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Cathodic Reduction of Oxygen and Hydrogen Peroxide at Cobalt and Iron Crowned Phthalocyanines Adsorbed on Highly Oriented Pyrolytic Graphite Electrodes

Nagao Kobayashi,*[1] Pavel Janda,*[2] and A. B. P. Lever*

Department of Chemistry, York University, 4700 Keele Street, North York (Toronto),
Ontario, Canada M3J 1P3

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The surface electrochemistry of iron and cobalt crowned phthalocyanine (Fe^{II}CRPc(−2) and Co^{II}CRPc(−2)) adsorbed on a highly oriented pyrolytic graphite (HOPG) electrode has been explored under an argon atmosphere. The redox processes of surface bound Co^{II}CRPc(−2)/[Co^{I}CRPc(−2)]$^-$, [Fe^{III}CRPc(−2)]$^+$/Fe^{II}CRPc(−2), and Fe^{II}CRPc(−2)/[Fe^{I}CRPc(−2)]$^-$ couples were identified and their pH dependence reported in the range 1–13. Under an oxygen atmosphere at the Co^{II}CRPc(−2)/HOPG electrode, two reduction processes, oxygen to hydrogen peroxide and hydrogen peroxide to water, were clearly delineated and their pH dependences explored. Surface bound Fe^{II}CRPc(−2) catalyzes the four-electron reduction of oxygen in alkaline medium. The Co^{II}CRPc(−2)/HOPG electrode is very stable both in the presence and absence of oxygen, but the Fe^{II}CRPc(−2)/HOPG electrode is much less stable when electrocatalytic oxygen reduction takes place on its surface.

Introduction

There has been significant progress in our understanding of the electrocatalytic reduction of oxygen in the presence of organometallic catalysts.[3-6] In many cases, oxygen reduction has been carried out at catalyst-adsorbed or -modified electrodes. When monomeric cobalt porphyrins and phthalocyanines are used as catalysts, oxygen reduction usually proceeds only to hydrogen peroxide (H_2O_2),[3,4] however the four-electron reduction of oxygen to water catalyzed by a monomeric cobalt phthalocyanine[7] and by a cyano-bridged cobalt phthalocyanine[8] has recently been reported. Some cobalt derivatives of cofacial diporphyrin are known to catalyze the reduction of oxygen to water.[5] Moreover, iron porphyrins and phthalocyanines will catalyze the four-electron reduction of oxygen, in alkaline medium. However, the factors responsible for activating a four-electron rather than a two-electron pathway remain obscure. Oxygen reduction characteristics are influenced by various extrinsic factors such as, for example, differences in adsorption procedure and surface coverage by catalyst and even by changes of ionic strength of the experimental solution.[6k] Many catalysts are degraded by contact with hydrogen peroxide such that successive potential scans of a given modified electrode surface are not fully reproducible, necessitating a large number of studies with fresh surfaces. It is difficult to ensure that all such fresh surfaces are identical further complicating the study.

Recently, we reported the synthesis and properties of phthalocyanines with four 15-crown-5 ether voids at the 3,4 position,[9] MCrPc(−2)[10] (M = Co, Fe, Cu, H_2). In the course of purification, we noted that these phthalocyanines adsorbed onto silica gel and powdered charcoal very strongly. Also, they exhibited ideal spectroscopic (UV, MCD, ESR, NMR, emission, etc.) behavior.[9] The cobalt and iron derivatives (Figure 1) have therefore been studied as electrocatalysts for oxygen reduction and are shown here to have many desirable features; in particular, they (Fe, Co) can be used for preparation of stable electrodes with modified surfaces whose electrochemical properties are sufficiently reproducible for multiple-scan voltammetry. It is not necessary to constantly renew the surface, at least under argon. The iron derivative, under oxygen, is less stable. The cobalt species is more stable but shows some deactivation over time when deposited on the RDE while electrocatalytic oxygen reduction takes place.

During the progress of our studies, there has evidently been great interest in the properties of both crowned phthalocyanines[11] and crowned porphyrins,[12] but the properties of these with respect to oxygen electrocatalysis have not been explored.

Co^{II}CRPc(−2) adsorbed onto highly oriented pyrolytic graphite electrodes (HOPG)[13] is shown to catalyze the commonly observed two-electron reduction of oxygen to hydrogen peroxide. This is

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[1] Visiting professor from the Pharmaceutical Institute, Tohoku University, Sendai 980, Japan.

[2] Visiting scholar from the J. Heyrovsky Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Praha, Czechoslovakia.

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[10] Abbreviations: FeCRPc(−2), tetra(15-crown-5)ed (phthalocyaninato)iron; CoCRPc(−2), tetra(15-crown-5)ed (phthalocyaninato)cobalt; HOPG, highly oriented pyrrolytic graphite; CV, cyclovoltammetric; RDE, rotating disk electrode; SCE, saturated calomel electrode; DCB, dichlorobenzene, *i*, current.

