$\times 10^{-5}$ mol) (synthesized as in ref 9). Isolation and purification were performed as for FTF4*; yield 30%; UV–vis (λ_{max} nm) 370, 502 (sh), 536, 566, 644; MS *m,e* 955 (calcd 954).

Cobalt insertion into FTF3 and FTF4 was performed in an inert atmosphere box, with $CoCl_2$ in 1:3 THF–toluene, as previously described in ref 9. Co_2(FTF4)*: *m/e* 1097.4 (calcd 1096.4); Co_2(FTF3): *m/e* 1069.4 (calcd 1068.3).

Acknowledgment. This work derives from a collaborative effort that also includes the groups of Professors, F. C. Anson (Caltech), M. Boudart and H. Taube (Stanford), and Dr. H. Tennet, formerly of Hercules Inc. Research Center. Mass spectral analyses were carried out at the Middle Atlantic Mass Spectrometry Laboratory, a National Science Foundation Shared Instrumentation Facility. We thank R. R. Durand, Jr., Dr. E. R. Evitt, and Dr. L. J. Wright for helpful discussions. Initial studies were carried out at Stanford by Dr. R. B. Pettman; his work is gratefully acknowledged. This project was supported by National Science Foundation Grants CHE77-22722 and CHE81-10545. Use of the Stanford Magnetic Resonance Laboratory (NSF Grant GP23633 and NIH Grant RR00711) is also acknowledged. C.S.B. thanks the Venezuelan Council for Scientific and Technological Research (CONICIT) for her doctoral fellowship. We are deeply indebted to Dr. L. Tokes (Syntex) for a high-resolution mass spectrum and to G. Venburg for technical assistance.

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Mechanistic Aspects of the Catalytic Reduction of Dioxygen by Cofacial Metalloporphyrins

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Abstract: The mechanisms by which the reduction of dioxygen at graphite electrodes is catalyzed by cofacial dicobalt and related porphyrins adsorbed on the electrode surface have been scrutinized. The products of the reduction, the electrode potential where the reduction proceeds, and the mechanistic role of protons were among the topics examined. For the best catalyst it was possible to relate the electrochemical response of the adsorbed porphyrin to the potential where the catalyzed reduction of dioxygen proceeds. The electrocatalytic behavior of several new heterobinuclear cofacial porphyrins is reported as well as that of a new cofacial dicobalt porphyrin in which the bridge connecting the two porphyrin rings consists of only three atoms. A comparison of the behavior of the various catalysts has led to a more detailed proposal for the mechanisms by which they operate in catalyzing the electroreduction of dioxygen.

In previous accounts of the unusual catalytic potency of several dicobalt cofacial porphyrin molecules for the electroreduction of dioxygen to water,[1-3] the catalytic mechanism was surmised on the basis of limited experimental data. In particular, the reduction and oxidation of the catalysts themselves in the absence of O_2 were difficult to observe above the background response from the surface of the pyrolytic graphite electrode on which they were adsorbed. The effects of changes in the proton concentration on the catalysis were also examined only cursorily although it was shown that the course of the reduction was substantially different at electrodes deprived of protons.[1-3]

We have now found conditions that permit the electrochemical responses of the adsorbed catalysts to be observed clearly and reproducibly both in the absence and in the presence of O_2 and over a wide pH range. The rate constant for the first step in the catalytic reaction has been measured, and the effect of pH on the distribution of reduction products between H_2O_2 and H_2O has been determined. The catalytic activities of dicobalt cofacial porphyrins with six, five, four, and three atoms in the amide bridges have been compared, and the behavior of several new heterobinuclear cofacial porphyrins (Figure 1) has been examined. The results obtained have provided new insight into the mechanisms employed by these catalysts in reducing dioxygen.

Experimental Section

Materials. The detailed synthetic procedures employed to obtain the metalloporphyrin molecules utilized in this study are presented elsewhere.[4] Figure 1 lists the porphyrins employed and the abbreviations used to identify them. Pyrolytic graphite electrodes were obtained and mounted as previously described.[5] Reagent-grade chemicals and solvents were used as received. The electrodes were mounted to expose the edges rather than the basal planes of the pyrolytic graphite. Such edge-plane electrodes cannot be cleaved to renew the electrode surface so their surfaces were prepared by polishing with 600-grade SiC paper (3M Co.).

Procedures. Pyrolytic graphite electrodes were coated with porphyrin catalysts by syringing small volumes of stock solutions in dichloroethane onto the electrode surface and allowing the solvent to evaporate. Coulometric assays of the resulting coatings performed by measuring the areas under cyclic voltammograms recorded in the absence of dioxygen showed that they typically contained 2–4 $\times 10^{-10}$ mol cm^{-2}, which corresponds to a few close-packed monolayers on a smooth surface or to a single monolayer on a graphite surface with a roughness factor of 2–3. This quantity of adsorbed electroactive catalyst was reproducibly ob-

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[§] Contribution No. 6683.

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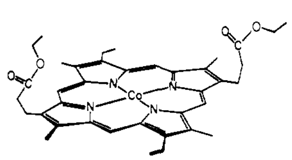

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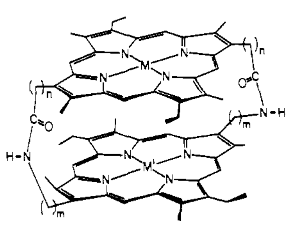

M	M'	n	m	Abbreviation
Co	Co	2	2	Co_2FTF6
Co	Co	1	2	Co_2FTF5
Co	Co	1	1	Co_2FTF4
Co	Co	0	2	Co_2FTF4^*
Co	Co	0	1	Co_2FTF3
Co	2H	1	1	CoH_2FTF4
Co	Fe	1	1	CoFeFTF4
Co	Mn	1	1	CoMnFTF4
Co	Ag	1	1	CoAgFTF4
Co	Al	1	1	CoAlFTF4
Ag	Ag	1	1	Ag_2FTF4

Figure 1. Molecular structures and abbreviations for the metalloporphyrins examined in this study.

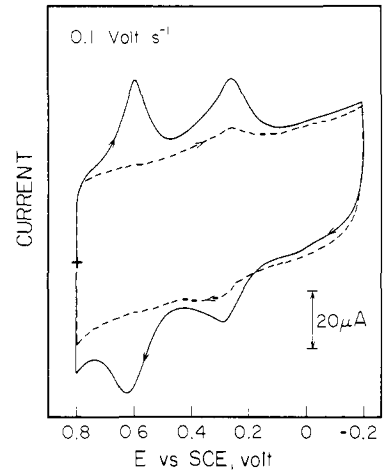

Figure 2. Cyclic voltammogram of Co_2(FTF4) adsorbed on an edge-plane pyrolytic graphite electrode in the absence of O_2: supporting electrolyte 1 M CF_3COOH saturated with argon; scan rate 0.1 V s^{-1}. The dashed line is the background response of the pyrolytic graphite before the porphyrin was adsorbed.

tained whether or not larger excesses of catalysts were applied to the electrode surface in the adsorption step. Conventional cyclic and rotating-disk voltammetry were carried out with the previously described apparatus and procedures. For cyclic voltammetry at scan rates above 1 V s^{-1}, a digital oscilloscope (Tektronix Model 5223) was employed to acquire the voltammetric data, which were subsequently read out with an x–y recorder for precise measurements of peak potentials and currents. Potentials were measured and are quoted with respect to a saturated calomel reference electrode (SCE).

