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Cobalt Porphyrin Electrode Films as H_2 Evolution Catalysts

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Electrochemical characteristics have been investigated for cobalt porphyrins attached to electrodes in a variety of ways, with a view toward examining their utility as H_2 evolution catalysts. Cobalt *meso*-tetraphenylporphine (CoTPP) adsorbed on a glassy-carbon electrode (GCE) is electroactive but is desorbed at potentials sufficiently negative to reduce Co(II). Cobalt *meso*-tetrakis(2-aminophenyl)porphine (CoTAPP), covalently attached to a GCE, shows effective catalysis (turnover number 4/s) for reduction of neutral aqueous buffer, at potentials less than 0.2 V negative of the reversible H^+/H_2 potential. The reaction, however, leads to rapid loss of the porphyrin from the surface. A polymer film formed by condensing cobalt *meso*-tetrapyrid-4-ylporphine (CoTPyP) with *p*-xylyl α,α'-dibromide showed good electroactivity and a large catalytic current at the Co(II)/Co(I) potential, but electroactivity decreased appreciably with each cyclic voltammetric scan. The inactivated film appeared largely intact, however, as judged by spectrophotometry on transparent SnO_2 electrodes, indicating that inhibition of electron transfer resulted from microscopic changes at the electrode–film or film–electrolyte interfaces. Similar results were obtained with electropolymerized cobalt protoporphyrin films. Cobalt(II) *meso*-tetrakis(*N*,*N*,*N*-trimethylanilinium-4-yl)porphine (CoTMAP), which has a 4+ charge, was taken up by a Nafion-coated electrode film; the loaded film supported H_2 evolution upon electrolysis, at −0.95 V vs. a saturated calomel electrode (SCE) for 90 min without deterioration, but at a low rate, consistent with the poor electron-transfer characteristics observed for this film. When Nafion on SnO_2 is loaded with cobalt(II) *meso*-tetrapyrid-4-ylporphine (CoTPyP) in acid solution (tetracation) and then placed in pH 7.0 buffer, the absorption spectrum shows a slight blue shift, suggesting that neutral CoTPyP migrates into Nafion hydrophobic domains. In contrast, CoTPyP adsorbed from acid solution onto a sulfonated polystyrene film shows a marked blue shift and broadening of the absorption spectrum at pH 7, consistent with Co coordination by neutral pyridine from a neighboring porphyrin; a strong negative shift, of nearly 0.5 V, is also seen for the Co(III)/Co(II) redox couple.

Introduction

Chemically modified electrodes are under extensive study because of their promise for greatly improving the efficiency and selectivity of a wide variety of electrochemical processes.[1,2] Electroactive molecules have been attached to electrodes by direct adsorption, covalent attachment, electropolymerization, prepolymerization and deposition, and uptake by ion-exchange coatings. In the present work we examined several procedures for attaching cobalt porphyrins to electrodes, intending to catalyze the reduction of H_2O to H_2. In a companion study,[3] we have demonstrated that cobalt(I) porphyrins react with water extremely rapidly and that H_2 generation by water electrolysis is catalyzed by cobalt(I) porphyrins in solution; however, the electrode kinetics are dominated by adsorption phenomena. Although platinum is an effective catalyst for H_2 evolution, it seemed worthwhile to explore the development of a molecularly based hydrogen electrode in order to understand the requirements for catalysis. In addition, porphyrins, which absorb light strongly in the visible region, offer promise for combining photoactivity and catalysis in one molecule. Thus, it is conceivable that cobalt porphyrins bound to electrodes might afford a convenient route to light-driven H_2 production.

There are formidable problems, however, in the development of catalytic electrodes based on chemical modification. The catalytic layer must accommodate good electron-transfer kinetics with the electrode, via electron "hopping" or diffusion within the layer, while resisting mechanical or chemical degradation due to the reaction being catalyzed. Problems associated with these requirements are illustrated by the experiments described herein. As the exploration of different surface attachment schemes continues, it can be expected that better understanding of the interaction of electrocatalytic centers and the matrix will lead to improved design criteria for effective and durable catalytic films.

Experimental Section

The free-base porphyrins *meso*-tetraphenylporphine, *meso*-tetrakis(2-aminophenyl)porphine, and protoporphyrin IX dimethyl ester were purchased from Mid-Century Chemicals (Posen, IL) and metalated to form CoTPP, CoTAPP, and CoPP, respectively, by standard procedures.[4] The syntheses of the water-soluble porphyrins cobalt *meso*-tetrakis(*N*,*N*,*N*-trimethylanilinium-4-yl)porphine chloride (CoTMAP), cobalt *meso*-tetrapyrid-4-ylporphine (CoTPyP), and cobalt *meso*-tetrakis(methylpyridinium)-4-yl)porphine chloride (CoTMPyP) have been described in the preceding paper.[3] Electrochemical, UV-vis spectrophotometric, and gas chromatographic instrumentation and methods were discussed as well. All electrochemical potentials are referred to the saturated calomel electrode (SCE).

