Inorg. Chem. **1998,** *37,* 1037−1043

(5,10,15,20-Tetramethylporphyrinato)cobalt(II): A Remarkably Active Catalyst for the Electroreduction of O_2 to H_2O

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Received October 10, 1997

Unlike most simple, monomeric cobalt porphyrins, the cobalt tetramethylporphyrin identified in the title catalyzes the electroreduction of O_2 to H_2O instead of H_2O_2. On graphite electrodes, coatings of the porphyrin prepared by irreversible adsorption from chloroform solutions catalyze the electroreduction of O_2 in aqueous $HClO_4$ at unusually positive potentials. Both the title porphyrin and the corresponding unsubstituted cobalt porphine are argued to derive their activity as four-electron reduction catalysts from their propensity to form dimers (or higher aggregates) in solution and, presumptively, on the surface of graphite electrodes.

In a recent communication, we reported the surprising finding that cobalt porphine, the simplest of all cobalt porphyrins, with no substituents on the porphyrin ring, is an active catalyst for the electroreduction of O_2 to H_2O at unusually positive potentials.[1] The unattractively low yields obtained in the synthesis of the porphine ligand and the propensity of cobalt porphine to undergo irreversible oxidation to produce a less active catalyst[1] led us to seek an alternative cobalt porphyrin that had comparable catalytic activity but that could be more easily prepared and was less subject to irreversible degradation. As the *meso* positions of the unsubstituted porphyrin ring of cobalt porphine were believed to be the likely sites of its irreversible oxidation, we chose to examine the otherwise identical cobalt porphyrin in which methyl groups were introduced at the 5-, 10-, 15-, and 20-positions of the ring. This (tetramethylporphyrinato)cobalt(II) complex, CoTMP, exhibited many of the attributes that we were seeking. Its electrochemistry and electrocatalytic activity toward the reduction of O_2, which have not previously been described, are the subject of this report.

Experimental Section

Materials. 5,10,15,20-Tetramethylporphine (TMP) was obtained from Porphyrin Products, Inc. (Logan, UT). Its purity was inspected using ^{1}H NMR. The spectrum of the as-received material was identical with that of a sample subjected to chromatography on an alumina column: δ (500 MHz; $CDCl_3$) 9.48 (s, 8H, H_β), 4.61 (s, 12H, *meso*-CH_3), 2.38 (s, 2H, −NH). The UV−vis spectrum of the TMP in CH_2Cl_2 agreed with a previously published spectrum.[2] Co(II) was inserted into the ring by mixing 25 mg of TMP with a 20% molar excess of cobalt acetate in 5 mL of DMF (EM Science) and bringing the mixture to reflux under Ar for 1 h. The resulting solution was cooled to room temperature and then in an ice−water bath. The dark crystalline solid that was precipitated was transferred to a Buchner funnel, washed successively with water, methanol, and hexane, and dried under vacuum. Yield: 77%. UV−vis: λ_{max} (in $CHCl_3$) 412, 538 nm.

All organic solvents were passed through a column of basic alumina (Brockman 1 Activated Basic) before use. Failure to do so sometimes resulted in oxidation of CoTMP samples exposed to the solvents. Laboratory-distilled water was further purified by passage through a purification train (MilliQ Plus). Other chemicals were of reagent grade and were used as received. Pyrolytic graphite rods with the edges of the graphitic planes exposed (Union Carbide Co.) were mounted to stainless steel shafts with heat-shrinkable polyolefin tubing (Alpha Wire Co.). The exposed graphite disk (0.32 cm^2) was polished with wet 600 grit SiC paper, sonicated in purified water, and dried with clean tissue just before it was coated with the porphyrin catalysts.

Apparatus and Procedures. Conventional electrochemical instrumentation and two-compartment cells were employed. A rotating platinum ring−graphite disk electrode with a collection efficiency of 0.39 was obtained from Pine Instrument Co. A gold disk electrode (0.02 cm^2) was obtained from Bioanalytical Systems, Inc. Potentials were measured and are quoted with respect to a saturated calomel reference electrode (SCE).

CoTMP and other cobalt porphyrins were adsorbed on electrode surfaces by means of a dip-coating procedure. Transferring aliquots of solutions of the porphyrin in organic solvents ($CHCl_3$, CH_2Cl_2) directly to the electrode surface followed by evaporation of the solvent produced coatings that exhibited less distinct and poorly reproducible voltammetric responses compared with the coatings resulting from the following dip-coating procedure: The freshly polished and dried electrode was dipped for 5 s in a 0.3 mM solution of CoTMP in $CHCl_3$, transferred rapidly to pure $CHCl_3$ for 2−3 s, and then exposed to air, where the adhering solvent rapidly evaporated. The quantities of porphyrin that were irreversibly adsorbed on the electrode were determined by coulometric assays as described in the following text.

Spectral data were obtained with a Hewlett-Packard Model 8452A or a Bruker 500 MHz spectrometer.

