Electroreduction of O_2 to H_2O at Unusually Positive Potentials Catalyzed by the Simplest of the Cobalt Porphyrins

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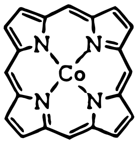
The search for metal complexes that act as electrocatalysts for the direct reduction of O_2 to H_2O at electrodes has led to the synthesis and testing of dimeric cofacial cobalt porphyrins,[1,2] of dimeric iridium porphyrins,[3−5] and of multinuclear cobalt porphyrins with back-bonding metal complexes bound to the periphery of the porphyrin ring.[6,7] The mechanisms through which these various electrocatalysts operate have been the subject of interesting speculations, but many details of the catalytic cycles remain to be elucidated. With the intention of establishing a baseline for the behavior of cobalt porphyrins that have been tested as electrocatalysts for the reduction of O_2, we examined the simplest of all cobalt porphyrins, cobalt porphine:



The electrocatalytic behavior of cobalt porphine has not been previously reported, probably because of the very low yields of the available methods for the synthesis of the porphine ligand which has been described as one of "the most difficult porphyrins to prepare in any quantity".[8] We utilized conventional procedures to prepare the ligand (in typically low yields) and to insert Co(II) into the porphyrin ring.[9] When the resulting complex was adsorbed on pyrolytic graphite electrodes and tested as an electrocatalyst for the electroreduction of O_2, we were surprised to find that it behaved significantly differently from most monomeric cobalt porphyrins: The reduction of O_2 occurred in two steps at unusually positive potentials, and the first step produced H_2O instead of H_2O_2 as the primary reduction product. The results indicate that simple, underivatized cobalt porphyrins can serve as electrocatalysts for the direct four-electron reduction of O_2 at potentials just as positive as those obtained with the less easily prepared cofacial or multinuclear cobalt porphyrins.[1,2]

Results. Cobalt(II) porphine is not highly soluble in typical organic solvents, but it is sufficiently soluble in $CHCl_3$ to obtain solutions from which satisfactory coatings can be adsorbed on edge plane pyrolytic graphite (EPG) electrodes by dip-coating. In Figure 1A (solid curve) is shown a cyclic voltammogram for a coating of cobalt porphine in the absence of O_2. The reversible response at 0.51 V, unusually sharp for an adsorbed cobalt porphyrin, can be assigned to the Co(III/II) couple. The area under the voltammetric peak in Figure 1A corresponds to 1.3×10^{-9} mol cm^{-2} of adsorbed cobalt porphine. The response is unaffected by continuous scanning of the electrode potential between +0.65 and −0.25 V. The relatively positive formal potential of the Co(III/II) couple is attractive because the catalysis of the electroreduction of O_2 requires that the cobalt center be reduced to Co(II). To check that the response shown in Figure 1A originated in the Co(III/II) couple and not in the oxidation/reduction of the porphine ring, the response was also measured in the presence of imidazole at a pH (8.3) where the ligand would be expected to coordinate to the cobalt center of the adsorbed porphyrin. As shown in Figure 1B, the reversible response is shifted to more negative potentials in the presence of imidazole, which is the behavior to be expected for the response from the Co(III/II) couple but not the oxidation/reduction of the porphine ring. The greater peak width of the response obtained in the presence of imidazole is reminiscent of the behavior exhibited by most monomeric cobalt porphyrins adsorbed on EPG electrodes,[10] which suggests that axial coordination of the ligand may break up the dimeric porphine structure that is believed to be present on the electrode surface (*vide infra*).

In Figure 1C is shown a current−potential curve for the reduction of O_2 at a rotating graphite disk electrode coated with the cobalt porphine. The reduction occurs in two well-separated steps. The first step occurs near the formal potential of the Co(III/II) couple (Figure 1A). The plateau current on the second step is considerably larger than the diffusion-convection-limited current for the reduction of O_2 to H_2O_2, the usual stoichiometry obtained with monomeric cobalt porphyrins. The rotating platinum ring−graphite disk voltammetry shown in Figure 1D was used to determine that >90% of the current at the half-wave potential of the first step (0.53 V) arises from the four-electron reduction of O_2. On the plateau of the second step, where the ratio of the ring to the disk current is 0.19, this percentage decreases to ca. 35%. Even though the first reduction step involves primarily the four-electron reduction of O_2, its plateau current is smaller than that of the second step, where 65% of the current arises from the two-electron reduction of O_2. The reason is that the currents are controlled, in part, by the rate with which the O_2 molecules coordinate to the Co(II) centers of the adsorbed porphyrin. We speculate that two parallel reaction pathways are accessible, one involving the binding of O_2 to two Co(II) centers and yielding the four-electron reduction of O_2 and the second involving only a single Co(II) center and yielding the two-electron reduction of O_2. The rate of formation of the intermediate containing two Co−O_2 bonds might well be slower than the rate at which the singly

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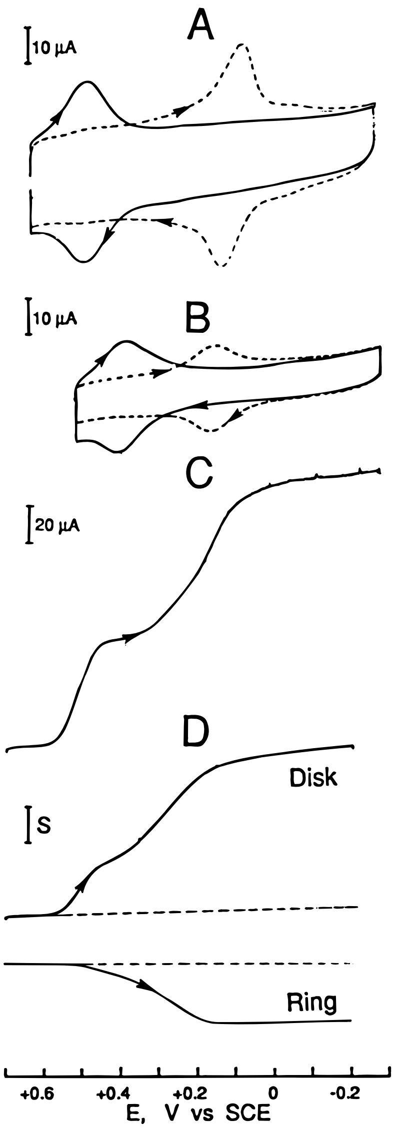