Glassy-carbon electrodes (GCE) obtained from Bioanalytical Systems (West Lafayette, IN) were used for most experiments. Glassy-Carbon disks (1-mm thickness; 5-, and 15-mm diameter) were purchased from Atomergic Chemetals (Plainview, NY) and could be spun for uniform coating and then sealed with heat-shrinkable tubing, from Ace Glass (Vineland, NJ), to the open end of glass tubing of comparable size. The construction of such electrodes has been described by Oyama and Anson.[5] Transparent electrodes, of tin oxide deposited on glass, were a gift from PPG Glass Industries (Pittsburgh, PA). Squares of this, cut to 1 cm on a side, were attached to a copper wire for external contact with conductive adhesive obtained from Acme Chemicals and Insulation Co. (New Haven, CT).

Spin coating of electrodes was performed with a precision balance spinner supplied by Headway Research (Garland, TX) set at 2000 rpm.

A Model 283 spectrophotometer from Perkin-Elmer (Norwalk, CT) was used to obtain IR spectra.

Toluene was refluxed over sodium metal for several hours and distilled in an argon atmosphere. Dimethyl sulfoxide (Me_2SO) was vacuum distilled twice from calcium hydride. Chloroform was dried over anhydrous calcium sulfate and distilled from a fresh batch of the drying agent in a nitrogen atmosphere. Absolute ethanol was used without further purification.

Poly(sodium *p*-styrenesulfonate) (poly-SS), obtained as a 20% w/v aqueous solution, and α,α'-dibromoxylene were purchased from Aldrich Chemical Co. (Milwaukee, WI). Nafion-125 was bought from C. G. Processing, Inc. (Rockland, DE) as a 5% w/v solution in ethanol. The anionic polymers, Nafion and poly-SS, were diluted to 0.5% w/v with their respective solvents before use. Thionyl chloride was distilled under nitrogen immediately preceding use.

CoTPP was adsorbed on to electrode surfaces by depositing microliter portions of a chloroform solution directly onto the electrode, followed by evaporation of the solvent under a stream of nitrogen.

CoTMAPP was covalently attached to a GCE, by a method analogous to that described previously by Lennox and Murray.[6,7] The GCE, after being polished with alumina, was held at oxidizing potentials in 1 M nitric acid, until oxygen bubbles were evident. The electrode was then placed in an oven at 140 °C for 1 h. The dried electrode was fitted into the neck of a three-neck boiling flask and refluxed in the presence of thionyl chloride, under nitrogen, for 2 h. Vacuum was applied to remove the excess thionyl chloride, and without exposure of the electrode surface

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to air, 20 mL of toluene containing 1 mg of CoTAPP was introduced by injection. The solution was then refluxed for 5 h, while the electrode was bathed. The electrode was used for electrochemical studies immediately after cooling.

A method adapted from Factor and Heinsohn[8] was employed to synthesize the copolymer poly(xylyl–CoTPyP) bromide. A 10^{-5} M solution of CoTPyP, previously dried in a vacuum desiccator, in 2:1 chloroform–ethanol was mixed with a twice as concentrated portion of dry α,α'-dibromoxylene and stirred under nitrogen. The liquid gradually turned cloudy over several hours. An IR band at 1200 cm^{-1} developed over this time period. The completion of the reaction was indicated when the magnitude of the peak height remained constant. Aliquots of the reaction mixture, usually several microliters, were pipetted onto electrode surfaces, and the solvent was evaporated under a gentle stream of nitrogen or the electrode was spun to evenly distribute the material.

Electropolymerized CoPP films were prepared according to the method of Macor and Spiro.[9,10]

Nafion and poly-SS films were prepared by evaporating the equivalent of 10 μL of solution/cm^2 of electrode area under nitrogen. The Nafion films were ready for metalation in about 10 min, but the poly-SS films required at least 1 h to dry so that they would maintain integrity during subsequent procedures. These films could be loaded with cationic porphyrins by soaking them in a 5 mM porphyrin solution for at least 15 min.

Results

A. Adsorbed Cobalt Tetraphenylporphine. In our initial experiment, cobalt(II) tetraphenylporphine (CoTPP) was dissolved in chloroform and a drop was evaporated onto a glassy-carbon electrode (GCE). When this electrode was immersed in aqueous electrolyte, its cyclic voltammogram (CV) showed a well-developed Co(III)/Co(II) wave, at +0.33 V vs. the saturated calomel electrode (SCE), showing electroactivity for the adsorbed molecules. Scanning to −1.0 V produced a large cathodic current, suggestive of water decomposition via Co(I), but electroactivity was abolished after one scan. We infer that the CoTPP molecules were desorbed upon H_2 generation.