Results

Behavior of Co_2(FTF4) in Acidic Electrolytes. The most impressive catalysis of the reduction of dioxygen is achieved by the dicobalt cofacial porphyrin in which four atoms comprise the two bridging groups that link the porphyrin rings, Co_2 (FTF4) (Figure 1). We have therefore concentrated most of our attention on the behavior of this molecule. The pair of prominent cyclic voltammetric waves exhibited by this catalyst when it is adsorbed on a pyrolytic graphite electrode and examined in the absence of O_2 are shown in Figure 2. The wave appearing near 0.6 V is easily distinguished from the background current, but the wave near 0.3 V falls close to that of a component of the background response (dashed curve in Figure 2) believed to arise from the presence of reducible quinone-like functional groups on the graphite surface. The position of the latter wave depends upon pH while the catalyst waves show no pH dependence below pH 6. This feature permits the background wave to be shifted away from the catalyst waves so that the formal potentials corresponding to both waves of the adsorbed catalyst can be measured under conditions where the background reactions do not interfere. The resulting values are E_f = 0.62 and 0.27 V.

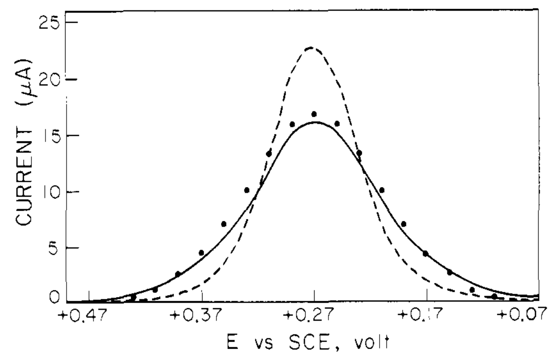

Figure 3. Comparison of the background-corrected voltammetric wave of Co_2(FTF4) at +0.27 V (solid line) with the calculated Nernstian response (dashed line). The solid points represent the calculated response when a nonideality parameter is introduced into the Nernst equation as described in ref 6. The best fit resulted with $r\Gamma_T = -0.7$.[6]

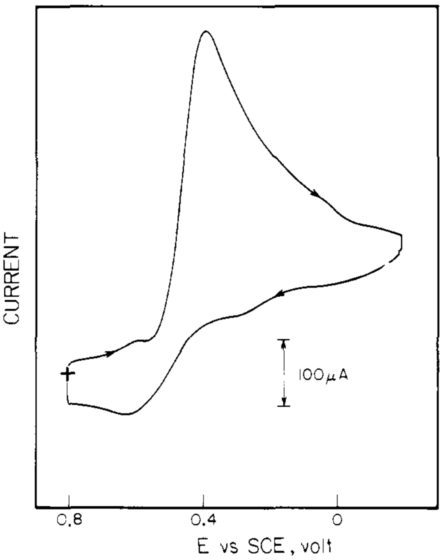

Figure 4. Cyclic voltammogram for the reduction of O_2 at a graphite electrode on which Co_2(FTF4) is adsorbed: supporting electrolyte 1 M CF_3COOH saturated with O_2; scan rate 0.1 V s^{-1}.

The shapes of the waves for the reduction of the adsorbed complex resemble those expected for a one-electron, surface-confined couple that exhibits small deviations from the Nernst equation. For example, Figure 3 shows how the experimental wave differs from that calculated from the Nernst equation for the same peak potential and quantity of adsorbed reactant. A reasonable fit of the experimental curves results if a nonideality parameter is introduced into the Nernst equation[6] as shown by the solid points in Figure 3.

The presence of two waves for the adsorbed Co_2(FTF4) molecule is expected on the basis of its cyclic voltammetry in nonaqueous solution where two waves are also obtained.[7] Both waves result from the reduction of the virtually identical cobalt(III) centers to cobalt(II). The reductions appear at different potentials because of the repulsive interactions between the cobalt centers that are held in close proximity (~4 Å) by the structure of the ligand. The splitting of cyclic voltammetric waves by such intramolecular interactions in reactant molecules has been discussed in several previous studies.[8]

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Table I. Half-Wave Potentials and Limiting Levich Current Densities for the Reduction of O_2 at Rotating Graphite Disk Electrodes Coated with Co_2(FTF4)[a]

pH[b]	$E_{1/2}$, V vs. SCE	I_{lim}, mA cm^{-2}
0	0.47	1.3[c]
1	0.40	1.3
2	0.33	1.2
3	0.27	1.2
4	0.23, −0.15[d]	0.9[d]
7	−0.07	0.9
10.8	−0.17	0.8
14	−0.21	0.55

[a] The electrode was rotated at 100 rpm in dioxygen-saturated solutions. [b] Phosphate buffers were used for pH 7 and 10.8. Other solutions were not buffered. [c] The calculated Levich current density for the four-electron reduction of O_2 is 1.3 mA cm^{-2}. [d] Two waves present, see text. The value of I_{lim} is the total plateau current on the second wave.

The peak potentials of the waves in Figure 2 are shifted only slightly when the scan rate is increased to 100 V s^{-1}, showing that the catalyst can be reduced and reoxidized rapidly at potentials close to its formal potential.

Catalyzed Reduction of O_2 in Acidic Electrolytes. The reduction of dioxygen at an electrode surface on which Co_2(FTF4) is adsorbed is shown in the cyclic voltammogram in Figure 4. The first reduction peak for the adsorbed catalyst can be seen followed by the large current resulting from the catalyzed reduction of O_2. The peak potential for the reduction of O_2 (0.42 V) is near the foot of the second reduction wave for the catalyst with a peak potential of 0.27 V (Figure 2). This indicates, as proposed previously on the basis of less well-resolved voltammograms,[1-3] that reduction of the second cobalt center in the adsorbed catalyst to cobalt(II) produces the dicobalt(II) species that is active toward the reduction of dioxygen.

The effect of changes in the proton concentration on the reduction of dioxygen was investigated at a rotating-disk electrode coated with Co_2(FTF4). At low rotation rates (~100 rpm) the limiting disk currents obey the Levich equation[9] and the half-wave potentials depend on the pH of the supporting electrolyte in the way shown in Table I. Between pH 0 and 3, the half-wave potential shifts by about 60 mV per pH unit even though the peak potential for the reduction of the adsorbed catalyst shows no pH dependence in this range. The sensitivity of the catalyzed reduction to the proton concentration must arise from a step in the catalytic cycle subsequent to the reduction of the catalyst.

The magnitudes of the Levich currents[9] for dioxygen reduction show a small decrease between pH 0 and 3 but remain close to the value expected for a four-electron reduction (Table I). At higher pH values the Levich current decreases toward the value corresponding to a two-electron reduction, from which it may be concluded that the dioxygen is being reduced to a mixture of hydrogen peroxide and water. Tests showed that Co_2(FTF4) is not a catalyst for the reduction or the disproportionation of hydrogen peroxide so that these Levich currents indicate that direct reaction pathways for both two- and four-electron reductions of O_2 must be accessible.

Behavior of Co_2(FTF4) at High pH. When a catalyst-coated electrode that yields voltammograms such as those in Figure 2 is transferred to a dioxygen-free solution at pH 14, the voltammogram shown in Figure 5A is obtained. The pair of waves observed at low pH is replaced by a single wave at a much more negative potential. The area under the single wave is no greater than that under either of the waves in Figure 2, and the single wave does not have the narrower width expected for a two-electron Nernstian process.[6] Thus, it does not appear that the waves present in acidic media have merged to form the single wave at pH 14. The diminished response is not the result of loss of catalyst from the surface because both of the original waves reappear with the same magnitudes if the electrode is returned to acidic supporting electrolytes.

