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Catalytic Electroreduction of Molecular Oxygen Using Iron or Cobalt 4,4′,4″,4‴-Tetracarboxyphthalocyanine

Nagao Kobayashi* and Yoshiyuki Nishiyama

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai 980, Japan

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The electroreduction of oxygen was examined in aqueous solution containing iron or cobalt 4,4′,4″,4‴-tetracarboxyphthalocyanine (FeTCPc or CoTCPc). In the presence of FeTCPc ([FeTCPc] > ca. 3×10^{-5} M), oxygen was reduced quantitatively to water via hydrogen peroxide (H_2O_2) and the reaction could be explained by an electrochemical (EC) catalytic regeneration mechanism. In the presence of CoTCPc ([CoTCPc] > ca. 3×10^{-5} M), oxygen was reduced quantitatively to H_2O_2 at a potential closely coincident with that for Co^{II}- to Co^{I}TCPc reduction, and moreover the resultant H_2O_2 was partially reduced to water at the same and more negative potentials. Magnetic circular dichroism and electronic absorption spectra have suggested that FeTCPc and CoTCPc as the reaction intermediates are low-spin divalent and low-spin monovalent complexes, respectively. The results are stated in comparison with those so far reported for iron and cobalt porphyrins and phthalocyanines.

Introduction

There has been much recent interest in the electrocatalytic properties of phthalocyanine and porphyrin complexes which are used to activate the cathodic reduction of oxygen with hydrogen in fuel cells.[1-13] As metals in the macrocycles, iron and cobalt have frequently been examined. And now, there appears to be a general agreement that monomeric cobalt complexes promote the O_2 reduction process via two electrons to give H_2O_2 whereas water is produced in the presence of iron complexes. In addition to water-insoluble catalysts, water-soluble "porphyrins" have been employed in the past five years.[7,8] The use of such catalysts has been valid especially in identifying the oxidation, spin, and ligand states of active species of the catalysts. In this study, we examined O_2 electroreduction in the presence of "water-soluble iron and cobalt phthalocyanines" as catalysts, i.e., FeTCPc and CoTCPc.[14] Because of the lower solubility of phthalocyanines[15] and accordingly the difficulty in preparing water-soluble phthalocyanines, there is, to our knowledge, no report in which phthalocyanines are dissolved in water of mild pH for the purpose of O_2 electroreduction. By introduction of FeTCPc and CoTCPc, not only was information on the active species of the catalysts obtained but also several intriguing facts were found as summarized in the Concluding Remarks.

Experimental Section

Materials. The chemicals were commercially available guaranteed reagents and were used without further purification. FeTCPc and CoTCPc were prepared according to the literature.[16] The ratio of N:Fe:COOH in FeTCPc was experimentally determined to be 2.01:1.04:3.29 as compared to a theoretical value of 2.01:1.00:3.22. Similarly, the ratio of N:Co:COOH in CoTCPc was 1.93:0.97:3.11 vs a theoretical value of 1.90:1.00:3.06. A GC (16 mm square × 3 mm thick) electrode used as the working electrode was purchased from Tokai Carbon Co. (GC-20, the area exposed to the solutions was 0.70 cm^2) and polished on one side to a bright surface with fine emery paper and alumina powder (final polish with 0.05 μm particle size, Buehler) just prior to use. It was then washed with 2 and 0.1 N H_2SO_4 and distilled water in a supersonic water bath to remove any alumina. The RRDE consisted of a GC disk surrounded by a platinum ring mounted in a Teflon rod (Nikko Keisoku Co.). The area of the disk was 0.22 cm^2. The collection coefficient was determined to be 0.43 at 100 rpm with the ferrocyanide–ferricyanide redox couple. The working surface of the RRDE was first polished with no. 1500 or 2000 emery paper and then with alumina slurry (particle sizes 1 and 0.05 μm) and well rinsed with 2 and 0.1 N H_2SO_4 and distilled water before each run to maintain its efficiency in the detection of H_2O_2. A large platinum foil (5 cm^2) was used as a counterelectrode. Small rectangular OTTLEs (Figure 1) that contained a platinum or a gold minigrid as the working electrode and could fit into the cell holders of the absorption and MCD apparatus were constructed according to the literature.[17] For

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(14) Abbreviations: FeTCPc, 4,4′,4″,4‴-tetracarboxyphthalocyaninatoiron; CoTCPc, 4,4′,4″,4‴-tetracarboxyphthalocyaninatocobalt; Pc, phthalocyanine dianion; MCD, magnetic circular dichroism; OTTLE, optically transparent thin-layer electrode; T, tesla; SCE, saturated calomel electrode; RRDE, rotating ring–disk electrode; GC, glassy carbon.