B. Covalently Attached Cobalt *meso*-Tetrakis(2-aminophenyl)porphine. Lennox and Murray[6,7] have demonstrated the covalent attachment of CoTAPP to a GCE. Surface carboxylic acid groups were converted to the acyl chloride, which formed amide links to the free base upon refluxing in dry toluene, followed by metalation in dimethylformamide (DMF). In an attempt to increase the quantity of immobilized porphyrin we first electrochemically oxidized the GCE surface. Anderson and Lung[11] have previously shown that the extent of coverage for the analogous ferrocene attachment was dependent upon surface treatment although the electrochemical oxidation method was not tested. Following acylation, direct covalent attachment of CoTAPP by refluxing in toluene was thought to be less damaging overall than the attachment and final metalation procedure originally prescribed.[6,7] However, the coverage of approximately 20 electroactive monolayer equivalents[10] was comparable to those previously demonstrated. The modified electrode showed a reversible CV wave in dry Me_2SO at −0.83 V, as expected for the Co(II)/Co(I) couple (Figure 1). When placed in pH 7.0 aqueous phosphate buffer, this electrode exhibited a large cathodic current and no return wave, as expected for catalytic H_2 generation. The cathodic wave at pH 7.0 is approximately 10-fold greater than the Co(II) reduction wave in dry Me_2SO. Since the catalytic current was 500 μA, a turnover number of roughly 4/s is suggested. The reversible H^+/H_2 potential at pH 7.0 is −0.66 V vs. SCE, so that the overpotential in this experiment is less than 0.2 V.

On successive CV scans, however, the cathodic current decayed quite rapidly and reached background levels within a few scans. Apparently the covalent attachment is not stable under conditions where H_2 is formed.

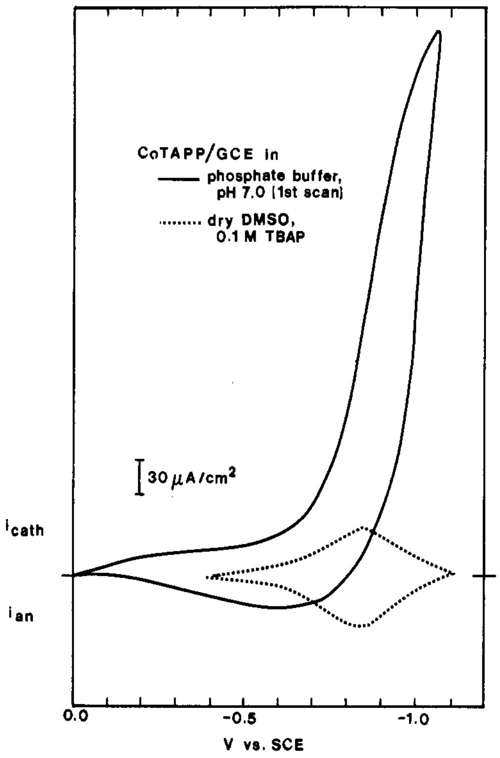

Figure 1. Cyclic voltammograms of CoTAPP linked covalently to a GCE (scan rate 50 mV/s).

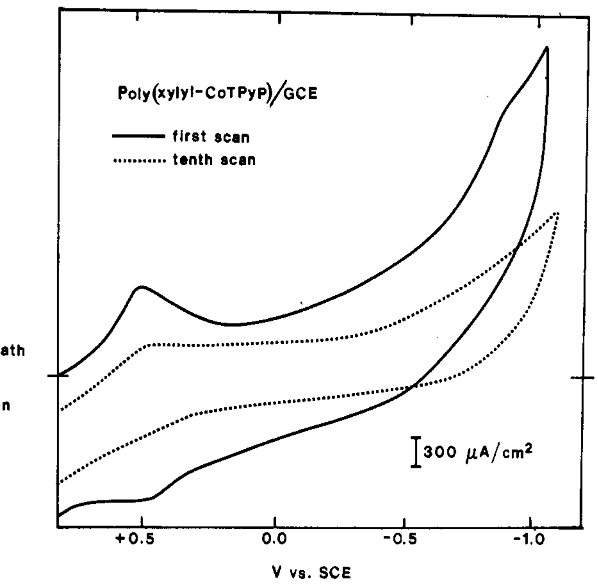

Figure 2. Cyclic voltammograms of poly(xylyl–CoTPyP) bromide on a GCE in acetate buffer, pH 4.8 (scan rate 100 mV/s).