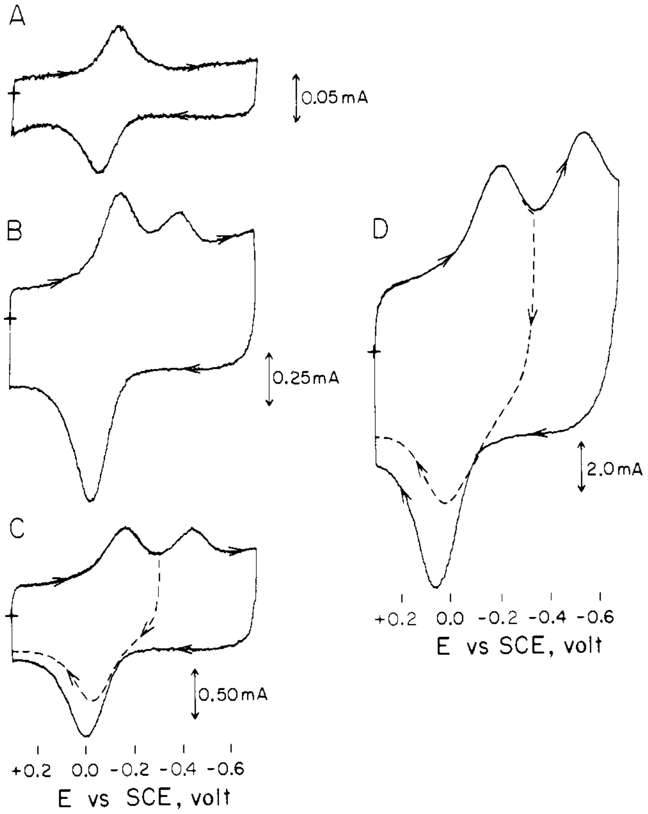

Figure 5. Cyclic voltammograms of Co_2(FTF4) adsorbed on graphite: supporting electrolyte 1M NaOH saturated with argon; scan rates (A) 1, (B) 10, (C) 20, (D) 100 V s^{-1}. The dashed curves show the result of reversing the direction of potential scan before the second reduction peak is traversed.

The single reduction wave shown in Figure 5A develops a satellite wave at scan rates above ca. 1 V s^{-1} that grows at the expense of the original wave as the scan rate increases (Figure 5, B, C, and D). However, only a single oxidation wave is present under the same conditions, and its magnitude is influenced by both of the reduction waves when two are present (Figure 5, curves C and D). Increasing the solution temperature to 80 °C eliminates the satellite wave while decreasing the temperature to 5 °C causes the satellite wave to appear at lower scan rates. Decreasing the pH from 14 to 12 (at 25 °C) diminishes the magnitude of the satellite wave. Once the peak currents of the satellite wave and the original wave become about equal, their relative magnitudes are insensitive to further increases in scan rate.

A less prominent satellite wave develops at high scan rates when the Co_2(FTF5) catalyst, with five atoms in the struts separating the porphyrin rings, is substituted for Co_2(FTF4). With Co_2(FTF6), with six atoms in the bridges, no satellite wave is observed at scan rates up to 100 V s^{-1}. The same is true for both Co_2(FTF3), with three atoms in the bridges, and the monomeric cobalt porphyrin, I (Figure 1). Co_2(FTF4*), in which the four atoms in the bridges have been rearranged so that the carbonyl group of amide linkage is directly attached to one porphyrin ring, gives voltammograms in which the satellite wave appears at scan rates as low as 0.1 V s^{-1}.

To account for the behavior of the adsorbed Co_2(FTF4) catalyst at high pH, we suggest equilibria such as those depicted in Scheme I in which μ-oxo and μ-hydroxo bridges are assumed to form within the cavity of the catalyst. In writing Scheme I we have assumed that the cofacial porphyrin molecules adsorb on the electrode because of strong interactions between one of the porphyrin rings and the graphite surface. We have no direct evidence for the orientation of the adsorbed molecules, but the maximum obtainable coverages are consistent with a monolayer of porphyrin rings adsorbed in a flat orientation and it is known that flat

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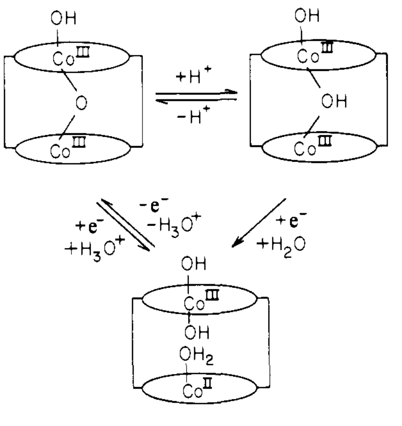
Scheme I



molecules with aromatic centers show high affinities for graphite surfaces.[10] This implies that the axial ligand site on the cobalt ion in the adsorbing ring may be inaccessible to ligands other than those that are present on the graphite itself.[11] The lower ring in the molecules shown in Scheme I is assumed to be bound to the electrode surface.

If the oxo- and hydroxo-bridged dicobalt(III) complexes in Scheme I were reduced at different potentials, the double waves in Figure 5 could be understood. As the distance separating the two cobalt centers increased such bridging would become less likely and this could account for the decrease in the magnitude of the satellite wave with Co_2(FTF5) and its disappearance with Co_2(FTF6). The relative magnitudes of the waves for the reduction of the μ-oxo and μ-hydroxo species would depend on the rate with which these two forms could be interconverted.

The lack of the satellite peak in the voltammograms of Co_2(FTF3) could reflect the absence of intercavity bridging when the separation of the cobalt centers becomes too small. The appearance of the satellite peak at lower scan rates with Co_2(FTF4*) than with Co_2(FTF4) might be the result of a somewhat smaller separation between the cobalt centers in Co_2(FTF4*) arising from conjugation of the carbonyl groups in the amide bonds with the porphyrin rings. One result might be a somewhat smaller ring-to-ring separation in Co_2(FTF4*) than in Co_2(FTF4). The rate of interconversion between the two bridged complexes proposed in Scheme I might also be altered, and this could account for the appearance of the satellite peak at lower scan rates with Co_2(FTF4*) than Co_2(FTF4).

At sufficiently high potential scan rates the magnitudes of the peak currents for the two waves in Figure 5 should become independent of scan rate and provide a measure of the equilibrium concentration of each form of the complexes. These predictions are in qualitative accord with the behavior shown in Figure 5, although quantitative features such as the relative magnitudes of the two peak currents at pH 12 and 14 are not. The origin of this discrepancy remains uncertain.

The cobalt(III) center in the half-reduced form of the catalyst shown in Scheme I is proposed to be converted to a dihydroxo complex. If the reduction of this species were kinetically much slower or had a formal potential that lay at inaccessibly negative values, the lack of a second catalyst reduction wave would be explained. Previously we have observed that the reduction wave of the adsorbed monomeric cobalt porphyrin, I, remains clear and undiminished at pH 14.[5] This is the anticipated result if the formation of the trans-dihydroxo form of the monomer were blocked by its adsorption on the electrode surface similar to the lower rings in the dimeric porphyrins of Scheme I.

There is only one form of the half-reduced catalyst in Scheme I so that only one oxidation wave is expected even at scan rates where the reduction wave is split into two parts. This accords with the behavior shown in Figure 5. Scheme I would also predict that the reduction of O_2 would proceed to H_2O_2 instead of H_2O in alkaline media if each end of the O_2 molecule must be coordinated to a cobalt center as the O_2 is reduced in order to avoid the release of H_2O_2. This also corresponds to the observed result (vide infra).