Results and Discussion

Electrochemistry of CoTMP in Solution. No previous descriptions of the electrochemical behavior of CoTMP, either dissolved in solution or adsorbed on electrode surfaces, could be found. We therefore began by examining the cyclic voltammetry of the porphyrin in solution. Tetrahydrofuran proved to be a useful solvent for this purpose. Shown in Figure 1A is a cyclic voltammogram obtained with a gold disk electrode to minimize the adsorption of the CoTMP on the electrode surface. The reversible response centered at 0.44 V can be assigned to the Co(III/II) couple on the basis of its similarity to

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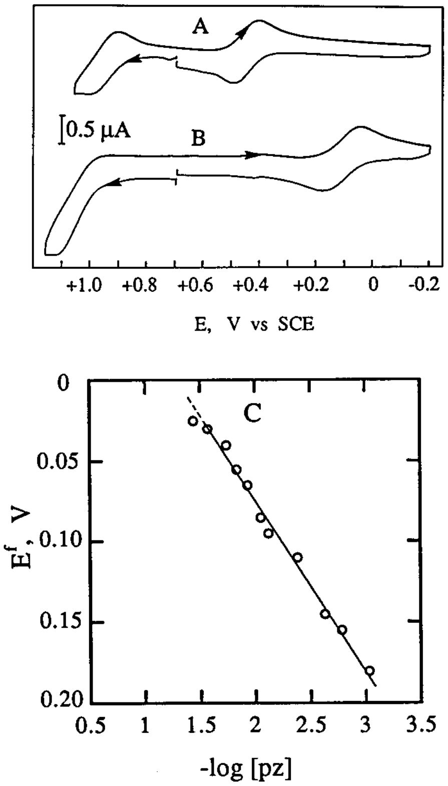

Figure 1. Cyclic voltammetry of 0.27 mM CoTMP dissolved in tetrahydrofuran. (A) Supporting electrolyte: 0.2 M tetrabutylammonium perchlorate. A gold disk electrode was used. The initial potential was 0.75 V, and the initial scan was toward more positive potentials. Scan rate = 50 mV s^{-1}. (B) Repeat of (A) in the presence of 5.3 mM pyrazine. (C) Dependence of the formal potential for the Co(III/II) couple on the logarithm of the molar concentration of pyrazine, [pz]. The slope of the least-squares line drawn through the data points is 114 mV per decade.

the behavior of many cobalt porphyrins in nonaqueous solvents.[3] The response at 0.95 V is assignable on the same basis to the one-electron oxidation/reduction of the porphyrin ring to its radical cation.[3] In the presence of ligands such as imidazole or pyrazine, which can coordinate to the axial positions of the cobalt center, the formal potential of the Co(III/II) couple (taken as the average of the anodic and cathodic peak potentials) shifts to less positive values. For example, the voltammogram obtained when the supporting electrolyte also contained 5.3 mM pyrazine is shown in Figure 1B. The behavior resembles that reported by Manassen for several cobalt tetraphenylporphyrins in which the affinity of Co(III) for the added ligands is much greater than that of Co(II).[4] The shift in formal potential of the Co(III/II) couple caused by the addition of pyrazine is independent of the oxidation state of the CoTMP in solution. The cathodic peak potential in the presence of pyrazine is the same in solutions of $Co^{II}TMP$ or $Co^{III}TMP$. Such behavior is indicative either of substitutional lability for Co(III) as well as Co(II) (an unusual property for Co(III) that has been previously reported[5] and attributed to metal−porphyrin orbital mixing that effectively introduces some "Co(II) character" into the oxidized (nominally Co(III)) form of the cobalt porphyrin to produce a substantial enhancement in its substitutional lability) or of rapid homogeneous electron transfer between substitutionally inert $Co^{III}TMP$ and substitutionally labile $Co^{II}TMP$(pyrazine).[6]

The increase in the anodic current near 1.0 V and disappearance of the cathodic peak in Figure 1B appear to be the result of more extensive oxidation of the porphyrin ring in the presence of the added, basic pyrazine ligand.

The formal potential of the Co(III/II) couple was measured in tetrahydrofuran solutions containing varying concentrations of pyrazine, and the results are shown in Figure 1C. A least-squares line drawn through the data points has a slope of 114 mV per decade, which indicates that two more pyrazine ligands are coordinated to the Co(III) form of the porphyrin than to the Co(II) form. As only two open coordination sites are available in CoTMP, the slope of the line in Figure 1C indicates that there is no coordination of pyrazine by the Co(II) porphyrin in the range of ligand concentrations investigated. In the absence of pyrazine, the open coordination sites of $Co^{III}TMP$ are presumably occupied by THF molecules. The equilibrium binding constant evaluated from the data in Figure 1C and the formal potential of the Co(III/II) couple in the absence of pyrazine (0.44 V) was $\beta_{III} = [CoTMP(pz)_2]/[CoTMP][pz]^2 = 2.8 \times 10^{10}\ M^{-2}$.

