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[5,10,15,20-Tetrakis(4-((pentaammineruthenio)cyano)phenyl)porphyrinato]cobalt(II) Immobilized on Graphite Electrodes Catalyzes the Electroreduction of O_2 to H_2O, but the Corresponding 4-Cyano-2,6-dimethylphenyl Derivative Catalyzes the Reduction Only to H_2O_2

Beat Steiger and Fred C. Anson*

Arthur Amos Noyes Laboratories, Division of Chemistry and
Chemical Engineering, California Institute of Technology,
Pasadena, California 91125

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Introduction

The electroreduction of O_2 at graphite electrodes coated with most cobalt porphyrins usually proceeds exclusively via a two-electron pathway to yield H_2O_2.[1] However, the direct four-electron reduction of O_2 to H_2O has been demonstrated using cobalt porphyrins that have $Ru(NH_3)_5^{2+}$ complexes coordinated to π-acid ligands pendant to the porphyrin ring.[1−5] Recently,[6] evidence was presented that, in the conversion of two-electron to four-electron catalysts, π-back-bonding interactions between the Ru(II) centers and the cobalt porphyrin are more important than intramolecular electron transfer. In continuing efforts to understand the mechanistic behavior of ruthenated cyanophenyl cobalt porphyrins as electrocatalysts for the reduction of O_2, we have now prepared [5,10,15,20-tetrakis(4-cyano-2,6-dimethylphenyl)porphyrinato]cobalt(II) and its tetraruthenated derivative (Figure 1) and compared their electrocatalytic behavior with that of the corresponding nonmethylated derivatives. The choice of these new cobalt porphyrin catalysts was inspired by the reports of Taube et al.[7] and Haim et al.[8] on intramolecular electron transfer between $[Ru(NH_3)_4(OH_2)]^{2+}$ or $[Fe(CN)_5]^{3-}$ and $[Co(NH_3)_5]^{3+}$ when the reductant and oxidant were both coordinated to the opposite ends of various bridging bipyridine ligands. In particular, the introduction of methyl groups at the 3- and 3′-positions of the 4,4′-bipyridine ligand prevented the pyridine rings from adopting a coplanar conformation, thereby interrupting π-conjugation between the two rings. This decrease in coplanarity diminished the transmission of electronic effects between the coordinated donor and acceptor metal complexes, but the rates of intramolecular electron transfer were changed very little by the presence of the methyl groups.[7,8] On the basis of these previous results, we reasoned that the introduction of methyl groups at the 2- and 6-positions of the 4-cyanophenyl ligands pendant to the porphyrin ring would reduce π-conjugation between the ligand and the porphyrin ring and diminish the transmission to the porphyrin ring of the electron density resulting from π-back-bonding of the Ru(II) complexes into the cyanophenyl rings without affecting significantly the rate of any electron transfer from the Ru(II) sites to reducible sites in the porphyrin. We therefore prepared and ruthenated the unmethylated and dimethylated (4-cyanophenyl)porphyrins and compared their catalytic behaviors both before and after they were ruthenated.

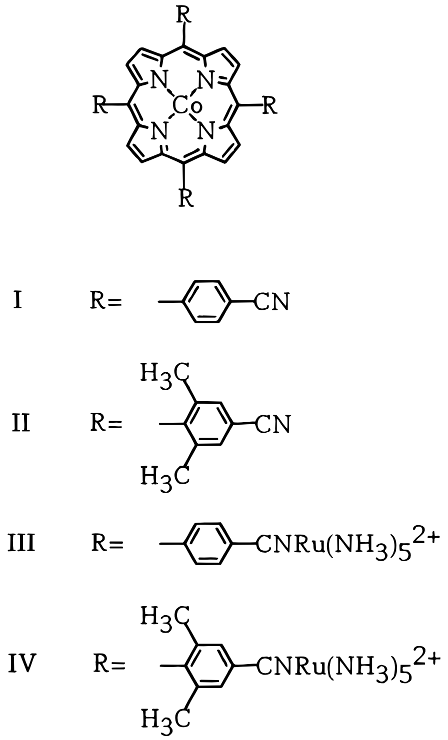

Figure 1. Structures of cobalt(II) porphyrins examined in this study.

The contrasting behaviors observed, as described in this report, provide additional support for a catalytic mechanism in which π-back-bonding interactions between the $Ru(NH_3)_5^{2+}$ groups and the cobalt porphyrin−O_2 adduct are more important than intramolecular reduction of the latter by the former.

Results

Syntheses of the Catalysts. The four cobalt porphyrins synthesized and examined in this study are shown in Figure 1.