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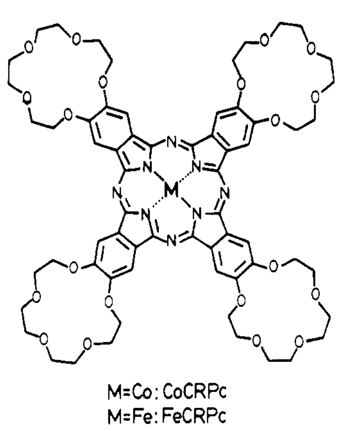

Figure 1. Cobalt and iron crown phthalocyanines.

followed at a significantly more negative potential by the further reduction of hydrogen peroxide to water. While such a double-step reduction has been observed previously,[3g,6g,13-16] the very clean separation observed here between these two processes affords us the rare opportunity of a more detailed study of the pH dependence.

Electrocatalytic data for Fe^{II}CRPc(−2) adsorbed onto a HOPG electrode are also described. As with other iron phthalocyanines, Fe^{II}CRPc(−2) catalyzes the four-electron reduction to water at alkaline pH. Interestingly, the pH dependence for oxygen reduction at the Fe^{II}CRpc(−2)-adsorbed electrode is quite similar to that of hydrogen peroxide reduction at the Co^{II}CRPc(−2)/HOPG electrode. However the data are not of such highly quality as with Co^{II}CRPc(−2)/HOPG due to decomposition of Fe^{II}CRPc(−2).

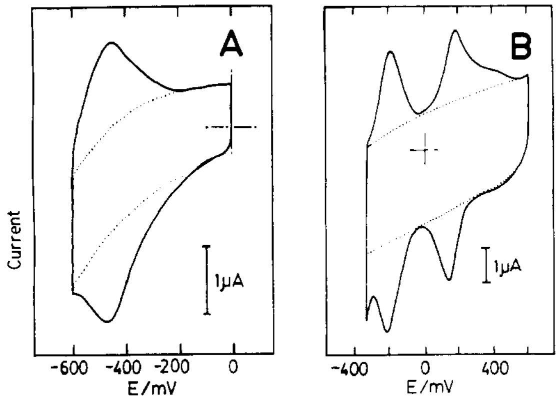

Figure 2. CV diagrams of (A) Co^{II}CRPc(−2)/HOPG at pH 3.0 and (B) Fe^{II}CRPe(−2)/HOPG at pH 0.9. Dotted lines indicate CV response at a bare HOPG surface. Scan speed = 100 mV/s.

Experimental Section

Materials. Argon gas (Linde) was purified by passage through heated copper filings, anhydrous $CaSO_4$ (Drierite), molecular sieves (Bolf, Type 3A), and glass wool. Oxygen gas (Linde) was purified by passage through anhydrous $CaSO_4$, NaOH pellets (AnalaR analytical grade), anhydrous $CaSO_4$, molecular sieves, and glass wool.

The cobalt crown phthalocyanine Co^{II}CRPc(−2) was prepared according to a literature procedure.[9a,b] The iron crown phthalocyanine Fe^{II}CRPc(−2) was prepared and purified in a similar fashion,[8b] from 2,3-(3′,4′-dicyanobenzo)-1,4,7,10,13-pentaoxycyclopentadeca-2-ene and $FeCl_2$ in refluxing ethylene glycol. Anal. Calcd for $C_{64}H_{72}FeN_8O_{20}$: C, 57.83; H, 5.46; N, 8.43. Found: C, 57.59; H, 5.40; N, 8.38.

Electrochemical Measurements. These were undertaken using equipment (Pine 4-electrode potentiostat, Princeton Applied Research Corp. PARC potentiostat) and techniques as previously described.[17] The electrode was mounted in Teflon to expose a circular area of 0.440 cm^2. Prior to adsorption of the catalyst, the HOPG (Union Carbide) surface was renewed using adhesive Scotch tape. A freshly exposed HOPG surface was modified by dipping and rotating it in 0.1 mM Fe^{II}CRPc(−2) or Co^{II}CRPc(−2) in DCB/ethanol (19:1 v/v) solution for about 5–10 min. The electrode was then washed with ethanol and doubly distilled water. Current–potential (i–E) curves were recorded in aqueous 0.1 M phosphate buffer (prepared from a 0.1 M solution of Na_2HPO_4 and KH_2PO_4), and the pH was adjusted by addition of small amounts of KOH and H_3PO_4 (AnalaR, BDH chemicals) as required. Measurements at pH 1–2 were carried out in dilute H_2SO_4 (Suprapur, Merck).