C. Cobalt *meso*-Tetrapyrid-4-ylporphine Copolymer. In an effort to produce a durable, thick electroactive film, we copolymerized CoTPyP with *p*-xylyl α-α'-dibromide to form a cross-linked pyridinium-based polycation. A similar technique has been used by several investigators[8,12,13] to form viologen polymers. Alkylation of the pyridine groups was confirmed by the IR absorption spectrum of the polymeric product, which showed a prominent band at 1200 cm^{-1} and a red-shifted Soret band (442 nm in 2:1 chloroform–ethanol) relative to that of CoTPyP (410 nm), as is also exhibited by Co^{II}TMPyP (428 nm).

When the polymeric porphyrin in chloroform–ethanol solution was evaporated onto a GCE and placed in contact with aqueous buffer (pH 4.8), the CV shown in Figure 2 was obtained. The Co(III)/Co(II) wave can clearly be seen at +0.5 V, and its am-

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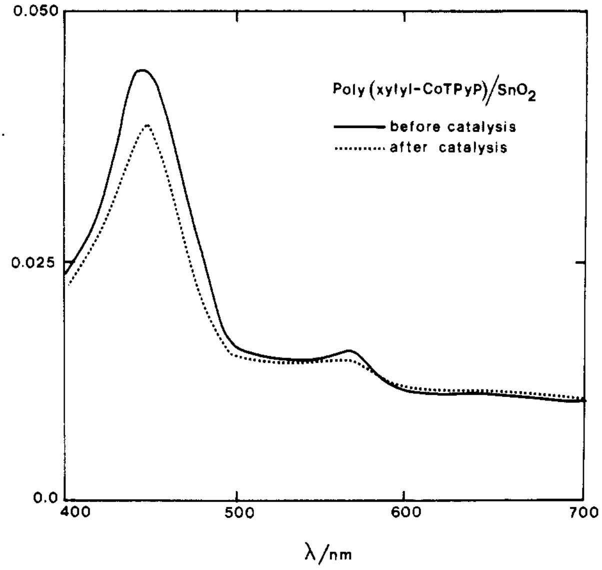

Figure 3. Visible absorption spectra of poly(xylyl–CoTPyP) bromide on a SnO_2–glass electrode.

plitude corresponds roughly to 100 monolayer equivalents (assuming a coverage of 1×10^{-10} porphyrin molecule per layer/cm^2),[10] although the large background current, presumably associated with charging of the polyelectrolyte, introduce a large uncertainty in this estimate. At −0.8 V one sees a large cathodic current, and no return wave, indicating catalytic H_2 production, as in the case of covalently bound cobalt porphyrin.

Again, successive scanning reduces the cathodic current, and by the tenth scan, it is diminished by a factor of 2 (Figure 2). Moreover, electroactivity is considerably decreased at the Co(III)/Co(II) wave as well. To check the film composition, we monitored this process via spectrophotometry at a transparent SnO_2 electrode. Similar CV's were obtained, and the absorption spectrum of the film before and after inactivation by scanning in aqueous buffer are shown in Figure 3. Although the amplitude of the Soret band (442 nm) is slightly reduced (15%) upon inactivation, there is no shift in its position or shape nor in that of the visible absorption band. Since the absorption spectrum is sensitive to most chemical influences, including porphyrin reduction and changes in cobalt ligation, we conclude that there is no chemical change in the bulk of the cobalt porphyrin units in the film and that only a small loss of material occurs from the film. Inactivation must, therefore, specifically inhibit electron transfer with the electrode, presumably via microscopic changes at the electrode–film interface or, conceivably, at the film–electrolyte interface. These changes might be chemical in nature (one or a few layers of chemically modified porphyrins would not show up in the spectrophotometric assay), or they might involve physical disruption of the electrode–film interface, perhaps via H_2 bubble formation, without separation of the entire film from the electrode.

D. Electropolymerized Cobalt Protoporphyrin. Work from this laboratory[9] has previously shown that a number of metal complexes of protoporphyrin IX, the most ubiquitous of the naturally occurring porphyrins, can be induced to undergo electropolymerization via the peripheral vinyl substituents, when the electrode is cycled to a potential sufficient to produce a porphyrin ring radical cation. These films show good electroactivity, although oxidative scanning in water led to rapid inactivation.[10] This was attributed to the susceptibility of the protoporphyrin methine bridges to oxidative attack.

We tested a cobalt protoporphyrin film for H_2 catalysis but again found inactivation upon reductive cycling, which was even more rapid than for the CoTPyP copolymer.