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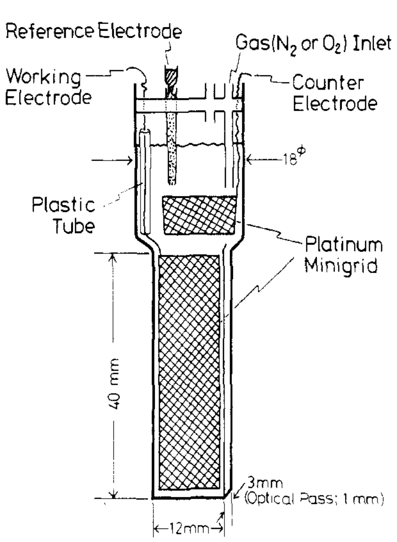

Figure 1. Structure of the OTTLE used.

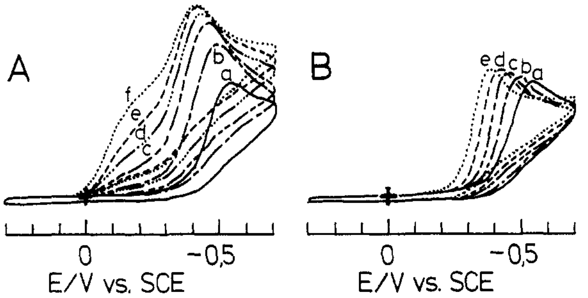

Figure 2. (A) Cyclic voltammograms for the reduction of O_2 (air saturated, ca. 0.24 mM) in 0.1 N bicarbonate solution (pH 9.0) containing various concentrations of FeTCPc (in M): (a) 0.0; (b) 1.43×10^{-7}; (c) 2.28×10^{-6}; (d) 1.14×10^{-5}; (e) 3.42×10^{-5}; (f) 1.14×10^{-4}. (B) Same as (A) but in the presence of various concentrations of CoTCPc (in M): (a) 0.0; (b) 1.44×10^{-7}; (c) 2.30×10^{-6}; (d) 3.44×10^{-5}; (e) 1.38×10^{-4}. Scan rate = 0.08 V s^{-1}.

pH variation experiments, concentrated H_2SO_4 or NaOH solution was added with stirring to a calcium carbonate saturated 0.1 N sodium bicarbonate solution (pH 9.0).

Measurements. Cyclic potential sweeps were generated by an NF circuit design block FG-100AD function generator in conjunction with a potentiostat which was built according to the literature.[18] An electrode rotator (Nikko RRD-1) was used for RRDE experiments. Nitrogen (99.9% pure) was used for deaeration of all solutions, and 20 min of vigorous air or pure O_2 bubbling was conducted in order to saturate solutions with oxygen. Absorption spectra were measured by use of a Jasco J-500 spectrodichrometer equipped with a data processor and with an electromagnet which produced magnetic fields up to 1.17 T, with parallel and then antiparallel fields. Its magnitude was expressed in terms of molar ellipticity per T, $[\theta]_M/10^4$ deg mol^{-1} dm^3 cm^{-1} T^{-1}.

Results and Discussion

Cyclic Voltammetry. Cyclic voltammograms of an N_2-saturated FeTCPc solution (1.14×10^{-4} M (1 M = 1 mol dm^{-3}), pH 9.0) showed a slight cathodic current increase at ca. −0.2 and −0.4 V, while that for a CoTCPc solution (1.38×10^{-4} M, pH 9.0) increased at ca. −0.4 V. With the introduction of air, the cathodic current increased dramatically especially at −0.4 V. Plots of the peak currents (i_p) at ca. −0.4 V vs. the square root of scan rates ($v^{1/2}$) for an air-saturated CoTCPc solution gave clear linearity, while that for a FeTCPc solution deviated from the linearity when $v^{1/2}$ was large. Yet, if the contribution at ca. −0.2 V was added, clear linearity was observed.