Results and Discussion

(i) Studies under an Argon Atmosphere, in the Absence of Oxygen. (a) Voltammetric Response of Co^{II}CRPc(−2)/HOPG. Figure 2A shows cyclic voltammetric (CV) potentiodynamic waves obtained at bare HOPG and Co^{II}CRPc(−2)/HOPG electrodes, with data collected in Table I. An anodic and a cathodic peak of practically equal area appeared (solid line), with peak currents (i_p) directly proportional to scan rate, typical of a Faradaic process involving an adsorbed species. Assuming that the surface redox couple obeys the Nernst equation, the number of electrons participating per adsorbed molecule (also estimated from the slope of the i_p versus scan rate plot) is 0.972 ± 0.002,[18] i.e. a one-electron redox process. The charge under this peak is then 4.1 μC and corresponds to a surface concentration of 4.2×10^{-11} mol/cm^2. From the Corey–Pauling–Koltun molecular model, the length of one side of Co^{II}CRPc(−2) is about 20 Å. Using the above surface concentration and assuming that Co^{II}CRPc(−2) lies flat on the electrode, the calculated coverage corresponds to almost exactly one monolayer. This limiting coverage of adsorbed Co^{II}CRPc(−2) was independent of the concentration of Co^{II}CRPc(−2) in the DCB used during adsorption. The Co^{II}CRPc(−2)/

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Table I. Redox Potentials (V) for the CoPc Oxygen and Hydrogen Peroxide Redox Processes vs SCE[a,b]

pH	$Co^{II}Pc(-2)/[Co^{I}Pc(-2)]^-$ $E_{1/2}$ CRPc	$[Co^{I}Pc(-2)]^-/[Co^{I}Pc(-3)]^{2-}$ $E_{1/2}$ TsPc	pH	O_2/H_2O_2 E_p CRPc	H_2O_2/H_2O E_p CRPc
1.0	–0.34		1.0	–0.29	
1.6	–0.38	–0.48	1.6	–0.30	–0.80
2.1	–0.42	–0.51	2.0	–0.29	–0.84
3.0	–0.46	–0.57	2.1	–0.32	–0.84
4.0	–0.54	–0.64	3.0	–0.35	–0.94
5.0	–0.59		4.0	–0.38	–1.06
5.7	–0.62		5.0	–0.37	–1.06
6.0	–0.60		5.7	–0.35	–1.08
7.0	–0.60	–1.04	6.0	–0.36	–1.15
8.1	–0.60	–1.10	7.0	–0.37	–1.15
9.0	–0.60	–1.15	8.1	–0.32	–1.34
10.0	–0.60	–1.21	9.0	–0.32	–1.39
11.0	–0.59	–1.26	10.0	–0.33	
12.0	–0.62	–1.32	11.0	–0.33	–1.40
13.0	–0.62	–1.37	13.0	–0.37	

[a] All data are from cyclic voltammetry. Averages of the anodic and cathodic waves of the reversible metal-centered couples are quoted. The irreversible cathodic peak potential is quoted for the oxygen reduction processes. [b] Additional data: A second $Co^{II}CRPc(-2)$ reduction potential was observed at –0.47 V for pH = 1. The oxidation process forming $[Co^{III}CRPc(-2)]^+$ was observed at 0.67, 0.52, and 0.28 V at pH 1, 7, and 10, respectively.

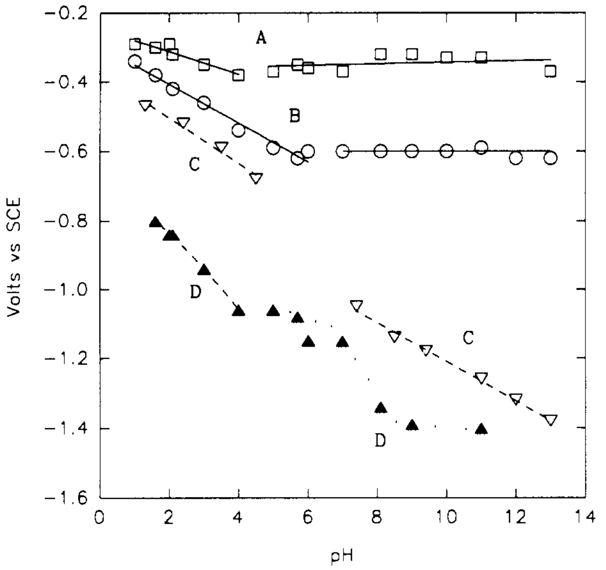

Figure 3. pH dependencies of (A) oxygen reduction potentials at $Co^{II}CRPc(-2)/HOPG$, (B) $Co^{II}CRPc(-2)/[Co^{I}CRPc(-2)]^-$ couple at HOPG, (C) $[Co^{I}TsPc(-2)]^-/[Co^{I}TsPc(-3)]^{2-}$ couple at an ordinary pyrolytic graphite (OPG) electrode, and (D) hydrogen peroxide reduction at $Co^{II}CRPc(-2)/HOPG$.

HOPG electrode was stable after several hundreds cycles in the potential range, shown in Figure 2, in the whole pH range and was not affected by rotation of the electrode.

The pH dependence of the redox potential calculated as a mean value of anodic and cathodic peak potentials is shown in Figure 3B and Tables I and II. High regression coefficients provide some confidence for the accuracies of the slopes and intercepts. In the range pH 5–1.6, the potential shifts to a more negative direction with increasing pH with slope of about –63 mV/pH, suggesting participation of one proton. Above pH 5, it becomes essentially pH-independent. The potential values, and their dependence on pH, are fully comparable to earlier studies with $Co^{II}TNPc(-2)$($TNPc(-2)$ = tetraneopentoxyphthalocyanine)[13] and $Co^{II}TsPc(-2)$($TsPc(-2)$ = tetrasulfonylphthalocyanine),[3h,19] and the wave in question undoubtedly arises from the Co^{II}/Co^{I} couple.