E. Cobalt Porphyrins in Nafion or Sulfonated Polystyrene Films. The instabilities encountered with porphyrin-based polymers led us to explore the utility of Nafion as a carrier for cobalt porphyrin electrocatalysts. Nafion is a sulfonated polyfluorocarbon that adheres well to electrode surfaces. It appears to have a domain structure, with hydrophilic polysulfonate pockets distributed among hydrophobic fluorocarbon regions.[14,15] These hydrophilic pockets can maintain access to the electrode surface, since multiply charged electroactive species, e.g. $Ru^{II}(bpy)_3^{2+}$ or methylviologen,[16] are electroactive when taken up into Nafion films.

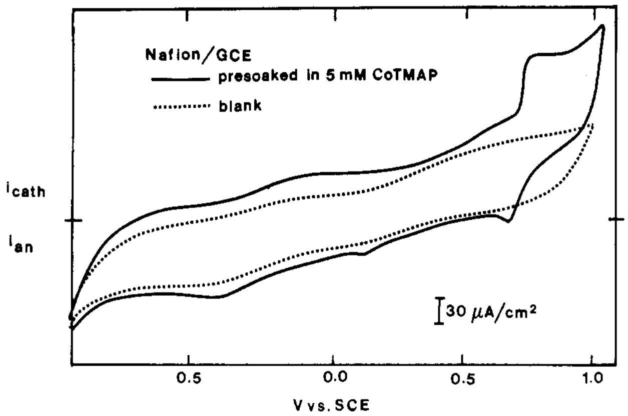

Figure 4. Cyclic voltammograms of a Nafion-coated GCE in 0.1 M TFA (scan rate 100 mV/s).

We found that positively charged cobalt porphyrins, such as CoTMPyP and CoTMAP, were avidly taken up by Nafion electrode films from 5 mM aqueous solutions, as judged by the deep colors produced and the absorption spectra of films on SnO_2. Electroactivity, however, was surprisingly poor. Figure 4 shows CV's of Nafion-coated GCE's in 0.1 M trifluoroacetic acid (TFA) with and without adsorbed CoTMAP. Electroactivity in the Co(III)/Co(II) region (approximately +0.3 V) is barely above background. A distinct cathodic current is seen, however, at the potential where Co(II) reduction is expected, around −0.8 V, although its amplitude is low; for example, it is about 10-fold lower than the currents seen for CoTPyP copolymer deposited directly on a GCE (see Figure 3).

Despite these low currents, H_2 was positively identified, via gas chromatography, as the product of electrolysis when CoTMAP–Nafion–GCE in 0.1 M TFA was potentiostated at −0.95 V. Ninety minutes of electrolysis produced 9×10^{-7} mol of H_2 for a 1.7-cm^2 electrode that was estimated to contain 3.4×10^{-8} mol (approximately 340 monolayers) of CoTMAP, as judged by spectrophotometry on a similarly treated SnO_2 electrode. The turnover number per Co in the film is, therefore, 26 for the 90-min run (0.005 turnover/s), although the turnover number for those few CoTMAP molecules in electrical contact with the electrode must be very much higher (the catalytic current corresponds to 6 monolayers/s).

The current was quite stable during the 90-min electrolysis, and afterward the electrode showed no signs of deterioration. The measured current efficiency was only 30%, but this may be associated with the low yield and the possibility of short-circuiting via diffusion of electrolyte from the auxiliary electrode compartment into the working electrode compartment during the lengthy run.

Buttry and Anson[15] have reported poor electroactivity for CoTPP-loaded Nafion prepared by uptake of the TPP diacid (2+ charge) followed by in situ insertion of Co. The lack of electroactivity, which could be remedied by coadsorption of an electronic relay molecule, $Ru(NH_3)_6^{2+}$, was attributed to migration of the neutral CoTPP into the hydrophobic regions of the Nafion. We examined the effect of charge on the porphyrin by adsorbing CoTPyP into Nafion from aqueous acid (pH 0), in which the pyridine groups are protonated, and then contacting the electrode with fresh acid or with pH 7.2 buffer. Electroactivity was minimal in both cases, but the absorption spectrum of the material coated

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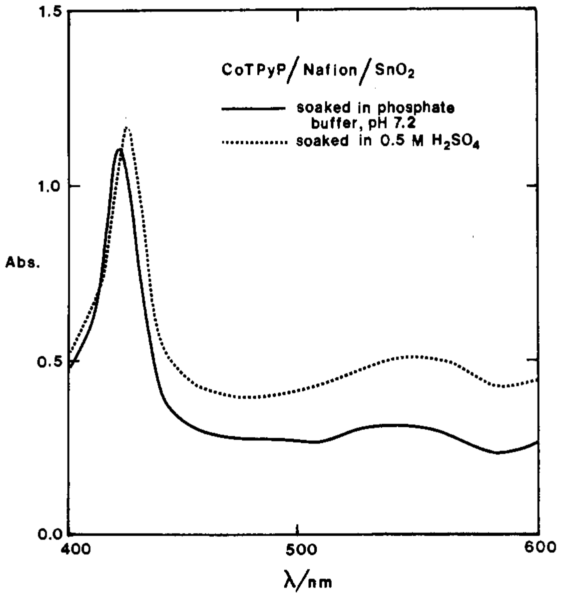

Figure 5. Visible absorption spectra of a SnO_2-glass electrode coated with Nafion, with CoTPyP incorporated.

