic voltammograms that were attributed to possible oxidation of the polymer were reported with poly(vinylpyridine) coatings.[6] No similar phenomena were observed within Nafion coatings even when the incorporated complex was cycled repeatedly between the IV and II oxidation states. Thus, Nafion coatings may offer general advantages for attaching highly oxidizing electrocatalysts to electrode surfaces.

The catalytic utility of Nafion–Ru(trpy)(bpy)(OH)$^{2+}$ coatings was examined by holding the electrode potential at 0.5 V in a pH 13 supporting electrolyte that also contained 0.1 M benzyl alcohol. Enhanced currents corresponding to the catalyzed oxidation of the alcohol were obtained. The currents were much larger than those that resulted at the pH values (6.5–7) employed by Samuels and Meyer,[6] but regardless of the pH, the current decayed to near zero within a few minutes. Approximately 150 turnovers by each ruthenium complex in the coating were obtained before the demise of the catalyst.

The cause of the loss of catalytic activity can be discerned from the cyclic voltammograms shown in Figure 11B. At the same time as the catalyst serves to oxidize the benzyl alcohol it is gradually converted into a new, catalytically inactive form of unknown structure that exhibits a reversible voltammetric response near 0.55 V. Once all of the catalyst has been transformed into this new species, the catalytic oxidation of alcohols ceases. The transformation of the active catalyst into the inactive form requires that the ruthenium center be oxidized. There is no loss of initial catalytic activity in the presence of benzyl alcohol when catalyst-coated electrodes are maintained at potentials where the ruthenium remains as Ru(II).

Although the nature of the catalytically inactive species was not pursued in detail, it was possible to monitor its formation spectrally by preparing a Nafion coating on a transparent tin oxide electrode. The initial spectrum of the Ru(trpy)(bpy)(OH$_2$)$^{2+}$ complex incorporated in the coating exhibited an absorption maximum at 485 nm. After the coated electrode was used to electrooxidize benzyl alcohol until the catalyst had become inactive, the absorption maximum had shifted to 502 nm and its magnitude was ca. 65% as great.

The loss of catalytic activity is not irreversible. The activity is restored spontaneously if the coated electrode is allowed to

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(16) (a) Martin, C. R.; Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4817. (b) White, H. S.; Leddy, J.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4811. (c) Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 5007.

stand for several hours in a buffer solution at pH 6.4. The initial cyclic voltammetric response of the coating in the absence of substrate is also restored to its initial state. The catalytic activity can be recovered somewhat more rapidly at lower pH values, but we found no conditions where the restoration rate was close enough to the rate of catalyst degradation to prevent the loss of activity of the catalyst.

Conclusions

The slow chemical transformation that converts $Ru(trpy)(bpy)(OH)^{2+}$ from an unoxidizable into an oxidizable form has been argued to involve the replacement of a Ru(III)–terpyridine bond with a $Ru(III)–OH_2$ or Ru(III)–OH bond. Both the disproportionation of the Ru(III) complex and reversible proton-transfer reactions were ruled out as reactions that limit the rate of the transformation. $Ru(trpy)(bpy)(OH)^{2+}$ incorporated in Nafion coatings on graphite electrodes produces very stable electrochemical responses that persist for many days in the absence of oxidizable substrates. The latter undergo catalytic electrooxidations at the coated electrodes, but the catalyst is gradually degraded until it loses its activity after about 150 turnovers. Catalyst activity can be restored, but conditions where it remained active for extended periods could not be found. Nafion coatings appear more attractive than previously examined polymers as a means for holding highly oxidizing complexes on electrode surfaces.

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Registry No. $[Ru(trpy)(bpy)(OH_2)](ClO_4)_2$, 16389-43-8; $Ru(trpy)(bpy)(OH_2)^{3+}$, 89463-61-6; $Ru(trpy)(bpy)(OH_2)^{2+}$, 20154-63-6; $Ru(trpy)(bpy)(OH)^{2+}$, 81971-63-3; $Ru(trpy)(bpy)(O)^{2+}$, 73836-44-9; OH^-, 14280-30-9; HSO_4^-, 14996-02-2; N, 7727-37-9; Ru, 7440-18-8; Nafion, 39464-59-0; graphite, 7782-42-5; benzyl alcohol, 100-51-6.

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Electrochemistry of the μ-Carbido Iron Tetraphenylporphyrin Dimer, $((TPP)Fe)_2C$, in Nonaqueous Media. Evidence for Axial Ligation by Pyridine

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The electron-transfer reactions of the μ-carbido iron tetraphenylporphyrin dimer, $((TPP)Fe)_2C$, were investigated by electrochemical and spectroscopic techniques. In CH_2Cl_2 two reductions and four oxidations were observed between −1.90 and +1.60 V vs. SCE. All reactions involved single-electron-transfer steps and were reversible on the cyclic voltammetry time scale. Addition of pyridine to oxidized and reduced solutions of $((TPP)Fe)_2C$ indicated the formation of both mono and bis adducts. Values of $\log \beta_2$ ranged between 7.7 ± 0.4 for $[((TPP)Fe)_2C(py)_2]^{2+}$ formation and 2.6 ± 0.4 for formation of $((TPP)Fe)_2C(py)_2$. A weak interaction of pyridine was also observed with $[((TPP)Fe)_2C]^-$. An overall oxidation–reduction mechanism is given in CH_2Cl_2/pyridine mixtures, and comparisons are made with ligand-binding properties of neutral and oxidized $((TPP)Fe)_2N$ and $((TPP)Fe)_2O$.

Introduction

Two iron porphyrins may be linked through a single bridging atom X:

$$(P)Fe{-}X{-}Fe(P)$$

where P = porphyrin and X = O, N, or C.[1] Most characterizations of these iron porphyrin dimers have involved μ-oxo complexes.[2] However, during recent years the structural and physicochemical properties of μ-nitrido[3-12] and μ-carbido[12-16] dimers have also generated considerable interest, especially in regard to the oxidation-state assignment of the iron center. The formal oxidation state is +3.5 for the $((TPP)Fe)_2N$ complex and +4 for the $((TPP)Fe)_2C$ species, but neither of these assignments is unambiguous, given the existing spectroscopic data. Also, for the diamagnetic μ-carbido dimer two resonance structures are possible:[1]

$$(P)Fe^{IV}{=}C{=}Fe^{IV}(P) \rightleftarrows (P)Fe^{II}{\leftarrow}{:}C{:}{\rightarrow}Fe^{II}(P)$$

The formalism of divalent iron best fits the solution spectroscopic data but does not agree with the Mössbauer spectra, which clearly indicate Fe(IV) at 131 K.[16]

Our own interest is in the redox properties and spectroscopic characterization of oxidized and reduced μ-oxo,[6,17,18] μ-ni-

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