During our variable-pH study, some experiments revealed a wave at more positive potentials (as noted in Table I). This was generally poorly developed. It is almost certainly the $[Co^{III}CRPc(-2)]^+/Co^{II}CRPc(-2)$ wave, but its identification was not pursued.

In our studies with cobalt tetrasulfonated phthalocyanine,[19] $Co^{II}TsPc(-2)/HOPG$, a second reduction process was observed occurring negative of the $Co^{II}TsPc(-2)/[Co^{I}TsPc(-2)]^-$ couple, namely the $[Co^{I}TsPc(-2)]^-/[Co^{I}TsPc(-3)]^{2-}$ process. This is observed relatively close to the former process in acid medium, but its different pH dependence causes it to be separated therefrom in basic medium. The pH dependence data for the latter process are reproduced in Figure 3C since they are relevant to the discussion below. In the $Co^{II}CRPc(-2)$ case, this second reduction process was detected in strong acid medium (see Table I). However, $Co^{II}CRPc(-2)$ catalyzes proton (water) reduction, and the solvent cutoff through this process obscures this second reduction step for all solutions except those with pH near 1.

For completion note that a $Co^{II}CRPc(-2)/HOPG$ electrode studied in DCB/TBAP solution showed a cyclic voltammogram, using a RDE electrode, with surface-bound couples appearing at –0.53 V (vs SCE) attributable to the couple $Co^{II}CRPc(-2)/[Co^{I}CRPc(-2)]^-$ and at +0.32 and +0.46 V attributable to the couples[20] $[Co^{II}CRPc(-1)]^+/Co^{II}CRPc(-2)$ and $[Co^{III}CRPc(-1)]^{2+}/[Co^{II}CRPc(-1)]^+$, respectively.

(b) Voltammetric Response of $Fe^{II}CRPc(-2)/HOPG$. In oxygen-free solution, a $Fe^{II}CRPc(-2)/HOPG$ electrode shows two redox couples (Figure 2B) in the potential range from ca. +0.2 to –0.4 V, with pH-dependence as shown in Figure 4A. From comparison with literature data on pH dependence,[6e,19,21] the more positive potential couple is assigned to $[Fe^{III}CRPc(-2)]^+/Fe^{II}CRPc(-2)$ and the less, to $Fe^{II}CRPc(-2)/[Fe^{I}CRPc(-2)]^-$. Although the $[Fe^{III}CRPc(-2)]^+/Fe^{II}CRPc(-2)$ couple looks sharper than that of $Co^{II}CRPc(-2)/[Co^{I}CRPc(-2)]^-$ in Figure 2A, the actual surface concentration of $Fe^{II}CRPc(-2)$ (4.8×10^{-11} mol/cm^2) estimated from the charge involved in the process (4.0 μC/cm^2) is approximately the same as that of $Co^{II}CRPc(-2)$, i.e. a monolayer. Regression data are collected in Table II.

At pH above 7, it was not possible to observe the $Fe^{II}CRPc(-2)/[Fe^{I}CRPc(-2)]^-$ wave due to solvent limit (proton reduction). It is clearly observed[19] with $Fe^{II}TsPc(-2)$, which must evidently be less effective in catalyzing proton reduction.

(c) Studies Using Hydrogen Peroxide and $Co^{II}CRPc(-2)/HOPG$. Cyclic voltammetric studies were briefly undertaken, of the reduction of oxygen-free, argon-saturated H_2O_2 at a bare HOPG electrode and at a $Co^{II}CRPc(-2)/HOPG$ electrode, for comparison with the oxygen reduction data below. The bare electrode shows rising reduction current at -1.0 V, at pH 3, while the $Co^{II}CRPc/HOPG$ electrode shows a reduction peak at –0.88 V corresponding almost exactly with the second oxygen reduction process described below.

(ii) Studies in Oxygen-Saturated Buffer Solutions. (a) Voltammetric Response of $Co^{II}CRPc(-2)/HOPG$. Figure 5A displays the CV curves for the reduction of O_2. Two cathodic peaks were recognized before the current due to H_2 evolution obscured further processes. The first is due to the reduction of oxygen to H_2O_2, and the second, to the reduction of the H_2O_2 so produced. The second peak corresponds with that observed when hydrogen peroxide is studied alone (see immediately above) and increases in current if hydrogen peroxide is added to the oxygenated solution. The second cathodic peak potential permits clear definition of the pH dependence of both peak potentials (vide infra).