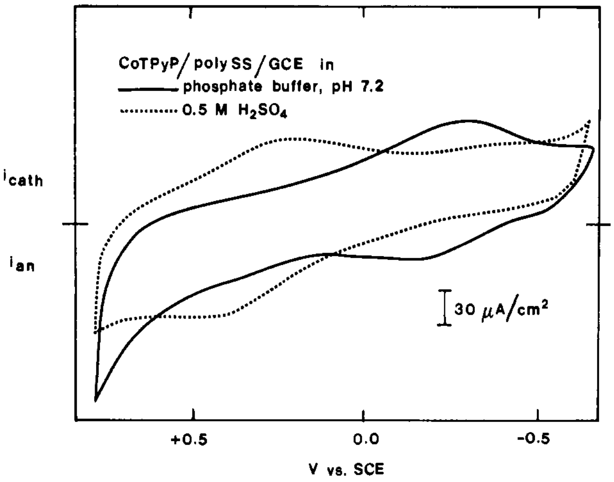

Figure 6. Cyclic voltammograms of a GCE coated with poly-SS, with CoTPyP incorporated (scan rate 100 mV/s).

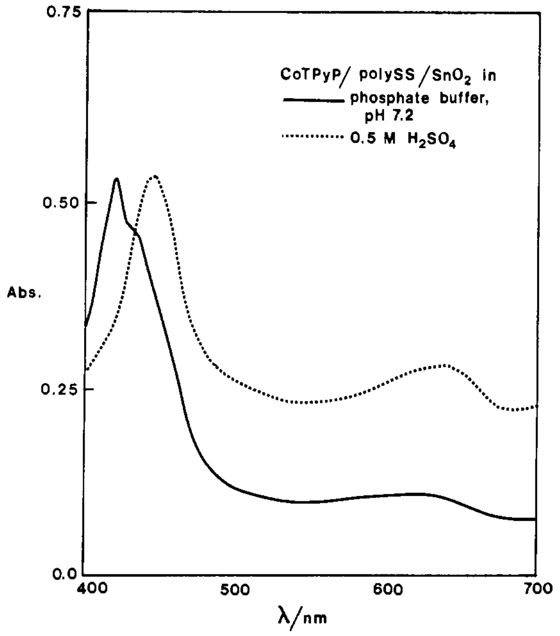

Figure 7. Visible absorption spectra of a SnO_2-glass electrode coated with poly-SS, with CoTPyP incorporated.

on SnO_2 showed a definite blue shift (426 → 422 nm) of the CoTPyP absorption band after the electrode was contacted with the neutral buffer, as shown in Figure 5. In 2:1 chloroform–ethanol solution, the Soret maximum for CoTPyP occurs at 410 nm while in acidic media it appears at 426 nm. Therefore, the shift of Nafion-incorporated CoTPyP with pH is consistent with deprotonation of the pyridinium units and partitioning of the CoTPyP into the hydrophobic region of the polymer. While the possibility exists that the porphyrin was not completely deprotonated at neutral pH, no further shifts were observed after transferring the coated electrode to pH 9.2 buffer. Nonetheless, the shift is not as large as expected and indicates other factors may be responsible for the observed spectra.

A quite different result was obtained when the same experiment was tried with a film of sulfonated polystyrene (one sulfonate group per styrene residue). In this case, electroactivity could be seen, albeit weakly, at the Co(III)/Co(II) potential, as shown in Figure 6. When the electrode was placed in contact with neutral buffer, this wave shifted strongly to negative potentials, from +0.3 to −0.2 V (Figure 6). Moreover, the Soret band of the absorption spectrum was strongly blue shifted (426 → 412 nm) at neutral pH, and a shoulder developed on the low-energy side, as shown in Figure 7. A similar blue-shifted Soret band (412 nm) and shoulder are seen for CoTPyP when dissolved in pyridine. We infer that, in the sulfonated polystyrene case, deprotonation of the pyridine groups is accompanied by coordination of the Co axial sites by the pyridine substituents of neighboring porphyrins. Consistent with this interpretation is the Co(III)/Co(II) potential shift, which is similar to that observed (+0.2 → −0.2 V) when pyridine is added to an aqueous solution of CoTMAP. In thiis experiment, desorption of neutral CoTPyP from the electrode film is presumably inhibited by its low solubility in water; coordination to an adjacent CoTPyP molecule within the film provides an energetically preferred environment. In Nafion, by contrast, partitioning into the hydrophobic domains seems to be preferred: these domains are presumably absent for the polystyrene film because of the high sulfonate content.