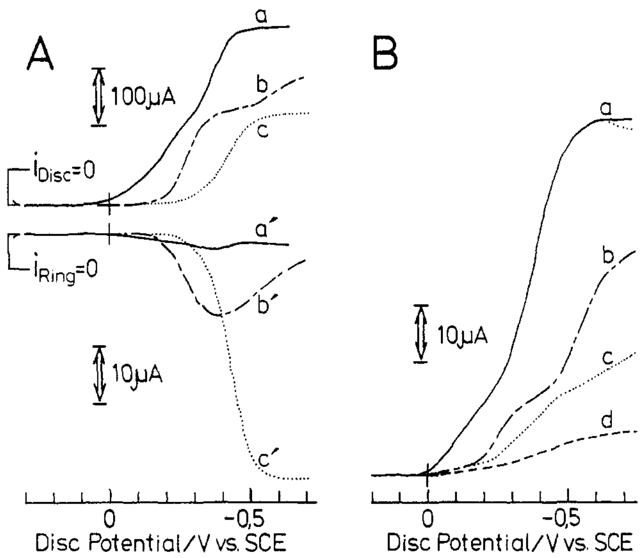

Figure 3. (A) Ring–disk *i–E* curves for the reduction of O_2 in the presence of 1.14×10^{-4} M FeTCPc (curves a and a′) or 1.20×10^{-4} M CoTCPc (curves b and b′) and in the absence of catalysts (curves c and c′). The solution was pure O_2-saturated, 0.1 N bicarbonate solution (pH 9.0), and the ring potential was set at +1.2 V. (B) *i–E* curves for the reduction of 0.8 mM H_2O_2 at a rotated GC disk (a) in the presence of 1.14×10^{-4} M FeTCPc, (b) in the presence of 1.20×10^{-4} M CoTCPc, and (c) in the absence of catalyst. Curve d is an *i–E* curve for N_2-saturated, 0.1 N bicarbonate solution (pH 9.0) in the absence of H_2O_2.

The concentration dependence of catalysis was examined at a fixed scan rate (Figure 2, A and B). As the [FeTCPc] was increased, a main O_2 reduction peak potential moved toward positive potentials with a concomitant increase in its current, and at [FeTCPc] = ca. 3×10^{-5} M, the change saturated, while the prewave at ca.-0.2 V kept increasing with an increase in [FeTCPc]. For the CoTCPc catalyst also, an anodic shift of the O_2 reduction peak was observed with an increase in its concentration. However, the accompanying increase in i_p was not so obvious. As for FeTCPc, i_p saturated at ca. 3×10^{-5} M.

The potential dependence of the catalysis was examined at pH values from 7.8 to 13. So long as the concentrations of the catalysts were fixed, the potentials were pH independent. For example, at [FeTCPc] = [CoTCPc] = 2×10^{-5} M, reduction peaks appeared at −0.39 and −0.38 V for FeTCPc and CoTCPc systems, respectively.

Rotating Ring–Disk Voltammetry. In N_2-saturated FeTCPc and/or CoTCPc solutions, the ratio of ring to disk currents matched the value expected from the collection efficiency (0.43), confirming the stability of the catalysts in the absence of oxygen. Their diffusion coefficient was evaluated to be 1.9×10^{-6} cm^{-2} s^{-1} from the limiting disk current.