Electrochemistry of CoTMP Adsorbed on Graphite. Shown in Figure 2A is a cyclic voltammogram recorded in aqueous acid with CoTMP irreversibly adsorbed on the surface of an edge plane pyrolytic graphite (EPG) electrode. The response corresponding to the Co(III/II) couple at 0.3 V is remarkable for its prominence and reversibility. Most cobalt porphyrins adsorbed on graphite or glassy carbon electrodes exhibit much broader and less distinct voltammetric peaks for the Co(III/II) couple in aqueous solution.[7] Only with adsorbed cobalt porphine have we observed voltammetric responses as clearly defined as the one in Figure 2A.[1] The difference in the formal potentials for the Co(III/II) couple of CoTMP dissolved in THF (0.44 V) or adsorbed on graphite in aqueous acid (0.3 V) can be attributed to the differences in solvation energies and reference electrode junction potentials in the two solvents as well as to the differences in the local environments of the CoTMP in the adsorbed and dissolved states.

The CoTMP adsorbed irreversibly on EPG electrodes by the dip-coating procedure is very stable. Cycling the potential of a coated electrode between +0.55 and −0.2 V for several hours in 1 M $HClO_4$ resulted in the loss of only a few percent of the adsorbed porphyrin. The area encompassed by voltammograms such as the one in Figure 2A corresponds to ca. 9×10^{-10} mol cm^{-2} of CoTMP based on the geometric area of the roughened electrode surface that results from polishing with 600 grit SiC paper. Electrodes polished on a polishing wheel with 0.05 μm alumina to produce a mirrorlike finish adsorbed about half as much porphyrin as did roughly polished electrodes so that the microscopic area of the roughly polished electrodes was apparently increased by a factor of only about 2. A monolayer of CoTMP contains ca. 10^{-10} mol cm^{-2} so that the area of the response in Figure 2A corresponds to several equivalent monolayers of the porphyrin on the electrode surface.

The shift in the formal potential of the Co(III/II) couple of adsorbed CoTMP produced by the addition of pyrazine to the supporting electrolyte is similar to the shift obtained when CoTMP is dissolved in THF as shown in Figure 2B. The negative shift of 68 mV produced by the addition of 2 mM pyrazine to the 1 M $HClO_4$ supporting electrolyte (where only

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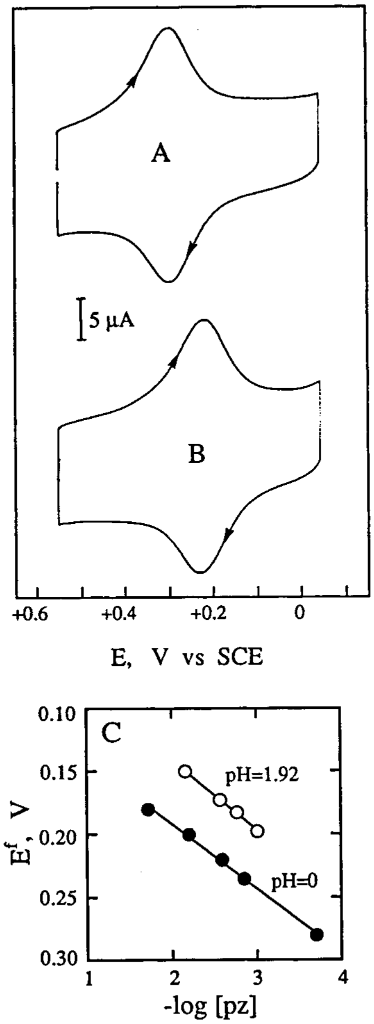

Figure 2. Cyclic voltammetry of CoTMP dip-coated onto an edge plane pyrolytic graphite electrode using the procedure given in the Experimental Section. (A) Supporting electrolyte: 1 M $HClO_4$. (B) Repeat of (A) in the presence of 2 mM pyrazine. (C) Dependence of the formal potentials of the Co(III/II) couple of adsorbed CoTMP on the concentration of pyrazine added to the supporting electrolyte which was 1 M $HClO_4$ (●) or 0.01 M $HClO_4$−0.2 M $NaClO_4$ (○). The slopes of the lines drawn through the points are both 55 mV per decade.