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Table II. Regression Data for pH Dependence (Data in V vs SCE)

redox process	pH range	slope[a]	intercept[a]	R	no.[a]
$Co^{II}CRPc(-2)/[Co^{I}CRPc(-2)]^-$	1.6–5	–0.063 (0.002)	–0.28 (0.008)	0.997	6
	5–13	0[b]			
$Co^{I}TsPc(-2)]^-/[Co^{I}TsPc(-3)]^{2-}$	1.25–4.5	–0.054 (0.006)	–0.41 (0.015)	0.988	4
	7.4–13	–0.056 (0.002)	–0.64 (0.01)	0.997	6
$O_2 \rightarrow H_2O_2$	1.6–4	–0.033 (0.005)	–0.25 (0.012)	0.950	6
	5–13	0[b]			
$H_2O_2 \rightarrow H_2O$	1.6–7	–0.110 (0.004)	–0.62 (0.008)	0.998	5
$[Fe^{III}CRPc(-2)]^+/Fe^{II}CRPc(-2)$	0.9–5	0	+0.18		
	7–13	–0.054 (0.001)	+0.45 (0.007)	0.999	5
$Fe^{II}CRPc(-2)/[Fe^{I}CRPc(-2)]^-$	1–5	–0.089 (0.005)[c]	–0.12 (0.016)	0.994	6
oxygen reduction	1–4	–0.049 (0.007)	+0.17 (0.017)	0.952	7
	8–13	–0.034 (0.005)	+0.12 (0.020)	0.953	7

[a] Least-squares analysis using number of points as indicated and with regression coefficient as indicated. [b] Assumed zero slope; in fact a least-squares analysis would yield a very small negative slope. [c] Omission of the point at pH = 7 provides a better correlation with a slope of –0.069 V/pH.

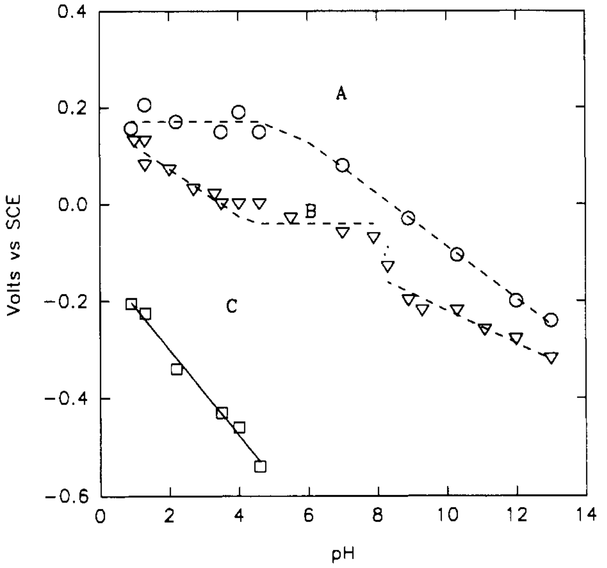

Figure 4. pH dependencies of (A) $[Fe^{III}CRPc(-2)]^+/Fe^{II}CRPc(-2)$ at HOPG, (B) oxygen reduction potentials at $Fe^{II}CRPc/HOPG$ from CV peak potentials, and (C) $Fe^{II}CRPc(-2)/[Fe^{I}CRPc(-2)]^-$ couples at HOPG.

Figure 5B shows the i–E responses for the first oxygen reduction wave obtained as $Co^{II}CRPc(-2)/HOPG$ rotating disk electrode (RDE) at several pH values. Multiple potential scans of the same surface give good reproducible data. The onset of oxygen reduction and the limiting current depend upon the solution pH. However, this last observation is due to the difference of solubility of oxygen: greater in basic than in acidic solution. The number of electrons, n, involved in the reaction was calculated from the Levich equation:[13,18,22]

$$i_l = 0.62\, nFA\omega^{1/2}C_{ox}D_0^{2/3}\nu^{-1/6} \qquad (1)$$

Here C_{ox} is the bulk oxygen concentration, D_0 is its diffusion coefficient, ν is the kinematic viscosity, and the other symbols have their usual electrochemical meanings. A value of $C_{ox}D_0^{2/3}\nu^{-1/6} = 1.77 \times 10^{-9}$ was derived via calibration with a platinum electrode (assuming a well-behaved 4-electron reduction process at Pt)[23] and led to an average experimental value of 1.99 ± 0.03 electrons, confirming that oxygen is reduced to H_2O_2.

RDE data show (Figure 5C) linear dependence of i_l on the square root of the rotation rate indicating a fast diffusion-driven reaction. Note the rising current (Figure 5B), beyond the plateau, at more negative potentials corresponding to the ensuing reduction of H_2O_2 and especially noticeable at lower pH. The data were analyzed by plotting them as i^{-1} vs $\omega^{-1/2}$ (Figure 5D) (Koutecky–Levich plots[13,22]). The line is almost perfectly straight, indicating first-order dependence of the overall reaction on oxygen concentration. The intercept is indistinguishable from zero within experimental error indicating a very fast reaction rate. Figure 5E shows a Tafel type plot from RDE data, for the first reduction process, at several representative pHs. The slope of the plot changes slightly in the pH range of 1.6 to 5 from −116 to −130 mV/decade, but above pH 5 this value remains constant (−130 mV/decade). This may be indicative of an irreversible (non-Nernstian) process possibly with a one-electron rate-determining step. Curve A in Figure 3 represents the pH dependence of the half-wave potential, $E_{1/2}$, for oxygen reduction at $Co^{II}CRPc(-2)/HOPG$. $E_{1/2}$ for oxygen reduction is always more positive than the Co^{II}/Co^{I} process. $E_{1/2}$ for oxygen reduction is always more positive than the Co^{II}/Co^{I} process (Figure 3, curve B) but with a much shallower pH dependence, −33 mV/pH, in the pH regime 1–4.