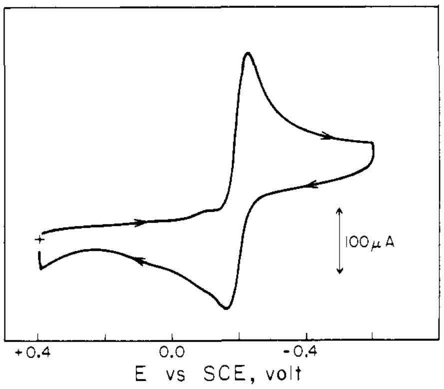


Figure 6. Reduction of O_2 at a graphite electrode on which Co_2(FTF4) is adsorbed; supporting electrolyte 1 M NaOH saturated with O_2; scan rate 0.1 V s^{-1}.

Although Scheme I manages to accommodate most of the experimental observations, we regard the mechanistic implications to which it leads as reasonable possibilities, not demonstrated facts.

Catalyzed Reduction of O_2 at High pH. The reduction of dioxygen from pH 14 solutions at electrodes coated with Co_2(FTF4) is a reversible process that yields hydrogen peroxide quantitatively. Figure 6 shows a typical cyclic voltammogram. The magnitude of the cathodic peak current matches that calculated from the Randles–Sevcik equation[12] for a two-electron nernstian reduction, and the equal magnitude of the anodic wave confirms that hydrogen peroxide is the only reduction product. The response obtained is indistinguishable from that exhibited by the monomeric cobalt porphyrin, I, under the same conditions.[5] This suggests that at high pH Co_2(FTF4) catalyzes the reduction of O_2 by a pathway that does not involve the participation of more than one of the cobalt centers in the catalyst molecule.

The adsorbed catalyst is not permanently altered by exposure to 1 M NaOH because transferring the electrode used to record Figure 6 to an acidic solution saturated with dioxygen produces the same, four-electron reduction of dioxygen that is obtained in the acidic solution with a freshly coated electrode.

Rotating-Disk Voltammetry. In a previous report,[1-3] current–potential curves for the reduction of dioxygen at rotating-disk electrodes coated with Co_2(FTF4) were recorded only in acidic electrolytes. Data for a wider pH range are now available, and they reveal a pronounced pH dependence in the responses (Table I). As noted earlier, at pH 0 and 1 the Levich currents are essentially equal to the current calculated for the four–electron reduction of dioxygen. Above pH 3 the Levich current falls below this value, signaling an increase in the formation of hydrogen peroxide. The Levich current at pH 14 is less than half of that at pH 0 because of the decreased solubility of dioxygen in 1 M NaOH. When this factor is accounted for, the current at pH 14 matches that expected for the quantitative two-electron reduction of dioxygen to hydrogen peroxide.

In unbuffered solutions between pH 4 and 6 the current–potential curve exhibits two waves with relative magnitudes that are affected by the concentration of protons at the electrode surface (Figure 7). At potentials on the first wave, the reduction of O_2 proceeds to H_2O as indicated by the absence of ring current in Figure 7. When this process consumes all of the available protons, the pH at the electrode surface increases substantially and the reduction shifts to more negative potentials. The corresponding anodic ring current shows that H_2O_2 is now a significant reduction product.[13] The data in Table I indicate clearly that the stoi-

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(12) Bard, A. J.; Faulkner, L. "Electrochemical Methods"; Wiley: New York, 1980.

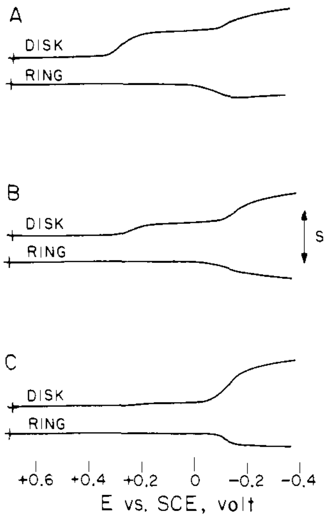

Figure 7. Disk and ring current vs. disk potential for the reduction of O_2 at a rotating-disk electrode coated with Co_2(FTF4): rotation rate 100 rpm; supporting electrolyte 0.1 M CF_3COONa saturated with air and adjusted with CF_3COOH to pH (A) 4.0, (B) 4.5, (C) 5.0. The platinum ring was maintained at +0.85 V. The values of S for disk and ring currents are 100 and 10 μA, respectively.

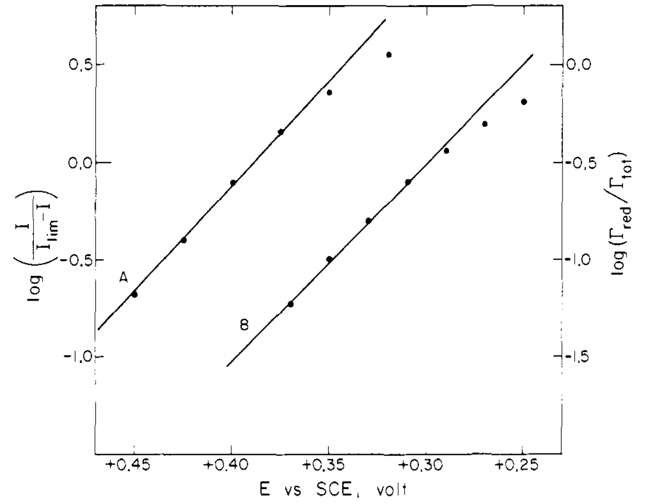

Figure 8. Potential dependences of (A) the catalyzed dioxygen reduction current and (B) the concentration of doubly reduced Co_2(FTF4) on the electrode surface. Data for line A (left-hand ordinate) were recorded in 1 M CF_3COOH saturated with air at ω = 400 rpm. Curve B (right-hand ordinate) was obtained by measuring the area under the solid curve in Figure 3 up to each potential of interest.

chiometry of the reduction of dioxygen as catalyzed by Co_2(FTF4) is influenced strongly by the hydrogen ion concentration.

Between pH 0 and 2 the limiting disk currents at low rotation rates (e.g., $\omega < 400$ rpm) increase linearly with $\omega^{1/2}$, which shows that the currents are controlled by the convective transport of O_2 to the electrode surface. The shape of the rising part of the rotating-disk current–potential curves recorded under these conditions was analyzed by plotting $\log I/(I_{lim} - I)$ vs. E. A typical plot, shown in Figure 8, is linear with a slope of 90 mV per decade. To analyze the slopes of such plots, it was desirable to compare them with the potential dependence of the quantity of the reduced form of the Co_2(FTF4) catalyst on the electrode surface. This was calculated from the solid curve in Figure 3 and is shown in the form of a plot of $\log(\Gamma_{red}/\Gamma_{tot})$ vs. E in Figure 8 (curve B). The slope of the linear portion of the curve that lies in the potential range where the catalyzed reduction of O_2 is observed is ca. 85 mV per decade. The agreement between the two slopes is the expected result if the current is controlled by the quantity of reduced catalyst on the electrode surface. This observation was important in deriving the catalytic mechanism described in the Discussion.

Table II. Electrochemical Responses of Cofacial Metalloporphyrins toward the Catalysis of the Reduction of Dioxygen[a]

porphyrin	E_f,[b] V. vs. SCE	E_f',[c] V vs. SCE	$E_{1/2}$,[d] V vs. SCE	I_{lim},[e] mA cm^{-2}
Co_2(FTF4)	0.62	0.27	0.47	1.3
CoFe(FTF4)	0.60	*f*	0.25, −0.07	0.7, 1.2
CoAl(FTF4)	*f*	*f*	0.22	0.8
CoAg(FTF4)	0.59	(0.25)	0.38	1.1
CoMn(FTF4)	*f*	*f*	0.23[g]	0.8[g]
CoH_2(FTF4)	0.60		0.20	0.8
Co monomer, I	0.54		0.20	0.8

[a] All data refer to 1 M CF_3COOH supporting electrolyte. [b] Formal potential of the cobalt center in the adsorbed porphyrin. Evaluated from cyclic voltammetric peak potentials recorded under argon at 100 mV s^{-1}. [c] Formal potential of the second metal center (if any). [d] Half-wave potential of the dioxygen reduction wave recorded in dioxygen-saturated solution with a coated disk electrode rotated at 100 rpm. [e] Limiting current density for the reduction of dioxygen at 100 rpm. [f] No clear peak evident above the background current. [g] A more positive $E_{1/2}$ (0.32 V) and a higher current (0.9 mA cm^{-2}) can be obtained by soaking the electrode in basic solution (see text).