18% of the added pyrazine remains unprotonated[8]) shows that Co^{III}TMP retains its high affinity for pyrazine when it is adsorbed on the surface of EPG electrodes. The change in the formal potential for the Co(III/II) couple as a function of the concentration of pyrazine is shown in Figure 2C at pH 0 and 1.9. The lines drawn through the data points are separated by 44 mV and have slopes of 55 mV per decade. The observed behavior is consistent with the Co(III) center of the adsorbed porphyrin coordinating one, unprotonated pyrazine ligand that is released when the cobalt center is reduced to Co(II). The 44 mV separation between the lines in Figure 2C compares favorably with the value, 43 mV, calculated from the known pK_a of pzH^+ (0.65[8]). The coordination of a single pyrazine ligand to the adsorbed porphyrin but of two pyrazines to the porphyrin dissolved in THF (Figure 1C) is understandable if the porphyrin is adsorbed with the ring parallel to the graphite surface so that only one axial coordination site is exposed and available for coordination by ligands such as pyrazine. The equilibrium constant for the binding of unprotonated pyrazine to the adsorbed porphyrin calculated from the data in Figure 2C is K_{ads} = [CoTMP(pz)]/[CoTMP][pz] = 3.7×10^4 M^{-1}. It is difficult to compare this value with the constant for the coordination of pyrazine to the porphyrin dissolved in THF because of the differences in the molecularity of the reactions and in the environments of the porphyrin. Nevertheless, the high affinity of Co^{III}TMP for axial bases such as pyrazine is clearly expressed in both the dissolved and adsorbed states.

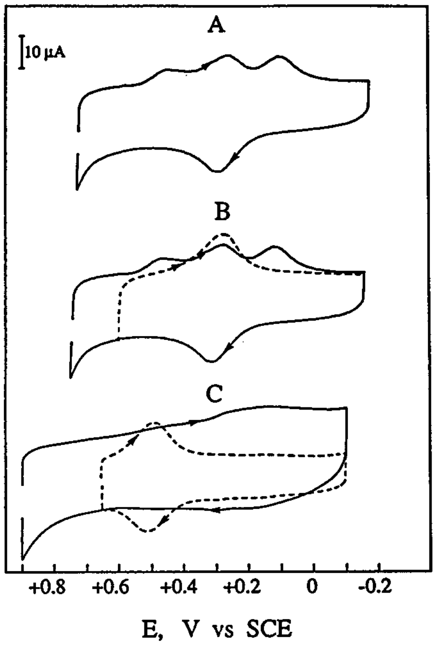

Figure 3. (A) Cyclic voltammogram for CoTMP adsorbed on an EPG electrode recorded from an initial potential of 0.75 V. (B) Repeat of (A) with the addition of a second scan to more negative potentials after reversing the scan direction at 0.6 V (dashed line). (C) Cyclic voltammograms for adsorbed cobalt porphine recorded from initial potentials of 0.65 V (dashed curve) or 0.9 V (solid curve). In all cases the supporting electrolyte was 1 M $HClO_4$ and the scan rate was 50 mV s^{-1}.

Oxidation of Adsorbed CoTMP. Metalloporphines which lack substitutents in the 5-, 10-, 15-, and 20-positions of the porphyrin ring are typically more readily oxidized than are porphyrins in which substituent groups are present in these ring positions. For example, in our recent investigation of cobalt porphine adsorbed on EPG electrodes, the adsorbed porphyrin was irreversibly oxidized at electrode potentials more positive than ca. 0.8 V or by exposure to H_2O_2.[1] This behavior is undesirable for cobalt porphyrins intended to serve as electrocatalysts for the reduction of O_2 because of the more negative potentials where the oxidized porphyrins are catalytically active. One of the reasons we decided to examine CoTMP in the present study was to determine if the presence of methyl groups in the 5-, 10-, 15-, and 20-positions of the ring would make CoTMP more resistant to oxidation than was cobalt porphine.

Shown in Figure 3A is the cyclic voltammogram obtained for adsorbed CoTMP when the initial electrode potential was 0.75 V. The cathodic response consists of three, separated peaks while only a single cathodic peak was present when the initial potential was 0.6 V (Figure 2A). It appears that the presence of the four *meso* methyl groups does not prevent the oxidation of the adsorbed CoTMP at 0.75 V. The single anodic peak obtained when the scan direction is reversed at −0.2 V is the same for both initial potentials (Figures 2A and 3A), and if the potential is scanned again from 0.6 V toward more negative

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(8) The pK_A of singly protonated pyrazine is 0.65: Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965.