Although the electron-transfer characteristics were somewhat better for sulfonated polystyrene than for Nafion when loaded with cobalt porphyrins, the polystyrene films were considerably less durable, detaching readily from the electrode surface upon slight mechanical disturbance, and were unsuitable for studying H_2 generation.

Discussion

From the results of the accompanying study,[3] it is clear that cobalt porphyrins have the potential to be effective H_2-evolution catalysts. The oxidation of Co(I) by water is extremely rapid for these species, and the Co(II)/Co(I) potential covers a range, −0.65 to −0.85 V, that is only moderately more negative than the H^+/H_2 potential in neutral solution; at the positive end of this range (i.e. CoTMAP or CoTAPP), the overpotential at pH 7 is near zero. When CoTAPP is covalently attached to a GCE, it does indeed show good turnover characteristics in aqueous buffer at the Co(II)/Co(I) potential, but the attachment is disrupted during the reaction. Poly(xylyl–CoTPyP) films also show favorable electron-transfer and catalytic properties, but short lifetimes are again observed. There is no evidence for physical separation of the films nor for chemical alteration of the bulk of the cobalt porphyrin units in the film. The inhibition to electron transfer may result from microscopic changes, either chemical or physical, at the electrode–film or film–electrolyte interfaces. How fundamental this problem is remains unclear. Conceivably, the generation of H_2 gas at the electrode inevitably disrupts the interface with a film whose structure is based on the catalyst itself. On the other hand, further attention to the anchoring of the film to the electrode may lead to improved stability.

Nafion films are known for their stability and afford a high capacity for uptake of electroactive cations into the anionic pockets. We find that CoTMAP loaded onto Nafion supports H_2 evolution for an extended period of time, without deterioration of the film. The rate of evolution is very low, however, reflecting the poor electron-transfer characteristics of the film.

Slow electron transfer has also been noted for other electroactive agents in Nafion. While well-developed CV's are seen for cations like $Ru(bpy)_3^{2+}$, the peak widths and anodic–cathodic peak separations are far from showing the reversible characteristics of the solution species.[16] The kinetics of the electron transfer no doubt depends upon the structural details of the anionic pockets in the film. The electroactive agents must be free to diffuse to the electrode surface or else must be packed in an arrangement that allows for electron "hopping". In addition, counterions must migrate freely through the film. Evidently, one or more of these critical pathways are inhibited in the cobalt porphyrin-loaded films.

On the hypothesis that the highly charged (4+) $Co^{II}TMAP$ may reduce film mobility in Nafion by strong Coulombic attraction to the polymer-bound sulfonate groups, we explored the use of CoTPyP, whose charge can be adjusted by varying the solution pH. At low pH, the cationic porphyrin was satisfactorily taken up by the Nafion and electron transfer was slow. At neutral pH, electron transfer remained slow and the absorption spectrum showed evidence that the neutral porphyrin was migrating to hydrophobic regions of the Nafion, as suggested for CoTPP by Buttry and Anson.[15] Thus, the attempt to improve electroactivity by loosening the charge interactions was thwarted by partitioning with the hydrophobic domains. The uniqueness of Nafion in this regard is emphasized by the behavior of sulfonated polystyrene in the same experiment. In this case, neutralization of the charged CoTPyP in the film led to coordination of Co by the pyridine groups of the adjacent porphyrins, producing a prominent blue shift in the optical Soret band, and a negative shift of the Co(III)/Co(II) redox potential. Unfortunately, this behavior is unhelpful with regard to H_2 generation, since the same intermolecular coordination shifts the Co(II)/Co(I) potential to more negative values, thereby reducing the effectiveness of this couple in water-reduction catalysis.

Thus, although the present experiments demonstrate the feasibility of H_2-evolution catalysis by electrode-bound cobalt porphyrins, the problem of finding a suitable substrate that affords favorable electron-transfer characteristics and resistance to inactivation during the H_2-generation reaction has yet to be solved.

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Registry No. CoTPP, 14172-90-8; $CoTPP^+$, 38414-01-6; CoTAPP, 96481-61-7; $CoTAPP^-$, 96481-62-8; $CoTMAP^{4+}$, 80137-20-8; $CoTMAP^{5+}$, 79619-73-1; CoTPyP, 14244-55-4; $CoTPyP^+$, 61136-56-9; (CoTPyP)–(*p*-xylyl α,α'-dibromide) (copolymer), 96481-64-0; ($CoTPyP^+$)–(*p*-xylyl α,α'-dibromide) (copolymer), 96481-63-9; H_2, 1333-74-0; C, 7440-44-0; H_2O, 7732-18-5; TFA, 76-05-1; SnO_2, 18282-10-5; poly(sodium *p*-styrenesulfonate), 25704-18-1; Nafion, 39464-59-0.