Levich plots (I_{lim} vs. $\omega^{1/2}$)[9] of the limiting dioxygen reduction current are shown in Figure 9A for a 1 M CF_3COOH solution. The increasing deviations from linearity at higher rotation rates reflect the intervention of a potential-independent chemical step as the current limiting factor. The reaction between the reduced catalyst and dioxygen is the most likely such step,[1-3] and its rate may be estimated from the intercepts of Koutecky–Levich plots (I_{lim}^{-1} vs. $\omega^{-1/2}$)[14] such as the two shown in Figure 9B for air- and dioxygen-saturated solutions. The reciprocal of the intercepts of the lines, I_{int}, can be related to the rate constant of the current-limiting reaction, k, via eq 1[14] where n is the number of electrons

$$I_{int} = n\mathcal{F}kC_{O_2}\Gamma_{cat} \qquad (1)$$

consumed in the reduction of dioxygen, i.e., 4, $\mathcal{F}$ is the Faraday, C_{O_2} is the concentration of oxygen in the bulk of the solution, and Γ_{cat} is the surface concentration of catalyst (assumed to be uniformly accessible to the dioxygen). The chemical reaction that limits the current is assumed to be first order in dioxygen and in catalyst. This was confirmed for dioxygen by noting that the values of I_{int} differ by a factor of 5 in dioxygen- and air-saturated solutions. The rate constants evaluated from the two lines in Figures 9B are 2×10^5 and 3×10^5 M^{-1} s^{-1}. Using the average of these constants and an estimate of the uncertainty in the measurement of the quantity of catalyst present on the electrode surface, we calculate a catalyst turnover number of $(4 \pm 2) \times 10^2$ per second in a dioxygen-saturated solution. This number compares very favorably with turnover numbers that have been estimated for platinum-based catalysts[15] and is within an order of magnitude of the rates of turnover achieved by some biological dioxygen reduction catalysts such as cytochrome *c* oxidase.[16]

Related Heterobinuclear Cofacial Porphyrins. In order to compare the catalytic effectiveness of Co_2(FTF4) with that obtained if a different metal cation (or two protons) were substituted for one of the two cobalt ions, we examined the behavior of several new binuclear cofacial porphyrins. These included the Co–Fe(II),

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(13) In a previous report (ref 5), we often experienced difficulties in maintaining a constant sensitivity of the platinum ring electrode toward the oxidation of H_2O_2 in buffered supporting electrolytes at pH values above ca. 2. For this reason we have preferred to use the magnitude of disk currents as a more reliable indicator of the stoichiometry of the reduction of O_2. However, the presence or absence of ring current remains a highly reliable qualitative means for detecting H_2O_2 among the reduction products.

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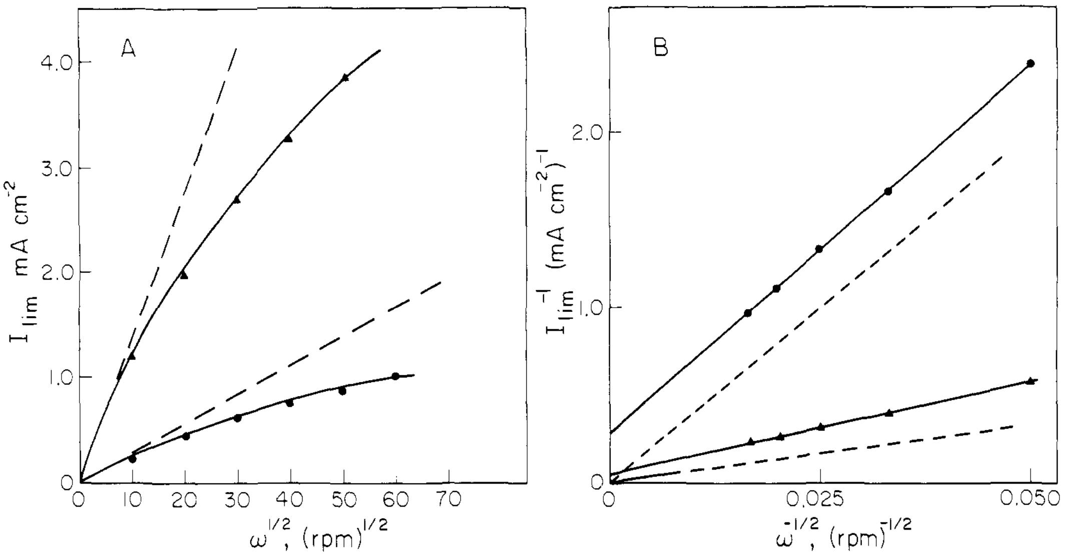

Figure 9. Levich (A) and Koutecky–Levich (B) plots of rotating-disk limiting currents in air (●) and dioxygen-saturated (▲) 1 M CF_3COOH. The dashed lines represent the calculated responses for the mass transfer limited, four-electron reductions of dioxygen in air- and dioxygen-saturated solutions.

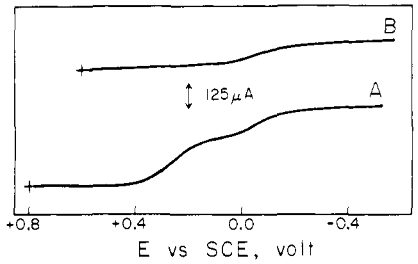

Figure 10. Rotating-disk voltammograms at electrodes coated with CoFe(FTF4): supporting electrolyte 1 M CF_3COOH, (A) dioxygen-saturated solution, (B) argon-saturated solution + ~1 mM H_2O_2; scan rate 0.5 V min^{-1}; electrode rotation rate 100 rpm; potential scanned at 0.5 V min^{-1}.

Co–Mn(III), Co–Al(III), Co–Ag(II) and Co–H_2 complexes. The behavior of the Co–Pd(II) complex was reported in our previous studies.[1-3] Table II lists the formal potentials of the cobalt centers in the adsorbed catalysts measured in the absence of dioxygen, the half-wave potential of the catalyzed dioxygen reduction wave for each catalyst at a graphite disk electrode rotated at a low rate, and the corresponding limiting reduction (Levich) currents. The responses obtained are clearly quite sensitive to the nature of the second cation in the cofacial complexes, which supports the previous contention[1-3] that interactions of both metal centers of the catalyst with the O_2 molecule are involved in determining the course of the catalyzed reduction reaction.

CoFe(FTF4). A single redox wave for the $Co^{III/II}$ couple appeared near 0.6 V with electrodes coated with this catalyst in the absence of dioxygen in 1 M CF_3COOH. This potential corresponds closely to that observed with the monomeric cobalt porphyrin I.[5] By comparison with monomeric iron porphyrins,[17] the $Fe^{III/II}$ response would be expected to appear at potentials about 0.5 V negative of the cobalt response, but we were unable to observe a clear wave above the background current. In dioxygen-saturated solutions, rotating disk electrodes coated with CoFe(FTF4) exhibited the two-step reduction shown in Figure 10, curve A. The first step appears at potentials considerably more negative than the potential where the catalyst is reduced. This behavior resembles the response obtained at electrodes coated with monomeric cobalt porphyrins,[5] where the catalyzed reduction proceeds only to hydrogen peroxide. The second reduction step in Figure 10 appears at about the same potential as that where adsorbed, monomeric iron porphyrins are active catalysts for the reduction of hydrogen peroxide,[17] and the total limiting current on the second plateau is closer to that expected for the four-electron reduction of dioxygen.