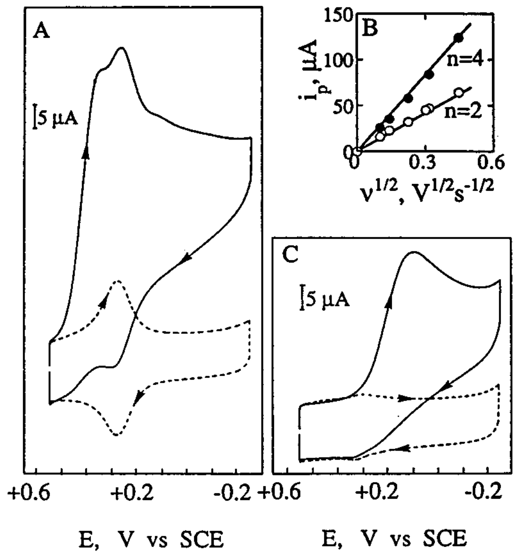

Figure 4. (A) Solid curve: Catalysis of the electroreduction of O_2 by CoTMP dip-coated on an EPG electrode. Supporting electrolyte: 1 M $HClO_4$ saturated with air. The dashed curve was recorded with an argon-saturated solution. Scan rate = 50 mV s^{-1}. (B) The current at the first cathodic peak in (A) (solid points) or (C) (open points) minus the current at the same potential in the dashed voltammogram plotted vs (scan rate)$^{1/2}$. The lines give the calculated currents for the diffusion-limited reduction of O_2 by two or four electrons assuming that the transfer of the first electron is rate-limiting, the transfer coefficient is 0.5, D_{O_2} = 1.7 × 10^{-5} cm^2 s^{-1}, and [O_2] = 0.28 mM. (C) Repeat of (A) using CoTPP instead of CoTMP as the catalyst.

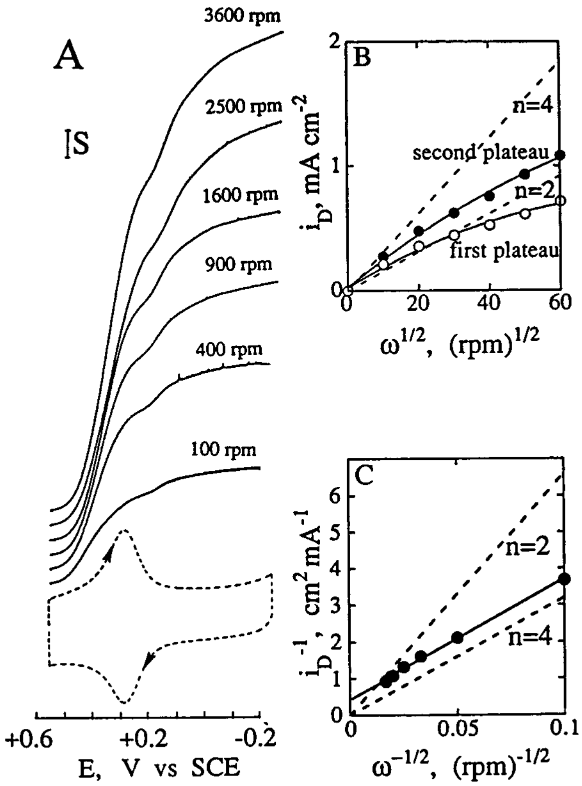

Figure 5. (A) Reduction of O_2 at an EPG disk electrode coated with CoTMP and rotated at the indicated rates in 1 M $HClO_4$ saturated with air. Scan rate = 5 mV s^{-1}. S = 20 µA. The dashed curve is the cyclic voltammetric response from the CoTMP coating in the absence of O_2 at a scan rate of 50 mV s^{-1} and S = 5 µA. (B) Levich plots of the plateau currents for both of the steps in (A). (C) Koutecky−Levich plots for the plateau currents of the second step in (A).

values, the subsequent cathodic peak is singular (Figure 3B) and indistinguishable from the response obtained when a freshly prepared electrode is scanned from +0.6 to −0.2 V. Thus, in contrast with cobalt porphine,[1] the oxidized CoTMP is apparently restored to its original form by the multiple-step, cathodic reduction of the adsorbed porphyrin. Different results are obtained when cobalt porphine is adsorbed on the electrode and subjected to potentials of 0.8−0.9 V. The reversible response exhibited by the unoxidized cobalt porphine (dashed curve in Figure 3C) is essentially removed by oxidation of the adsorbed cobalt porphine at 0.8−0.9 V (solid curve in Figure 3C), and the voltammetric response characteristic of the unoxidized porphyrin cannot be recovered in subsequent scans over any range of potentials. The contrasting behavior of adsorbed CoTMP and cobalt porphine suggests that the oxidation of the former involves the formation of radical cationic complexes without the breaking or making of new bonds while oxidation of the latter may involve the addition of oxygenated functionalities at the *meso* positions of the porphine ring.

Like cobalt porphine,[1] CoTMP undergoes chemical oxidation by the H_2O_2 to which it is exposed when the adsorbed porphyrin is used to catalyze the electroreduction of O_2. However, in contrast with cobalt porphine, the chemically oxidized CoTMP can be restored to its initial unoxidized form by electrochemical reduction so that exposure to H_2O_2 does not lead to a permanent degradation in the catalytic activity of CoTMP.