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Reactions of Diborane with Aromatic Heterocycles. 3.[1] Diborane-Catalyzed Polymerization of Imidazole–Borane

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Imidazole–borane eliminates hydrogen in ether solution over a period of 1–2 weeks to form an air-stable polymer. The polymerization is catalyzed by excess diborane. The rate law is first order in diborane and first order in NH protons with a rate constant of 9.6 ± 0.5 M^{-1} s^{-1}. A possible mechanism for the reaction is discussed.

Introduction

Primary and secondary amine–boranes undergo oligomerization by hydrogen elimination (eq 1). Several authors have studied

$$n(RR'NH)BH_3 \rightarrow nH_2 + (RR'NBH_2)_n \qquad R' = R \text{ or } H \quad (1)$$

the mechanisms of such reactions of group 13[7] hydrides and generally have found the condensations to be bimolecular.[2,3]

As part of our program to examine the action of diborane on aromatic heterocycles, we had occasion to prepare imidazole–borane, observe its thermal polymerization, and study its behavior in the presence of excess diborane. In the course of this research we discovered that diborane *catalyzed* the polymerization of imidazole–borane in ether media at room temperature. The purpose of this paper is to report the results of our studies on the properties of imidazole–borane and its condensation polymer and to describe the kinetics of the diborane-catalyzed polymerization.

Experimental Section

Reagents. Diborane was prepared by the reaction of sodium borohydride with warm polyphosphoric acid. Imidazole (Aldrich) was reagent grade and was used without further purification. The solvent 1,2-dimethoxyethane (monoglyme) was purchased from Aldrich Chemical Co., purified by distillation from lithium aluminum hydride, and stored over this material is evacuated bulbs. When needed, the monoglyme was vacuum transferred directly into reaction vessels.

Spectra. Boron-11 NMR spectra were obtained with a Varian HA-100 spectrometer operating at 32.1 MHz. Chemical shifts are relative to the ethtyl ether complex of boron trifluoride, and downfield shifts are positive. Proton NMR spectra were obtained with a Varian T-60 spectrometer. Chemical shifts are in ppm downfield tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer 337 spectrophotometer.

Synthesis and Characterization of Imidazole–Borane. In a typical reaction a 0.110-g (1.61-mmol) sample of imidazole dissolved in 8 mL of monoglyme was allowed to react with 3.30 mmol of diborane for 5 min at room temperature. Removal of volatile materials left a colorless crystalline solid. Recovery of unreacted diborane showed a borane:imidazole ratio of 0.981. The product could be recrystallized under dry nitrogen by dissolving in fresh monoglyme and adding hexane; mp 93–94 °C. ^{11}B NMR (monoglyme): δ −19.0 (quartet), $J = 91$ Hz. ^1H NMR: δ 7.1 (s, 1 H), 7.2 (s, 1 H), 8.0 (s, 1 H), 11.6 (br s, 1 H). IR (film on KCl disk, in cm^{-1}): NH 3820 s; BH 2370 s, 2260 s, 2140 sh, m. Methanolysis of the adduct gave unaltered imidazole.

Polymerization of Imidazole–Borane. A monoglyme solution of imidazole–borane at room temperature evolves 1 equiv of hydrogen over a 2-week period; hydrogen evolution is faster if diborane is present. In a typical experiment a solution of 3.04 mmol of the adduct was prepared by reaction of imidazole with a slight excess of diborane of 1 min followed by rapid removal of volatiles and addition of 10 mL of fresh monoglyme. After 4 days at room temperature, 0.25 mmol of hydrogen had formed. At this point 0.43 mmol of diborane was added to the mixture, and after 20 h, 1.97 mmol of hydrogen was collected.

Characterization of the Polymer. The colorless, glassy, ether- and chloroform-soluble product gave only 4–5% of the expected hydrogen open methanolysis. Although initial reaction was rapid, further exposure and even prolonged boiling in concentrated hydrochloric acid failed to degrade the substance. Treatment with alkaline hydrogen peroxide gave unaltered imidazole after workup. IR (freshly prepared film on KCl plate, in cm^{-1}): BH 2400 vs, 2340 s, sh, 2275 m; no NH. After the film was exposed to air for 2 h, the IR showed an additional weak band at 3200 cm^{-1}. No further change in band intensity was observed over an 8-day period. ^1H NMR (monoglyme): δ 7.1 (s, 2 H), 8.0 (s, 1 H). ^{11}B

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