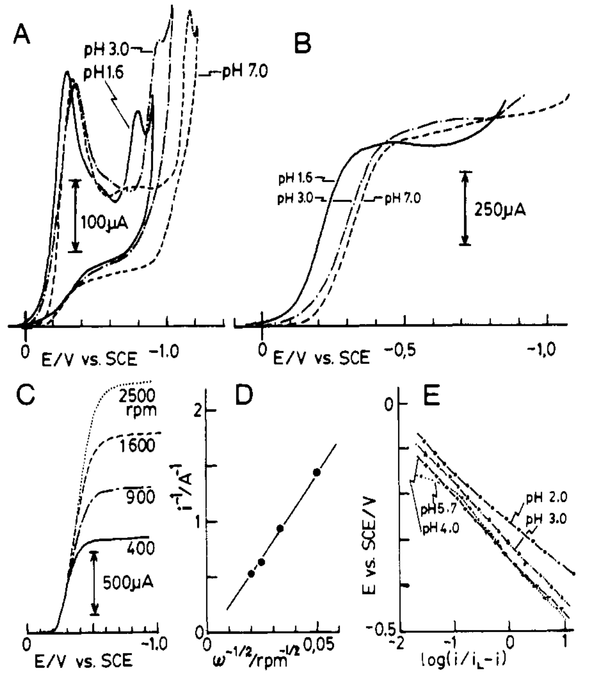

Figure 5. (A) CV curves for oxygen reduction at $Co^{II}CRPc/HOPG$ (scan rate 100 mV/s). (B) RDE responses for oxygen reduction at $Co^{II}CRPc/HOPG$ at various pH values (scan rate 10 mV/s). (C) RDE responses for oxygen reduction at $Co^{II}CRPc/HOPG$ at various rotation speeds (pH 13, scan rate 10 mV/s). (D) Koutecky–Levich plots constructed from the plateau current in (D). (E) Tafel type plots from RDE data at $Co^{II}CRPc/HOPG$ for the first oxygen reduction process.

The pH dependence for reduction of hydrogen peroxide to water at a $Co^{II}CRPc(-2)/HOPG$ electrode is shown in Figure 3D. It differs substantially from that of oxygen reduction at $Co^{II}CRPc(-2)/HOPG$, shown in Figure 3A. There are three

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(22) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1962. Koutecky, J.; Levich, V. C. *Zh. Fiz. Khim.* **1956**, *32*, 1565.

(23) Koryta, J.; Dvorak, J. *Principles of Electrochemistry*; John Wiley and Sons: New York, 1987; p 343.

regions of differing slope showing that the number of protons involved in the process varies as the mechanism varies from low to medium to high pH. At low pH, the slope is −110 mV/pH. Near neutral pH, the data are more scattered but the slope is evidently zero or small. Unfortunately it was difficult to collect data for this process at high pH since the process occurs very close to the reduction of water.

(b) Mechanism of Oxygen and Hydrogen Peroxide Reduction by $Co^{II}CRPc(-2)$. It is tempting to assume that the active catalyst for oxygen reduction is the $[Co^{I}CRPc(-2)]^-$ species since the pH dependence of oxygen reduction parallels that of the $Co^{II}Pc(-2)/[Co^{I}Pc(-2)]^-$ couple, at slightly more positive potentials. Indeed with a simplified assumption of reversibility, and ideal behavior of the phthalocyanine catalyst, one may calculate a rate constant for oxygen reduction,[24] using

$$k = (D_0/\Gamma_{CoCRPc}\delta)\exp[(F/RT)(E_{1/2} - E^\circ)] \qquad (2)$$

where δ is the thickness of the diffusion layer at the RDE (and $\delta = 4.98D_0^{1/3}\nu^{1/6}\omega^{1/2}$),[24c] Γ_{CoCRPc} is the surface concentration of the catalyzer, $E_{1/2}$ is the half-wave potential for oxygen reduction, and E° is the redox potential for the $Co^{II}CRPc(-2)/[Co^{I}CRPc(-2)]^-$ redox couple. The values (T = 20 °C) $D_0 = 1.7 \times 10^{-5}$ cm^2/s, $\Gamma = 4.2 \times 10^{-11}$ mol/cm^2, rotation rate ω = 42 rads/s, and kinematic viscosity $\nu = 10^{-2}$ cm^2/s and the value of $E_{1/2} - E^\circ$ = ca. 300 mV, from the data, yield k = ca. 10^{10} M^{-1} s^{-1} in basic medium. However, this does not prove the catalytic participation of $Co^{I}Pc(-2)$. Recently we have discussed the electrocatalytic reduction of oxygen by perchlorinated cobalt phthalocyanine ($CoCl_{16}Pc(-2)$).[25] In this case, oxygen reduction parallels the $Co^{II}Pc(-2)/[Co^{I}Pc(-2)]^-$ couple in acid medium but not in alkaline medium. In strong alkali, oxygen reduction occurs at some 400–600 mV more positive a potential than the $Co^{II}Pc(-2)/[Co^{I}Pc(-2)]^-$ couple. If $[Co^{I}Cl_{16}Pc(-2)]^-$ were the active species, oxygen reduction would have to occur at an unrealistically high rate (following the above analysis). Therefore, we proposed that the active species was $Co^{II}Cl_{16}Pc(-2)$. It is reasonable to suppose that $Co^{II}CRPc(-2)$ is the active catalyst here and that an intermediate oxygen adduct is involved:[13,25]