Catalysis of the Reduction of O_2 by CoTMP Adsorbed on Graphite Electrodes. When irreversibly adsorbed on the surface of EPG electrodes, CoTMP displays catalytic activity toward the electroreduction of O_2 that is unusual in several respects: (i) The reduction of O_2 begins near 0.5 V, which is significantly more positive than both the formal potential of the Co(III/II) couple of the adsorbed porphyrin (Figure 4A) and the potentials where most monomeric cobalt porphyrins exhibit catalytic activity.[9] (ii) With adsorbed CoTMP, the catalytic currents for the reduction of O_2 under typical cyclic voltammetric conditions are almost as large as the diffusion-limited value for the four-electron reduction of O_2 to H_2O, as shown by the plot of (corrected) cathodic peak currents vs (scan rate)$^{1/2}$ in Figure 4B (solid points). (iii) The contribution to the voltammetric response from the adsorbed CoTMP catalyst itself is prominent, and it remains visible even as the adsorbed porphyrin acts to catalyze the reduction of O_2 to H_2O. These unusual features are evident in the voltammograms shown in Figure 4A. Their novelty becomes particularly apparent when the voltammograms in Figure 4A are compared with those in Figure 4C, which was obtained with cobalt tetraphenylporphyrin (CoTPP) instead of CoTMP as the adsorbed catalyst. No clear response from the Co(III/II) couple of the adsorbed CoTPP is evident. The catalyzed reduction of O_2 begins near 0.3 V, but the reduction involves only two electrons as shown by the open points in Figure 4B. The differences between the behaviors of cobalt tetraphenyl- and tetramethylporphyrins are profound.

The electroreduction of O_2 was also examined at rotating EPG disk electrodes coated with CoTMP. Shown in Figure 5A are the current−potential curves obtained at various electrode rotation rates. The catalyzed reduction clearly occurs in two steps. The second step, with an $E_{1/2}$ value near 0.2 V, corresponds to the small peak near the same potential in the voltammogram in Figure 4A. With the larger currents (and correspondingly larger catalyst turnover rates) required at the rotating disk electrode, more of the reduction occurs at the

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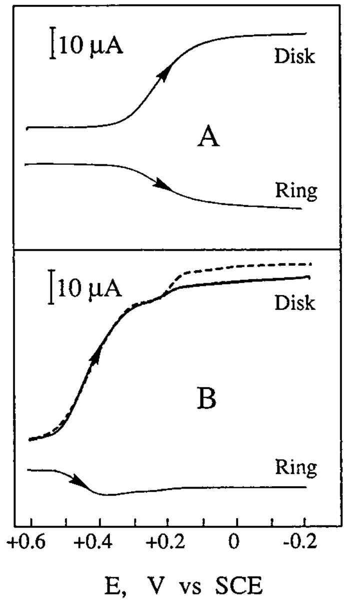

Figure 6. Reduction of O_2 at a rotated platinum ring−graphite disk electrode in 1 M $HClO_4$ saturated with air. The Pt ring was maintained at 1.0 V. The collection efficiency of the ring−disk electrode was 0.39. The disk was dip-coated with (A) CoTPP or (B) CoTMP. Rotation rate = 100 rpm. Scan rate = 5 mV s^{-1}. The dashed curve in (B) was obtained after the solution was made 0.16 mM in H_2O_2.

second step. The increase with rotation rate in the ratio of the plateau current for the second to that for the first wave in Figure 5A is consistent with this interpretation.

Levich[10] and Koutecky−Levich plots[11] of the plateau currents for both of the steps in Figure 5A are shown in Figure 5B,C. The Levich plots show that the plateau currents of the first step exceed the values corresponding to the two-electron reduction of O_2 at low rotation rates while those of the second step do so at all rotation rates. The slope of the Koutecky−Levich plot for the second plateau (Figure 5C) is close to the value corresponding to the reduction of each O_2 molecule by four electrons. The half-wave potentials of the first step in the disk current−potential curves in Figure 5A are in the same region as the potentials where the adsorbed Co^{III}TMP is reduced to Co^{II}TMP (dashed curve in Figure 5A). In addition, the values of $E_{1/2}$ shift to more negative values as the rotation rate of the electrode is increased and the disk current increases. This is the behavior expected for an irreversible electrode process catalyzed by an adsorbed catalyst.[12] The smaller catalytic current obtained under cyclic voltammetric conditions allows the reduction to begin at potentials that are somewhat more positive than the formal potentials of particularly active adsorbed catalysts because the small quantities of reduced catalyst generated at these potentials are nevertheless adequate to provide the cyclic voltammetric currents.

A comparison of the electroreduction of O_2 as catalyzed by CoTMP or CoTPP was also carried out using a rotating platinum ring−graphite disk electrode.[13] As shown in Figure 6A, with CoTPP as catalyst, the reduction of O_2 proceeds in a single step and H_2O_2 is the sole product of the reduction. However, with CoTMP as the catalyst (Figure 6B), the larger disk current and smaller ring current show that a portion of the O_2 is reduced to H_2O instead of H_2O_2. On the first plateau in the disk current−potential curve in Figure 6B, the magnitude of the ring current shows that 58% of the O_2 is reduced to H_2O_2 and 42% to H_2O. The smaller portion of four-electron reduction of O_2 at the rotating Pt ring−graphite disk electrode than at the rotating EPG disk electrode used in Figure 5 is a result of the difference in the graphite surfaces of the two electrodes. The pyrolytic graphite employed in the commercial ring−disk electrode typically adsorbs less porphyrin and yields catalyst coatings that are less active than coatings prepared from the same catalysts on homemade pyrolytic graphite disk electrodes in which the electrode surface is composed of the edges of the graphitic planes. Interactions of the adsorbed porphyrins with the graphite surface are known to be important in affecting the catalytic activities of cobalt porphyrins,[23] and these interactions are apparently different on authentic, polished EPG electrodes and the commercial Pt ring−graphite disk electrodes which cannot be polished to the same extent as the pure EPG electrodes without damaging the relatively fragile platinum ring electrode.