Figure 1. (A) Cyclic voltammetry of cobalt porphine adsorbed on an EPG electrode before (solid curve) and after (dashed curve) the electrode was used to reduce O_2. Supporting electrolyte: 1.0 M $HClO_4$ saturated with argon. Scan rate: 50 mV s^{-1}. (B) Solid curve: Repeat of (A) but with 0.2 M $NaClO_4$ buffered with borate at pH 8.3 as the supporting electrolyte. Dashed curve: After the supporting electrolyte was made 1 mM in imidazole. (C) Current−potential curve for the reduction of O_2 at a 0.32 cm^2 rotating EPG disk electrode coated with cobalt porphine. Supporting electrolyte: 1.0 M $HClO_4$ saturated with air. Rotation rate: 400 rpm. Scan rate: 5 mV s^{-1}. (D) Reduction of O_2 at a rotating platinum ring−pyrolytic graphite disk electrode (0.2 cm^2) having a collection efficiency of 39%. The potential of the ring electrode was maintained at 1.0 V. Rotation rate: 100 rpm. Scan rate: 5 mV s^{-1}. $S = 5$ and 10 μA for the ring and disk currents, respectively.

bonded intermediate is formed. If the doubly bonded intermediate were reduced at more positive potentials than the more rapidly formed singly bonded intermediate, the relative magnitudes of the two plateau currents in Figure 1C would be understandable.

Although the response from the Co(III/II) porphine couple (Figure 1A) is unaffected by repeated reduction−oxidation cycles in argon-saturated supporting electrolyte solutions, changes occur when the cycling is carried out in the presence of O_2. The dashed curve in Figure 1A shows the change in the Co(III/II) response that resulted after an electrode coated with cobalt porphine was used to reduce O_2 in air-saturated 1.0 M $HClO_4$. The cycling under O_2 converts the adsorbed cobalt porphine into a complex with a more negative formal potential for the Co(III/II) couple. Exposure of the cobalt porphine-coated electrode to solutions (~1 mM) of H_2O_2 produces the same result. Irreversible oxidation of the porphine ring by H_2O_2 is believed to be responsible for this change in the behavior of the adsorbed cobalt porphine. A similar oxidation of cobalt octaethylporphyrin has been reported.[11] The oxidation also occurs when a solution of cobalt porphine in $CHCl_3$ is exposed to aqueous H_2O_2 (1 mM). Electrodes coated from such oxidized solutions exhibit a Co(III/II) response at the more negative potential shown by the dashed curve in Figure 1A. Such oxidized coatings catalyze the reduction of O_2 in a single step at potentials that match the second step in Figure 1C. Although the plateau currents of the one-step reduction are somewhat smaller than the second plateau current in Figure 1C, they continue to exceed the value corresponding to the diffusion-convection-limited two-electron reduction of O_2 to H_2O_2.

Discussion. The unusually positive formal potential of cobalt porphine adsorbed on graphite and its ability to catalyze the four-electron reduction of O_2 are probably the result of the strong tendency of the porphine to form dimeric, cofacially disposed rings through van der Waals interactions.[12−14] Covalently-linked cofacial, dimeric cobalt porphyrins have been shown to accomplish the electroreduction of O_2 to H_2O at potentials similar to those observed in the present study.[2] However, the monomeric cobalt porphyrins used to prepare the covalently linked porphyrins yielded only two-electron reductions.[2,15] The two monomeric units must be strapped together to obtain the four-electron reduction of O_2, and this behavior has been attributed to the interaction of both ends of O_2 molecules with Co(II) centers in the transition state that leads to the reduction of O_2 to H_2O.[2,15] Apparently, a similar transition state is accessible to O_2 molecules that react with dimers (or oligomers) of cobalt porphine adsorbed on the electrode surface. The irreversible oxidation of the adsorbed cobalt porphine that occurs as it catalyzes the reduction of O_2 might well alter the extent of the van der Waals attraction between the rings and diminish the formation of structures that foster the simultaneous interaction of O_2 molecules with two Co(II) centers. A portion of the "four-electron transition state" would then give way to the more common "two-electron transition state" to produce the behavior observed in Figure 1C,D.

The rate of the oxidative degradation of the four-electron electrocatalytic activity of cobalt porphine can be decreased somewhat by employing more concentrated $HClO_4$ as the supporting electrolyte. The oxidation-sensitive *meso* positions of the porphine ring might also be protected by the attachment of substituents that are sufficiently small not to interfere with the spontaneous dimerization that is believed to be the key to the unusual electrocatalytic activity of the cobalt porphine. Experiments testing this approach with (5,10,15,20-tetramethylporphyrinato)cobalt(II) have been encouraging.

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Supporting Information Available: Text presenting procedures employed to synthesize and purify cobalt(II) porphine and to prepare graphite electrodes for the irreversible adsorption of the porphyrin (1 page). Ordering information is given on any current masthead page.

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