In Figure 3A, curves a, b, and c respectively show the *i–E* responses for O_2 reduction in pure O_2-saturated solution (pH 9) in the presence of FeTCPc or CoTCPc and in their absence. Although the homogeneously dissolved catalysts and oxygen are brought to the surface of the RRDE, a calculation based on the theory of RRDE[19] indicates that the contribution of the catalysts to the observed current is only a few percent (in the calculation, the concentration and the diffusion coefficient of O_2 were supposed to be 1.1 mM[12c] and 2.1×10^{-5} [7d,e] cm^2 s^{-1}, respectively). In the presence of FeTCPc, O_2 reduction commenced at ca. 0 V and when the disk electrode potential (E_{disk}) reached ca. −0.45 V, the amount of the current matched approximately that expected from the Levich equation[20] for a four-electron reduction of oxygen. As curve b shows, O_2 reduction in the presence of CoTCPc proceeded in

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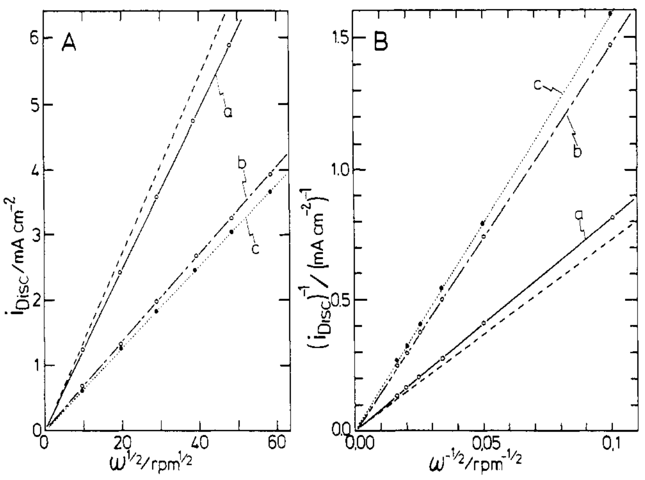

Figure 4. (A) Levich plots of limiting disk current vs. (rotation rate)$^{1/2}$ for pure O_2-saturated, 0.1 N bicarbonate solution (pH 9.0) (a) in the presence of 1.14×10^{-4} M FeTCPc, (b) in the presence of 1.20×10^{-4} M CoTCPc, and (c) in the absence of catalysts. The dashed line gives the calculated response for the four-electron, mass-transfer-limited reaction. (B) Koutecky–Levich plots for the reduction of O_2, constructed from the data in (A). Symbols are as in (A).

two steps. The cathodic current began to increase at E_{disk} = ca. −0.2 V but its rate of increase fell off in the region of $-0.4 < E_{disk} < -0.5$ V and again increased at more negative potentials. In curves a–c, the limiting currents were proportional to the O_2 concentration. That is, those in pure O_2-saturated solution were about 4.4–4.7 times larger than those in air-saturated solutions.

During O_2 reduction at disks, the responses at the ring electrode were also monitored. In order to detect H_2O_2, the ring electrode potential, E_{ring}, was maintained at +1.2 V.[7b,12] Corresponding to the above i–E curves a, b, and c, curves a′, b′, and c′ were obtained (Figure 3A). Although, the anodic current was detected in all cases, the amount was different, decreasing markedly in the sequence c′ > b′ > a′. In the presence of CoTCPc, the ring current increased but after reaching a maximum, it decreased. By comparing curves b and b′, the first stage is rationalized to be an O_2 to H_2O_2 process and the second step a partial reduction of H_2O_2 to H_2O. The disk current at the potential where the ring current reached a maximum corresponds to the current from a two-electron reduction of oxygen. Thus, it is suggested that the O_2 to H_2O_2 process occurs at more positive potential than that from H_2O_2 to H_2O. As curve a′ shows, O_2 reduction in the presence of FeTCPc also appears to proceed via H_2O_2.

Figure 4A demonstrates the Levich plots of the limiting current for the reduction of O_2 at a rotating electrode in the presence and absence of the catalysts (for CoTCPc system, the first limiting current was adopted). A clear linearity was obtained for all cases. Even at higher rotation speed, the disk current did not deviate from a straight line, indicating that the currents measured were entirely transport controlled. The number of electrons, n, involved in the reduction was then calculated from the Levich equation[20] (eq 1), where i_{lev} is the limiting disk current, ν is the kinematic

$$i_{lev} = 0.62FAD^{2/3}\nu^{-1/6}\omega^{1/2}C \qquad (1)$$

viscosity (0.01 cm s^{-1}), ω is the rotation speed (rad s^{-1}), C is the O_2 bulk concentration, and the other symbols have their usual meaning. The values were 3.78 and 2.08 for systems containing FeTCPc and CoTCPc, respectively, and 1.94 in the absence of catalysts. Thus, approximately a four-electron reduction was attained in the FeTCPc systems. Figure 4B shows the corresponding Koutecky–Levich plots.[20] The intercept at an infinitely high rotation rate (zero) indicates that the oxygen molecule is instantly reduced when it arrives at the electrode surface. The rates of reaction of the catalysts with oxygen were thus proved to be too fast to measure with the RRDE (>10^7 M^{-1} s^{-1}).