The concentration of H_2O_2 at the surface of the disk electrode on the first plateau of the curve in Figure 6B can be calculated as $I_R C_{O_2}/NI_L = 0.16$ mM, where I_R is the ring current, N is the collection efficiency of the ring−disk electrode, I_L is the Levich current for the reduction of O_2 to H_2O_2, and C_{O_2} is the bulk concentration of O_2 (0.28 mM). The further reduction of some of this H_2O_2 to H_2O seemed likely to be responsible for the second step in the disk current−potential curve in Figure 6B because of the decrease in anodic ring current that accompanied the increase in disk current. To test this possibility, the solution used to record the solid curve in Figure 6B was made 0.16 mM in H_2O_2 and the disk current−potential response recorded again. The plateau current for the second step approximately doubled (dashed curve in Figure 6B), as expected if the step corresponded to the reduction of H_2O_2. Thus, CoTMP is an electrocatalyst for the reductions of both O_2 and H_2O_2. However, the catalytic activity of the porphyrin toward H_2O_2 is much weaker: At equal bulk concentrations of 0.28 mM, the current plateau for the reduction of O_2 was 6.4-fold larger than that for H_2O_2 at a rotation rate of 100 rpm.

We attribute the more negative potential at which the catalytic reduction of H_2O_2 occurs to the more negative reduction potential of the CoTMP·H_2O_2 adduct, presumed to be the reducible intermediate, and the smaller catalytic reduction current to the lower rate at which this adduct is formed compared with the CoTMP·O_2 adduct responsible for the first stage of the reduction of O_2.

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Possible Origin of the Unusual Electrocatalytic Activity of CoTMP. The surprising difference in the catalytic behavior of CoTMP (and Co porphine) compared with CoTPP may originate in the greater tendency of the former porphyrin to spontaneously dimerize (or to form higher aggregates). Such dimerization of metalloporphines and metalloporphyrins has been the subject of several reports.[14−20] No corresponding studies of CoTMP have appeared, but the pronounced aggregation of porphyrin ligands containing larger and charged substituents in the *meso* positions of the ring[21,22] makes similar self-association of CoTMP seem likely. Pairs of cobalt porphyrins that are covalently linked in a cofacial configuration by amide or aryl groups attached to the rings of both porphyrins are known to catalyze the four-electron electroreduction of O_2,[23] while the unlinked porphyrins do not.[24] The hypothesis is that CoTMP (as well as CoP) adsorbed on graphite electrodes exists, at least in part, as a cofacial dimer that is held together by van der Waals interactions. Both experimental and theoretical evidence supporting such spontaneous dimerization has been presented.[14−16] Additional evidence in the case of CoTMP was obtained from measurements of the absorbance of solutions of the porphyrin in $CHCl_3$ as a function of its concentration. A plot of the data (given in the Supporting Information) exhibits marked deviations from Beer's law. The deviations, which are typical of aggregating porphyrins,[25] occur at concentrations above ca. 0.5 mM. The effective concentration of CoTMP molecules in coatings on electrode surfaces are much greater than 0.5 mM so that substantial attractions between pairs of porphyrin molecules could occur as they accumulate on the graphite surface during the dip-coating procedure. The dimers that resulted from the interactions could then serve as catalysts for the four-electron reduction of O_2 by means of the same mechanism utilized by covalently linked, cofacial cobalt porphyrin catalysts in which the O_2 molecule is believed to interact with both cobalt centers in the transition state.

The aggregation of the porphine ligand takes place whether or not a metal cation is inserted in the porphyrin ring.[14−17] Therefore, one might expect that, in mixtures of the metalated and unmetalated porphyrins, the quantity of dimeric species present in which both porphyrin rings contained a metal ion would be smaller than that in solutions containing only the metalated porphyrin. To be catalytically active for the four-electron reduction of O_2, dimers in which both porphyrin rings contain a Co(II) center are believed to be required; a dimer consisting of CoTMP linked to TMP would be expected to catalyze only the two-electron reduction of O_2. Thus, dilution of coatings of CoTMP with TMP should diminish the catalytic O_2 reduction current by diverting more of the O_2 from the four- to the two-electron reduction pathway. This speculation was tested by comparing the activities of catalyst coatings adsorbed from pure solutions of CoTMP with those of coatings containing the same quantities of CoTMP but also coadsorbed TMP as a diluent. The results, summarized in Table 1, show that the presence of TMP in catalyst coatings significantly decreases the catalytic current for the reduction of O_2. The observed behavior supports the proposal that dimers of CoTMP are important in producing the four-electron reduction of O_2. Additional support comes from the observation that the addition of pyrazine to test solutions caused the current for the reduction of O_2 to decrease to values corresponding to a two-electron reduction. The coordination of pyrazine to the Co(III) centers of the adsorbed CoTMP may interfere with the formation of the dimeric species that are believed to be essential to obtain the four-electron reduction of O_2.