When the experiment was repeated with a dioxygen-free solution of hydrogen peroxide, only the second reduction wave remained with a limiting current corresponding to a two-electron reduction (Figure 10, curve B). Thus, the two metal centers in the CoFe(FTF4) catalyst appear to function independently to yield behavior characteristic of monomeric porphyrin catalysts containing the same metal cations. Indeed, an electrode coated with a one-to-one mixture of monomeric cobalt and iron porphyrins produced a current–potential curve very similar to that in Figure 10A.

CoMn-, CoAl-, CoPd-, and CoH_2(FTF4). The behavior of all four of these catalysts is similar and resembles that obtained with the monomeric cobalt porphyrin: Limiting reduction currents at catalyst-coated rotating-disk electrodes correspond to the two-electron reduction of dioxygen with half-wave potentials between 0.20 and 0.23 V vs. SCE (Table II). Although the identity of the second metal has some influence on the potential where the cobalt center is reduced, these heterobinuclear cofacial porphyrins are catalytically no more effective than the monomeric cobalt porphyrin I. The corresponding monomeric porphyrin complexes of the second metals show no activity toward the reduction of dioxygen.

As noted in Table II, if the adsorbed CoMn(FTF4) was soaked in an alkaline solution and transferred back to an acidic supporting electrolyte, some changes resulted in the limiting current and half-wave potential. The monomeric manganese porphyrin exhibited no changes when subjected to the same treatment. It is possible that axial ligands initially coordinated to the Mn center are removed by exposure to alkaline solutions, but the phenomenon was not studied sufficiently to establish its origin.

CoAg(FTF4). In contrast to the other heterobinuclear catalysts, the cofacial porphyrin containing cobalt and silver ions shows two reduction waves when inspected under argon (Figure 11A). The more positive wave remains at about the same potential as that observed with the other porphyrins and seems clearly to arise from the cobalt center. The less positive wave probably originates in the silver center as it appears at a potential typical for the $Ag^{III/II}$ couple in porphyrins.[18] The reduction of dioxygen at a graphite rotating-disk electrode coated with CoAg(FTF4) is shown in Figure 11B. The reduction proceeds at positive potentials, and the limiting currents are well above the value corresponding to a two-electron reduction of dioxygen. The slope of the Koutecky–Levich plot prepared from curves such as those in Figure

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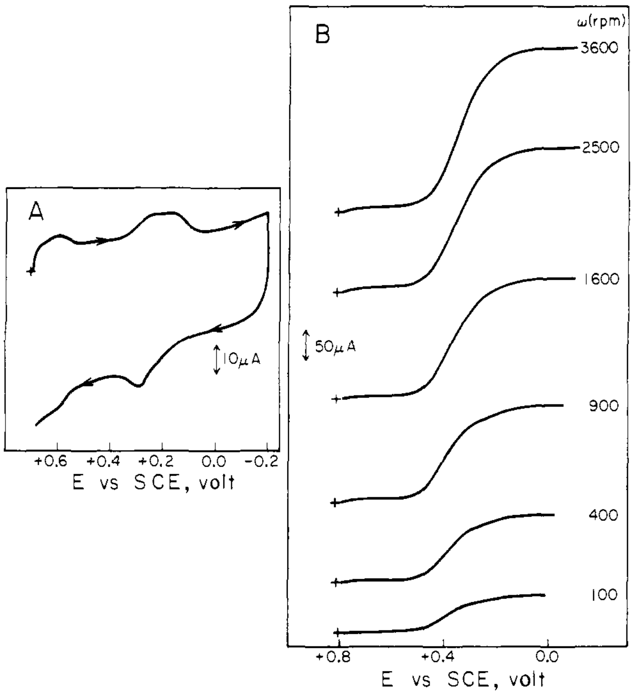


Figure 11. (A) Cyclic voltammogram of CoAg(FTF4) adsorbed on graphite: supporting electrolyte 1 M CF_3COOH saturated with argon; Scan rate 0.1 V s^{-1}. (B) Rotating-disk voltammograms for reduction of O_2 at graphite electrodes coated with CoAg(FTF4): supporting electrolyte 1 M CF_3COOH saturated with air. A new coating of complex was applied before each curve was recorded. Scan rate 0.5 V min^{-1}.

Table III. Effects of Increasing the Distance between Porphyrin Rings on Electrochemical Responses of Dicobalt Cofacial Porphyrins[a]

porphyrin	E_f, V vs. SCE	E_f', V vs. SCE	$E_{1/2}$, V vs. SCE	I_{lim}, mA cm^{-2}
Co_2(FTF3)	0.64	0.34	0.40	0.8
Co_2(FTF4)	0.62	0.27	0.47	1.3
Co_2(FTF4*)	0.64	0.35	0.44	0.8
Co_2(FTF5)	0.60	*b*	0.38	1.1
Co_2(FTF6)	0.59	*b*	0.32	0.8

[a] See Table II for explanation of column headings. [b] Wave not discerned.

11B corresponds to 2.9 electrons, suggesting that the reduction proceeds by two parallel pathways, one leading to hydrogen peroxide and the other to water.

Electrodes coated with a monomeric silver porphyrin or the disilver analogue, Ag_2(FTF4), showed no catalytic activity toward the reduction of dioxygen or hydrogen peroxide. Adsorption of a mixture of monomeric cobalt and silver porphyrins produced an electrode with a response similar to that obtained from the cobalt monomer alone. The CoAg(FTF4) complex resembles Co_2(FTF5) in its ability to catalyze the reduction of O_2. It is the most active cofacial porphyrin catalyst we have encountered that does not contain two cobalt centers, and the circumstantial evidence points strongly to the participation of both metal centers in generating the enhanced catalytic activity.

Variation in the Length of the Bridging Groups in Dicobalt Cofacial Porphyrins. Dicobalt cofacial porphyrins with three, four, five, and six atoms in the bridging groups have now been synthesized and tested as dioxygen reduction catalysts. Table III summarizes the results that have been obtained. The optimum separation between the porphyrin rings appears to have been reached with the four-atom bridge as indicated by the less positive value of $E_{1/2}$ and smaller limiting currents obtained for both Co_2(FTF3) and Co_2(FTF5).

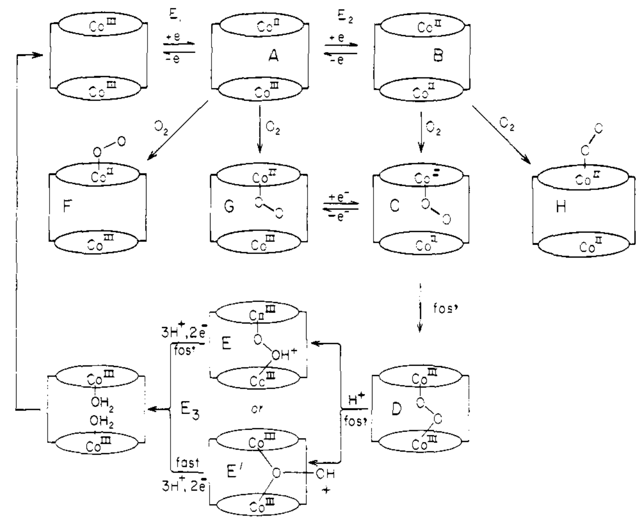
The effect of changing the order of the bridging atoms is clear from the difference in the behavior of Co_2(FTF4) and Co_2(FTF4*). The magnitude of the limiting O_2 reduction current obtained with Co_2(FTF4*) points to H_2O_2 as the primary reduction product. The half-wave potential of the catalyzed wave obtained with Co_2(FTF4*) is more positive than any peroxide-producing catalyst we have encountered. Its behavior is the subject of continuing studies.