Since the current originating from H_2O_2 was observed in Figure 4, reduction of H_2O_2 was examined in oxygen-free solutions (Figure 3B). In both FeTCPc and CoTCPc systems, H_2O_2 was reduced in the potential range where O_2 was reduced, although in the later system, more current was observed at potentials more negative than −0.5 V, as anticipated from Figure 3A. From the limiting current, the number of electrons involved was calculated to be 2.2 for the FeTCPc system (6.8×10^{-6} cm^2 s^{-1} was used as the $D_{H_2O_2}$ value).[21]

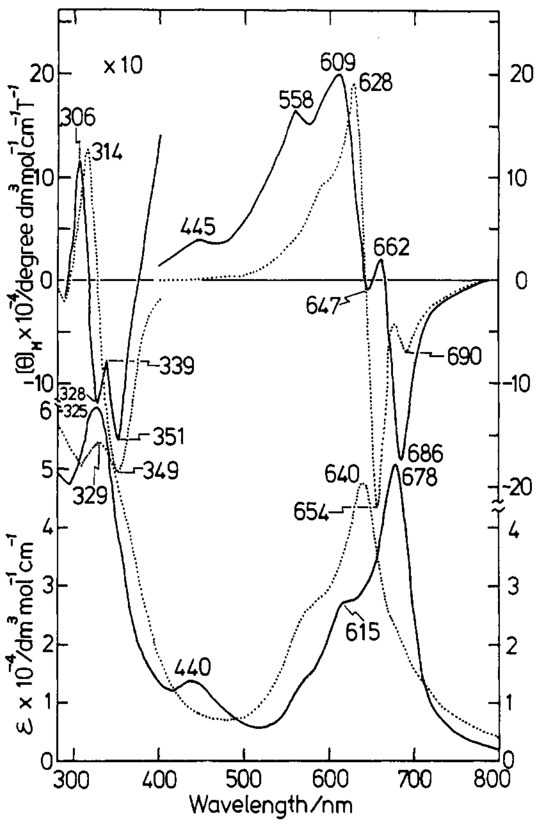

Figure 5. UV–visible absorption (bottom) and MCD (top) spectra of Fe^{III}FeTCPc (···) and electrogenerated Fe^{II}FeTCPc (—) in 0.1 N bicarbonate solution (pH 9.0). [Fe^{III}FeTCPc] = 1.14×10^{-4} M, path length = 1.0 mm, magnetic field = 1.1 T. Applied potentials were 0 and −0.45 V for Fe^{III}TCPc and Fe^{II}TCPc, respectively.

Electronic Absorption and Magnetic Circular Dichroism Spectroscopy. UV–visible and MCD spectra of FeTCPc and CoTCPc were obtained in order to get information on the oxidation and spin state of the central metals. Figure 5 shows the spectra for FeTCPc. Although the oxidation state of iron in iron phthalocyanines is generally 2+,[15] FeTCPc in pH 9 solution has been substantiated to exist as a mixture of at least iron(III) high- and low-spin state complexes because of the electron-withdrawing carboxyl groups.[22] Thus the MCD trough (dotted line) at 690 and 654 nm in the absence of an applied potential has been ascribed to the iron(III) low- and high-spin components, respectively. When the potential of the working electrode in the OTTLE was brought to ca. −0.25 V, the spectra changed slightly, but at ca. −0.45 V, well-defined spectra drawn as a solid line were obtained. Even if the pH value of the solution was changed within 7.8 ≤ pH ≤ 13 region, the situation was quite similar, i.e., the spectra changed dramatically at ca. −0.4 to −0.45 V where catalytic O_2 reduction occurs. From the presence of a diagnostic absorption peak at 440 nm which can be assigned to a charge-transfer transition from iron to the axial ligand,[23] the species is judged to be in the low-spin iron(II) state. MCD spectra are also appropriate as the species to be in a d^6 low-spin state. That is in agreement with the prediction from theory;[24] the Faraday A terms appeared