$$Co^{II}Pc(-2) + O_2 \leftrightarrow (O_2^-)Co^{III}Pc(-2) \qquad (3)$$

In (3), the most simple oxygen adduct is portrayed, on the basis of cobalt(III) dioxygen chemistry.[26] A binuclear peroxo-bridged species might also be invoked, though, in the surface environment, a mononuclear species is perhaps more readily conceived. The argument remains substantially equivalent if a mononuclear or a binuclear oxygen adduct is assumed. The equilibrium (3) is strongly driven to the left and therefore oxygen reduction is not generally observed at, or close to, the $[Co^{III}Pc(-2)]^+/Co^{II}Pc(-2)$ couple potential, nor are oxygen adducts seen when $Co^{II}Pc(-2)$ solutions are mixed with oxygen. However, oxygen adducts have been observed at low temperatures, with CoPc, proving that equilibria such as (3) do occur.[27]

The data are consistent with the supposition that reduction of the oxygen adduct in (3) occurs at the potential corresponding experimentally with the observed catalytic oxygen reduction process. Removal of the oxygen adduct via this reduction process then drives the equilibrium (3) to the right. The pH dependence follows the Co^{II}/Co^{I} couple in the acid regime for two possible reasons: (i) protonation of the peroxo bridge likely occurs and (ii) the $[Co^{I}CRPc(-2)]^-$ species is air (oxygen) sensitive so that it would also catalyze oxygen reduction at a potential close to the Co^{II}/Co^{I} process as $[Co^{I}CRPc(-2)]^-$ begins to build up. The involvement of an analogous Co^{II} porphyrin as the catalytically active species has also recently been suggested by Anson and co-workers.[28]

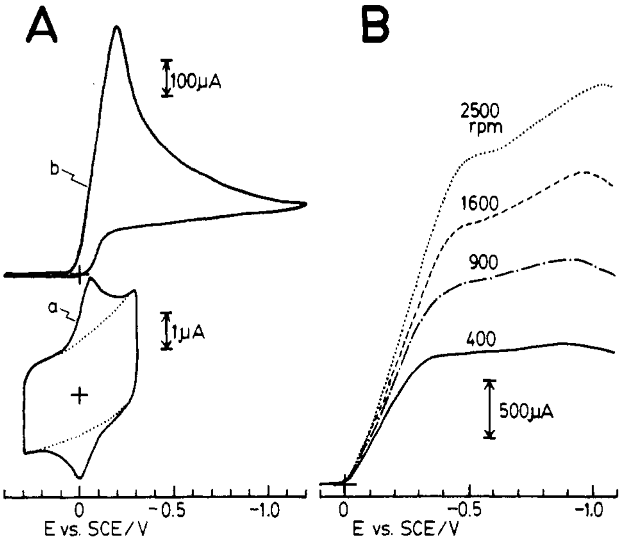

Figure 6. (A) CV diagrams at $Fe^{II}CRPc$/HOPG under argon (curve a) and in oxygen-saturated solution (curve b) at pH 8.9. Dotted lines indicate responses at bare HOPG (scan rate 100 mV/s). (B) RDE responses at $Fe^{II}CRPc$/HOPG in oxygen-saturated solution at pH 9.2 (scan rate 10 mV/s).

The reduction of hydrogen peroxide occurs at a potential somewhat negative of that for the next phthalocyanine reduction couple, $[Co^{I}Pc(-2)]^-/[Co^{I}Pc(-3)]^{2-}$, which was tracked as a function of pH in a parallel study of CoTsPc[19] (Figure 3C). Thus, the species $[Co^{I}CRPc(-3)]^{2-}$ will be the effective catalyst in peroxide reduction, probably via a complex similar to that described in (3).

This last couple is more accurately portrayed as $HCo^{I}Pc(-2)/H_2Co^{I}Pc(-3)$, in acid medium, where protonation (probably at a bridgehead aza link but conceivably also at the metal center) has occurred and where the number of protons is dictated by consideration of the pH dependences of the Co^{III}/Co^{II}, Co^{II}/Co^{I}, and $Co^{I}Pc(-2)/Co^{I}Pc(-3)$ couples shown in Figure 3. Assuming $Co^{II}Pc$ is not protonated, then the degree of protonation indicated above follows. In basic medium, $[Co^{I}CRPc(-2)]^-$ will then be unprotonated, while $[HCo^{I}CRPc(-3)]^-$ will retain one proton. Thus, the reduction of hydrogen peroxide will be catalyzed by these protonated $[Co^{I}Pc(-3)]^{2-}$ species. Presentation of a detailed mechanism awaits further study. However, note that mechanisms have been invoked to include coordination of HO_2^- to a reduced cobalt phthalocyanine, followed by bond breaking and generation of a hydroxide radical attached to cobalt, which is then immediately reduced to coordinated hydroxide anion.[3i]