Table IV. Rate Constants for the Reaction of Adsorbed Porphyrins with Dioxygen

porphyrin	$10^{-5}k$, M^{-1} s^{-1}
Co monomer, I	1.4
Co_2(FTF3)	1.2
Co_2(FTF4)	3
CoAg(FTF4)	2.2
CoAl(FTF4)[a]	1.0
CoMn(FTF4)[a]	2.0

[a] The quantities of these catalysts on coated electrodes were taken to be the same as that measured for Co_2(FTF4) because the voltammetric responses were not sufficiently well-defined for reliable measurements to be made.

Scheme II



Kinetics of the Reaction between Catalysts and Dioxygen. The rotating-disk procedure described earlier for measuring the rate constant governing the reaction of Co_2(FTF4) with O_2 was also applied to several additional porphyrins. The results, summarized in Table IV, show that the reaction rate constant does not vary extensively from porphyrin to porphyrin, suggesting a common rate-limiting step such as the substitution of dioxygen in the inner coordination sphere of cobalt(II).

Discussion

Dicobalt Porphyrins. The catalyst waves shown in Figure 2 are much more clearly defined than was true in our previous reports,[1-3] probably because the samples of Co_2(FTF4) used to coat the electrode in the present study were more abundant and more highly purified.[4] The two reversible waves observed in the absence of dioxygen represent the reduction of the dicobalt(III,III) complex successively to the (III,II) and (II,II) states. The absence of a pH dependence of the peak potentials below pH 6 indicates that hydroxy complexes of the oxidized and half-reduced catalyst are not important in this pH range. When a possible mechanism for the catalytic action of Co_2(FTF4) in dioxygen reduction is proposed, several facets of its behavior must be accommodated. These include the relative positions and pH dependences of the waves corresponding to the reduction of the catalyst itself and of dioxygen, the conversion of the dioxygen reduction product from water to hydrogen peroxide as acidic supporting electrolytes are made neutral or alkaline, the shape of the current–potential curve for the catalyzed reduction of dioxygen, and the intervention of a potential-independent step in the reaction mechanism when high rates of reaction are demanded by increasing the flux of dioxygen reaching the electrode surface. Scheme II presents a mechanism for acidic electrolytes that accommodates most of these points. As in Scheme I, it is assumed for each molecule shown in Scheme II that the lower porphyrin ring is adsorbed on the graphite surface so that the axial ligand site on the corresponding cobalt center is blocked. For purposes of exposition, we have depicted the first step in the catalytic sequence as the formation of an adduct between O_2 and a Co(II) center in which the formal oxidation states of the two reactants do not change. The actual electronic distribution within the adduct could, of course, differ from that depicted.

The reduction of dioxygen is catalyzed by Co_2(FTF4) at potentials near the foot of the second reduction wave of the catalyst (Figure 4) whose formal potential is labeled E_2 in Scheme II. The first catalyst wave, at potential E_1, is not altered in position or magnitude by the presence of O_2. This insensitivity of the first wave to O_2 shows that the equilibrium constants for the formation of adducts such as F and G in Scheme II are not large. If significant quantities of these species were formed, the peak potential of the first catalyst wave would be shifted toward more positive values in the presence of O_2. The same observation was made recently for the monomeric cobalt porphyrin I, whose single reduction wave precedes that for O_2 and is not affected by the presence of O_2.[5]

The dioxygen group present in F and G is not reducible before the second cobalt(III) center in species A or G is reduced to yield species B and C, respectively. At this point the catalyzed reduction of O_2 to H_2O ensues via species D and E. The potential, E_3, required for the reduction of the μ-hydroperoxo group in species E is assumed to lie positive of E_2 so that the final step of the reduction proceeds rapidly at the potential where species B is generated at the electrode. The dioxygen complex that is catalytically active in the four-electron pathway is proposed to be C, with the dioxygen molecule inside the cavity separating the two porphyrin rings, rather than F or H, because of the dramatic difference in behavior between Co_2(FTF4) and the monomeric porphyrin I or Co_2(FTF5), with only one additional atom in the bridging groups.[1-3] Although species such as F and H do not participate in the electrochemistry at potentials near E_2 because they are not reduced there, such O_2 adducts are reducible to H_2O_2 at more negative potentials.[5] This accounts for the appearance of H_2O_2 and the decrease in limiting disk currents when catalyst-coated electrodes are scanned to sufficiently negative potentials.[1-3] Further support for this proposal is provided by the behavior of Co_2(FTF3) with only three atoms in the amide bridging groups. Coatings of Co_2(FTF3) catalyze the reduction of O_2 to H_2O_2 but not to H_2O, a result to be expected according to Scheme II if the dioxygen molecule were unable to fit between the two porphyrin rings.

The formation of species E, the (μ-hydroperoxo)dicobalt(III) complex, is proposed in order to account for the unique ability of Co_2(FTF4) to avoid the formation of H_2O_2. The release of H_2O_2 from species D and E should be slowed down by the need to break two cobalt–oxygen bonds. Rapid protonation of D produces a hydroperoxo group with both ends coordinated to a cobalt center. We propose that this μ-hydroperoxo group is more easily reduced than any of its predecessors in the reaction sequence. Once formed, it rapidly accepts two electrons from the electrode to complete the reduction to H_2O and regenerate the catalyst. The (μ-hydroperoxo)- rather than the (μ-peroxo)dicobalt(III) complex is proposed as the rapidly reducible intermediate in order to account for the positive shift in the half-wave potential of the O_2 reduction wave produced by increases in the concentration of protons (Table I). Scheme II is compatible with this observation if the rate at which the dicobalt(II) form of the catalyst is consumed irreversibly by reaction with O_2 depends on the proton concentration. Indeed, if the formation of species E from species B and O_2 were fast, irreversible and first order in H^+, the observed 60-mV change in $E_{1/2}$ for each 10-fold change in proton concentration could be rationalized.[19]

Scheme II includes the possibility that the hydroperoxide intermediate formed in the catalytic cycle leading to H_2O might be isomer E′ because analogous (μ-hydroperoxo)cobaltammine complexes are known,[20-23] and in one case[24] such a complex was shown to be a more reactive oxidant than the corresponding μ-peroxo isomer. The molecular geometric requirements for the formation of E and E′ certainly differ, and all of our evidence indicates that the catalytic effectiveness of the cofacial porphyrins is exceedingly sensitive to the relative configurations of the two cobalt centers. For example, although both Co_2(FTF4) and Co_2(FTF4*) have been shown by ESR to form (μ-superoxo)dicobalt(III) complexes in nonaqueous media,[4c] they are not equally effective as dioxygen reduction catalysts: Co_2(FTF4*) catalyzes the two-electron reduction instead of the four-electron reduction achieved by Co_2(FTF4). The ESR spectra of the two μ-superoxo complexes show dissimilarities that suggest less structural symmetry in the Co_2(FTF4*) complex. This apparent structural difference has major consequences in the catalytic behavior of the two complexes.