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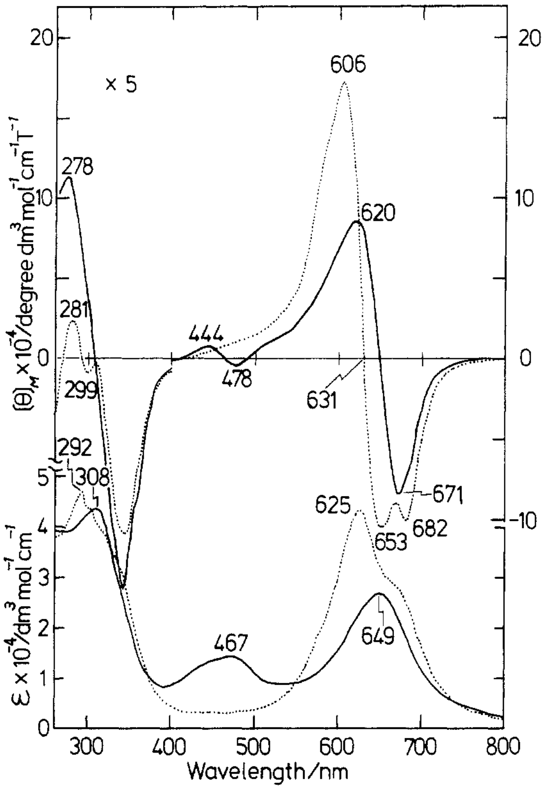

Figure 6. UV-visible absorption (bottom) and MCD (top) spectra of $Co^{II}TCPc$ (···) and electrogenerated $Co^{I}TCPc$ (—) in 0.1 N bicarbonate solution (pH 9.0). $[Co^{II}TCPc] = 1.20 \times 10^{-4}$ M. Applied potentials were 0 and -0.42 V for $Co^{II}TCPc$ and $Co^{I}TCPc$, respectively.

associated with an absorption peak and a shoulder at 678 and 615 nm, respectively.

Figure 6 shows the spectra of CoTCPc. In the absence of an applied potential, CoTCPc revealed spectra of cobalt(II) phthalocyanines.[25] However, when the potential of the OTTLE was brought close to that of catalytic O_2 to H_2O_2 reduction from the positive side within the ca. 100-mV region, the spectra began to change gradually, and finally at almost the same potential as that of catalytic O_2 reduction, the well-defined spectra shown as a solid line were recorded. Even if the solution pH was changed with $7.8 \leq pH \leq 13$, a drastic spectral change was always recognized in the -0.3- to -0.4-V region, precluding the participation of protons or hydroxyl anions. From the appearance of the characteristic new peak at 467 nm which can be assigned to charge transfer from cobalt to ligand,[25] the final spectrum is that of cobalt(I) phthalocyanine. Furthermore, as previously theoretically manifested,[25a] the MCD spectrum is that of low-spin d^7 cobalt phthalocyanine, by the corresponding negative *A* term. This band was lost immediately when oxygen was admitted. Thus the active species of CoTCPc is a low-spin cobalt(I) complex.

The results mentioned so far indicate that O_2 electroreduction in the presence of FeTCPc or CoTCPc dissolved in solution can be explained by an EC catalytic regeneration mechanism. As a pH-independent E step, eq 2 is appropriate, where $n = 3$ for Mt

$$Mt^{n}TCPc + e^{-} \rightarrow Mt^{n-1}TCPc \quad E_1^{0'} \qquad (2)$$

= Fe and 2 for Mt = Co. And as the C step, eq 3 and 4

$$Mt^{n-1}TCPc + {}^1/_2O_2 + H^+ \rightarrow Mt^{n}TCPc + {}^1/_2H_2O_2 \qquad (3)$$