Table 1. Effect of Co-Adsorbed TMP on the Catalytic Activity of Adsorbed CoTMP

$10^{10}\Gamma_{\text{CoTMP}}$,[a] mol cm^{-2}	$10^{10}\Gamma_{\text{TMP}}$,[b] mol cm^{-2}	I_{cat},[c] μA	$10^{10}\Gamma_{\text{CoTMP}}$,[a] mol cm^{-2}	$10^{10}\Gamma_{\text{TMP}}$,[b] mol cm^{-2}	I_{cat},[c] μA
0.62	0	77	0.43	0.67	59
0.62	0.48	66	0.15	0	60
0.43	0	75	0.15	0.96	47

[a] Quantity of CoTMP adsorbed on the rotating EPG disk electrode as evaluated from the area under a voltammogram recorded in the absence of O_2. [b] Quantity of TMP free base coadsorbed on the rotating EPG disk electrode estimated by assuming that $\Gamma_{\text{CoTMP}} + \Gamma_{\text{TMP}}$ remains constant as the molar ratio of CoTMP and TMP in the adsorption solution is varied while [CoTMP] + [TMP] is kept constant. [c] Plateau current for the reduction of O_2 at the coated EPG disk electrode rotated at 100 rpm in 1 M $HClO_4$ saturated with air.

It is worth noting that the shape of the voltammetric peaks corresponding to the Co(III/II) couple of the adsorbed CoTMP (Figure 2A) is close to that expected for a one-electron Nernstian redox couple (the width at half-height is only slightly greater than 90.6 mV).[26,27] Thus, the cobalt centers in the dimeric CoTMP believed to be present in the coating apparently do not interact strongly enough to produce either split peaks or the single, narrower (45 mV) peak that would correspond to a Nernstian two-electron redox couple. However, if the catalyst coating consisted of a mixture of both monomeric and dimeric porphyrins, the shape of the voltammetric response would not provide a simple basis for discerning the composition of the catalytically active ingredients in the coatings.

Comparison of the Catalytic Behaviors of Cobalt Porphine and CoTMP. Although both cobalt porphine (CoP) and CoTMP adsorbed on graphite electrodes catalyze the electroreduction of O_2 by four electrons, there are notable differences in the reactivity patterns exhibited by the two catalysts. Fresh coatings of CoP accomplish the reduction of O_2 at an unusually positive potential with H_2O as the primary reduction product at the first step of the two-step reduction.[1] However, the limiting rate of the reduction is relatively low.[1] By contrast, coatings of CoTMP yield considerably higher limiting rates at the first step of the reduction of O_2 (Figure 6B) but the product of the reduction is a mixture of H_2O_2 and H_2O. The ability of the CoP catalyst to avoid the production of H_2O_2 is no doubt related to the high potential at which it operates. The value of $E_{1/2}$ for the first reduction step at a CoP-coated rotating disk electrode in 1 M $HClO_4$ saturated with air is 0.53 V, which is very close to the $E_{1/2}$ value expected if the reduction were reversible (0.54 V) so that the quantity of H_2O_2 that could be produced at this potential is subject to thermodynamic constraints. The design or discovery of electrocatalysts for the reduction of O_2 that operate at potentials significantly more positive than the standard potential of the O_2/H_2O_2 couple is certainly one reliable method to ensure that only the four-electron reduction pathway is open.

Conclusions

The results of the present study and those in a previous report[1] show that both CoP and CoTMP irreversibly adsorbed on

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graphite electrodes exhibit unusual catalytic activities toward the electroreduction of O_2. These two catalysts operate at remarkably positive potentials and lead a large portion of the reaction along a four-electron reduction pathway. The presence of only methyl or of no substituents on the porphyrin ring appears to facilitate the dimerization of the porphyrin to produce the more catalytically potent species within coatings on electrodes. The susceptibility of CoP to apparent oxidative degradation makes it less attractive a catalyst than CoTMP, which, if oxidized, can be restored to its initial state by electrochemical reduction. Tests of related, lightly derivatized cobalt porphines as catalysts for the reduction of O_2 seem worth pursuing on the basis of the results reported here for CoTMP.

Acknowledgment. This work was supported by the National Science Foundation. Dr. Beat Steiger contributed a number of very helpful suggestions.

Supporting Information Available: A plot of the absorbance of solutions of CoTMP at the Soret maximum vs the concentration of CoTMP in $CHCl_3$ (1 page). Ordering information is given on any current masthead page.

IC971255P