Mixed-Metal Porphyrins. The results obtained with the heterobinuclear cofacial porphyrins add support to the mechanism depicted in Scheme II in that the metal center present in addition to cobalt is catalytically inert unless it is electroactive at potentials prior to that where species such as F, G, or H are reduced to H_2O_2. For example, the CoAg(FTF4) catalyst, with two electroactive metal centers, yielded currents well in excess of those corresponding to the two-electron reduction of O_2 and at potentials more positive than any catalyst except Co_2(FTF4). A reaction pathway leading to H_2O as the reduction product is apparently accessible with this catalyst, and it can be traversed in parallel with the pathway leading to H_2O_2 that is shared by all the catalysts. Since neither Ag_2(FTF4) nor the monomeric silver porphyrin analogous to I shows catalytic activity toward the reduction of O_2 or H_2O_2, the apparent activity of the reduced silver center in CoAg(FTF4) may reflect its ability to react with the unbound end of the O_2 molecule in the species corresponding to G of Scheme II to produce a hydroperoxo intermediate that is reduced to H_2O at the electrode in the same potential range where the O_2 in the species corresponding to F and H are reduced to H_2O_2.

By contrast, the CoFe(FTF4) complex, which also contains two electroactive metal centers, is no more active than the monomeric cobalt porphyrin because the electroactivity of the iron(III) center lies at potentials well beyond those where the O_2 in the species corresponding to F is reduced to H_2O_2.

Catalytic Mechanism in the Absence of Protons. In neutral and alkaline solutions the catalyzed reduction of O_2 occurs at significantly more negative potentials and leads to H_2O_2 instead of H_2O. In highly alkaline solutions this change could be interpreted in the light of Scheme II as resulting from μ-hydroxo or μ-oxo groups competing successfully against O_2 molecules for the cavity in the catalyst, access to which is required for the four-electron reduction according to Scheme II. The catalyzed reaction may then be forced to proceed via species such as F and H in Scheme II, which require more negative potentials for reduction of the coordinated O_2 and lead only to H_2O_2.

In neutral solutions, where the O_2 molecules may continue to be able to enter the cavity of the catalyst, the four-electron pathway may be blocked by the lack of protons necessary to convert the μ-peroxo intermediate, D, into species E (or E′), the only form of the intermediate that is reducible at the potential where it is generated. The coordinated peroxide is therefore released from the cavity as depicted in Scheme III instead of being further reduced. The resulting H_2O_2 accumulates in the solution because Co_2(FTF4) is inert toward the reduction of H_2O_2 at any pH.

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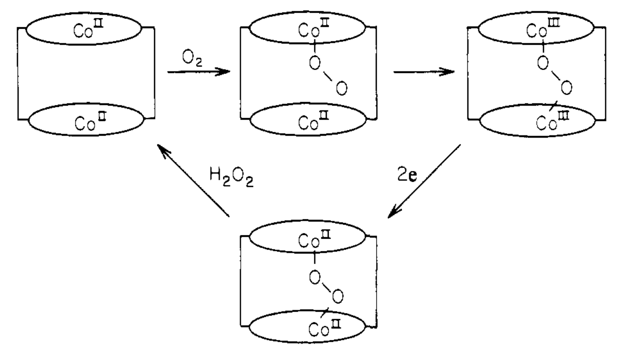
Scheme III



Conclusions

The combinations of observations we have made helps to identify two of the factors that are most important in the catalytic cycle by which the Co_2(FTF4) molecule reduces O_2 to H_2O without release of H_2O_2: (i) the two cobalt centers must be positioned so that the proposed μ-peroxo complex can be formed; (ii) protonation of the μ-peroxo bridge is required to render it reducible at the potential where it is formed. These two requirements are necessary but apparently not sufficient because the dicobalt cofacial porphyrin with four-atom bridges in the meso position of the porphyrin is not an effective catalyst for reduction of O_2 to H_2O.[1-3] Furthermore, the electroreduction in acidic media of stable, (μ-peroxo)dicobalt complexes of some other macrocyclic ligands produces cobalt(II) and H_2O_2, not H_2O.[25] Thus, the μ-peroxo group in the complex formed by Co_2(FTF4) is apparently unusually reactive toward protonation and further reduction. The combination of steric and electronic constraints imposed simultaneously on the μ-peroxo group and the cobalt centers by the cofacial porphyrin ligand with four atoms in its amide bridges seems of crucial importance to its unique catalytic action. We expect that additional studies of the coordination chemistry of Co_2(FTF4), Co_2(FTF4*), and Co_2(FTF3), including X-ray structural data, will lead to a more thorough understanding of the mechanistic details of their electrocatalytic behavior.

Acknowledgment. This work grew out of a collaborative research effort that also involved the groups of Professors M. Boudart and H. Taube (Stanford University) and Dr. H. Tennent (formerly of Hercules Inc. Research Center). It has been supported by the National Science Foundation. C.S.B. thanks the Venezuelan Council for Scientific and Technological Research (CONITCIT) for her doctoral fellowship.

Registry No. I, 71253-21-9; Co_2(FTF6), 71253-22-0; Co_2(FTF5), 74452-74-7; Co_2(FTF4), 71253-24-2; Co_2(FTF4*), 84928-54-1; Co_2(FTF3), 84928-53-0; CoH_2(FTF4), 84928-51-8; CoFe(FTF4), 84928-55-2; CoMn(FTF4), 84928-50-7; CoAg(FTF4), 84928-49-4; CoAl(FTF4), 84928-48-3; Ag_2(FTF4), 84928-52-9; O_2, 7782-44-7; H_2O, 7732-18-5; H_2O_2, 7722-84-1; graphite, 7782-42-5.

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Structure–Reactivity Effects in the Hydration of Benzaldehydes

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Abstract: Rate constants have been measured for the approach to hydration equilibrium for seven substituted benzaldehydes [4-Cl, 3-Cl, 4-CF_3, 3-NO_2, 4-NO_2, 3-NO_2-4-Cl, 3,5-$(NO_2)_2$]. The kinetic method involves the perturbing of the equilibrium position by forming hydrate anion in concentrated sodium hydroxide; addition of acid and buffer results in solutions containing excess hydrate. Hydration equilibrium constants have been calculated by knowing the rate constants in the two directions for the hydroxide ion catalyzed reaction, and a value for the 3,5-$(NO_2)_2$ system has been obtained by using a trapping technique. Literature values are also summarized; hydration has a ρ value of +1.7 in the hydration direction. General base catalysis is associated with Brønsted β values around 0.4 and ρ values near zero in the dehydration direction. The β values increase with decreased electron withdrawal, while the ρ values decrease with increased base strength ($\partial\beta/\partial\sigma = -0.06 = \partial\rho/\partial pK_a$). A three-dimensional reaction coordinate diagram is used to show that this behavior is consistent with a class n mechanism—in the dehydration direction, equilibrium deprotonation of the hydrate followed by acid-catalyzed expulsion of OH. The water rates fit the general base correlations, although rate constants at the diffusion limit are required in one step. Two distinct Brønsted plots are observed for general acids, one for RCOOH and a second for RPO_3H^-, including $H_2PO_4^-$. The line for the latter is about 1 log unit above that for the former; this is attributed to an electrostatic interaction and *not* bifunctional catalysis. A significant cross correlation is also found here, with $\partial\alpha/\partial\sigma = -0.12 = \partial\rho/-\partial pK_a$. This is shown to be consistent with a class e mechanism—in the dehydration direction, equilibrium protonation of the hydrate followed by base-catalyzed expulsion of water.

The reversible hydration of alkyl aldehydes has seen considerable investigation.[1] This represents perhaps the most simple example in the important class of carbonyl addition reactions, and the position of the equilibrium and the associated kinetics have been studied in detail for a number of simple aldehydes.[1-6] Aromatic aldehydes, on the other hand, are known not to be hydrated to a significant extent in water, due to the extra resonance stabilization in the unhydrated benzaldehyde. Some measurements or estimates of the extent of hydration have been reported.[7-10] The

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