$$Mt^{n-1}TCPc + {}^1/_2H_2O_2 + H^+ \rightarrow Mt^{n}TCPc + H_2O \qquad (4)$$

can be considered. Here, eq 4 may occur at the same or a slightly more negative potential than that of eq 3, especially for the CoTCPc system as would be anticipated from Figure 3. The results of Figure 3 also lessen the possibility of a direct four-electron reduction of O_2 to H_2O (eq 5). If we consider that H_2O_2

$$4Mt^{n-1}TCPc + O_2 + 4H^+ \rightarrow 4Mt^{n}TCPc + 2H_2O \qquad (5)$$

appears to be the initial product of O_2 reduction, reaction 2 followed by eq 6-8 may also be occurring:

$$Mt^{n-1}TCPc + H_2O_2 \rightarrow Mt^{n-1}TCPc(O_2H^-) + H^+$$

or

$$Mt^{n-1}TCPc + H_2O_2 \rightarrow Mt^{n-1}TCPc(H_2O_2) \qquad (6)$$

$$Mt^{n-1}TCPc(O_2H^-) + Mt^{n-1}TCPc + H^+ \rightarrow 2Mt^{n}TCPc + 2OH^-$$

or

$$Mt^{n-1}TCPc(H_2O_2) + Mt^{n-1}TCPc \rightarrow 2Mt^{n}TCPc + 2OH^- \qquad (7)$$

$$Mt^{n-1}TCPc(O_2H^-) + e^- + H^+ \rightarrow Mt^{n}TCPc + 2OH^-$$

or

$$Mt^{n-1}TCPc(H_2O_2) + e^- \rightarrow Mt^{n}TCPc + 2OH^- \qquad (8)$$

The type of $Mt^{n}TCPc$ species as well as whether OH^- or H_2O is present in the final products depends upon the solution pH.

Concluding Remarks

As for the systems containing water-soluble iron porphyrins,[7,8] electrocatalytic reduction of oxygen in the presence of dissolved FeTCPc could be explained by an EC catalytic regeneration mechanism, via H_2O_2 as an intermediate. This is different from the iron porphyrin adsorbed system[12c] in which catalytic O_2 reduction commences at a much more positive potential than that of the iron (III/II) redox couple. The results of optical measurements revealed that FeTCPc as the reaction intermediate is a low-spin iron(II) complex. For iron porphyrin, the active species were five-coordinated iron(II) high-spin state complexes.[7e,8cd] If we recall the fact that O_2 to H_2O reduction at a normal iron phthalocyanine adsorbed electrode was observed at a potential that nearly coincided with that from iron(II) to iron(I) reduction,[5] the oxidation state of iron does not appear to be a critical factor in O_2 electroreduction using iron phthalocyanines. Rather, O_2 reduction appears to occur at the first reduction potential of iron which exists, say, at 0 to -0.6 V vs. SCE, a potential appropriate for the catalytic reduction reaction, irrespective of the oxidation state of iron in the absence of an applied potential. Also, the present result offers a good example that what can be said of adsorbed catalysts is not necessarily true for dissolved catalysts. Namely, in the electrocatalytic reduction of oxygen at an iron phthalocyanine "adsorbed" electrode, active species are known to be in an intermediate or high-spin state but "not" in a low-spin state.[26]

The most notable result in the presence of dissolved CoTCPc was that the reduction proceeded by more than two electrons via H_2O_2. This appears to be an important difference between cobalt porphyrins and phthalocyanines, since hitherto reported O_2 reduction in the presence of monomeric cobalt porphyrins stopped at H_2O_2.[7c,12bc] In this case also, at least the O_2 to H_2O_2 process was rationalized by an EC mechanism. The H_2O_2 to H_2O process occurred, however, at the same and more negative potentials as compared with the above process. The active species of CoTCPc was confirmed to be a cobalt(I) low-spin state complex. The reaction was entirely controlled in O_2 in both FeTCPc and CoTCPc systems and the O_2 molecules were instantly reduced as soon as they arrived at the electrode.

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Registry No. O_2, 7782-44-7; CoTCPc, 69934-86-7; FeTCPc, 73533-56-9.

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