(c) Voltammetric Response of $Fe^{II}CRPc(-2)$/HOPG. At low pH, oxygen reduction starts (Figure 4B) slightly negative of the potential of the $[Fe^{III}CRPc(-2)]^+/Fe^{II}CRPc(-2)$ reduction couple (also see Figure 6A, curves a and b), strongly suggesting the participation of $Fe^{II}CRPc(-2)$ in the catalytic reduction process (Table III). The pH dependence for oxygen reduction (Figure 4B) roughly tracks that of the $[Fe^{III}CRPc(-2)]^+/Fe^{II}CRPc(-2)$ couple (Figure 4A). The separation between the $[Fe^{III}CRPc(-2)]^+/Fe^{II}CRPc(-2)$ process and the oxygen reduction process is proportional to the rate of oxygen reduction at the modified surface.[24] Thus, consideration of Figure 4 shows that the rate

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[24] (a) Oyama, N.; Oki, N.; Ohno, H.; Ohnuki, Y.; Matsuda, H.; Tsuchida, E. *J. Phys. Chem.* **1983**, *87*, 3642. (b) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1982**, *134*, 163; **1982**, *142*, 1. (c) Andrieux, C. P.; Dumas-Barchiat, J. M.; Saveant, J. M. *J. Electroanal. Chem.* **1982**, *131*, 1.

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Table III. Redox Potentials for $Fe^{II}CRPc$ Surface Potentials under Argon and Under Oxygen vs SCE[a]

			$Fe^{II}CRPc(-2)$ O_2 redn	
pH	$[Fe^{III}CRPc(-2)]^+$/ $Fe^{II}CRPc(-2)$ $E_{1/2}$	$Fe^{II}CRPc(-2)$/ $[Fe^{I}CRPc(-2)]^-$ $E_{1/2}$	pH	E_p
0.9	0.16	–0.21	1.0	0.13
1.3	0.21	–0.23	1.3	0.08
2.2	0.17	–0.34	1.3	0.13
3.5	0.15	–0.43	2.0	0.07
4.0	0.19	–0.46	2.7	0.03
4.6	0.15	–0.54	3.3	0.02
3.5	0.00		3.5	0.00
7.0	0.08		4.0	0.00
4.6	0.00		4.6	0.00
5.5	–0.03		5.5	–0.30
7.0	–0.06		7.0	–0.06
8.9	–0.03		7.9	–0.07
10.3	–0.11		8.3	–0.13
12.0	–0.20		8.3	–0.13
13.0	–0.24		8.9	–0.20
9.3	–0.22		9.3	–0.22
10.3	–0.22		10.3	–0.22
11.1	–0.26		11.1	–0.26
12.0	–0.28		12.0	–0.28
			13.0	–0.32

[a] See footnote *a* in Table I.

increases between about pH 3 and 7 and then is approximately independent of pH.

The *i*–*E* responses recorded at the $Fe^{II}CRPc(-2)$/HOPG RDE in pure oxygen saturated solution (pH 9.2) (Figure 6B) were analyzed by the conventional Koutecky–Levich[22] approach. The data are similar to those observed with FeTsPc.[6i] A Levich plot (not shown) of i_l vs $\omega^{1/2}$ from these curves is linear with the regression coefficient 0.999. An average value of *n* of 3.83 was obtained from the Levich equation (eq 1 above). The currents at the maxima then correspond to pure diffusion control for a four-electron reduction. The pH dependence for oxygen reduction (Figure 4B) is remarkably similar to that for H_2O_2 reduction catalyzed by CoCRPc (Figure 3D), suggesting that reduction may follow a similar mechanism at least insofar as proton dependence is concerned.

Thus, as for several other iron phthalocyanines,[4,6i,j] $Fe^{II}CRPc(-2)$ catalyzes the overall four-electron reduction in alkaline solution (in acidic solution, the catalytic current is smaller both in CV and RDE *i*–*E* diagrams).

Concluding Remarks

The crown phthalocyanine iron and cobalt species presents reproducible and well-behaved oxygen and hydrogen peroxide reduction data. In this preliminary report, we present an overview of these properties.

The excellent pH dependence data reported here, and the high stability of the surface, suggest that the CoCrPc system, in particular (the FeCRPc surface is less stable), could provide much more detailed mechanistic information concerning the catalytic processes involving the reduction of oxygen, hydrogen peroxide and indeed protons. The pH studies reported here may only be interpreted in rather simple terms in the absence of a more definitive study of the various steps which participate in what is likely a complex mechanism. However, the study would be worthy of expansion to other crown phthalocyanine species such as those with manganese, rhodium, and iridium. Studies involving the oxygen reduction of cobalt and iron crown phthalocyanine species as a function of the cation contained with the crown residue are in progress.

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