In our previous studies, the cobalt porphyrin catalysts were adsorbed on the surface of graphite electrodes, where they were ruthenated in place by reaction with $[Ru(NH_3)_5(OH_2)]^{2+}$. However, **I** and **II** adsorbed on the surface of graphite electrodes were too weakly solvated to undergo quantitative conversion to **III** and **IV**, respectively, upon lengthy exposure to aqueous solutions of $[Ru(NH_3)_5(OH_2)]^{2+}$. The ruthenation of **I** and **II** was therefore carried out by dissolving them in 1,2-dimethoxyethane (DME) and adding a 2.5-fold stoichiometric excess of $[Ru(NH_3)_5(O_3SCF_3)](CF_3SO_3)_2$ (prepared as described in the literature[9,10]) dissolved in DME/dimethylacetamide (DMA), 27:1 v/v, and reduced with zinc amalgam just prior to mixing. Details of the ruthenation procedure will be described elsewhere.[11] Comparison of the magnitudes of the Co(II/I) and Ru(III/II) responses in cyclic and rotating disk voltammograms of the ruthenated porphyrins in DME/DMA (20:3 v/v) showed that both **III** and **IV** contained at least 3.7 $Ru(NH_3)_5^{2+}$ groups per porphyrin molecule. Stock solutions of **I** and **II** in DME and of the $CF_3SO_3^-$ salts of **III** and **IV** in methanol were used

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* Corresponding author.

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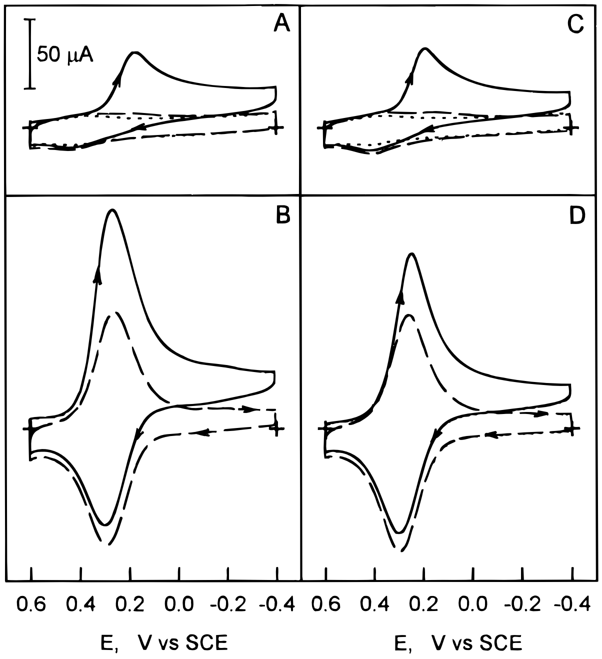

Figure 2. Cyclic voltammetry of the porphyrins of Figure 1 deposited on the surface of a pyrolytic graphite electrode: (A) 2.2 × 10^{-9} mol cm^{-2} of **I**; (B) 2.4 × 10^{-9} mol cm^{-2} of **III**; (C) 2.2 × 10^{-9} mol cm^{-2} of **II**; (D) 2.4 × 10^{-9} mol cm^{-2} of **IV**. Supporting electrolyte: 0.5 M $HClO_4$−0.5 M NH_4PF_6 saturated with argon (dashed curves) or air (solid curves). All of the coatings also contained 1.8 × 10^{-8} mol cm^{-2} of Nafion sulfonate groups. Scan rate: 50 mV s^{-1}. The dotted curves in (A) and (C) are the responses from the uncoated graphite electrode under argon.

to prepare coatings on the surface of graphite electrodes as described in the Experimental Section.

Electrocatalysis of the Reduction of O_2 by the Adsorbed Porphyrins. Cyclic voltammograms for the reduction of O_2 at graphite electrodes coated with **I** or **II** are shown by the solid curves in Figure 2A,C. These two unruthenated porphyrins behave essentially identically in catalyzing the two-electron reduction of O_2 to H_2O_2. After they are ruthenated, the two porphyrins behave quite differently as electrocatalysts, as is shown in the solid curves in Figure 2B,D: Larger peak currents for the reduction of O_2 are obtained with **III** than with **IV**.

The cyclic voltammetric responses from the $Ru(NH_3)_5{}^{3+/2+}$ complexes in coatings of **III** and **IV** in the absence of O_2 are also essentially identical (dashed curves in Figure 2B,D). The formal potential of the $[Ru(NH_3)_5(benzonitrile)]^{3+/2+}$ couple has been reported to be 0.24 V.[12] We measured the formal potentials of this couple and the corresponding couple having 3,5-dimethylbenzonitrile as the sixth ligand as 0.24 and 0.22 V, respectively. The difference between the formal potentials of these two complexes in solution is small, and it becomes too small to measure for the $Ru(NH_3)_5{}^{3+/2+}$ centers in **III** and **IV** adsorbed on graphite electrodes. Thus, the reducing strengths of the Ru(II) centers in **III** and **IV** adsorbed on graphite are the same and the difference in the catalytic behaviors evident in Figure 2B,D is not attributable to any difference in the driving force for intramolecular electron transfer from the Ru(II) centers.

To obtain more quantitative data, experiments were conducted using rotating ring−disk electrodes according to procedures that have been previously described.[5] The graphite disk electrode was coated with one of the porphyrins from Figure 1, and the concentric platinum ring electrode was maintained at 1.0 V to oxidize any H_2O_2 generated by the reduction of O_2 at the disk.

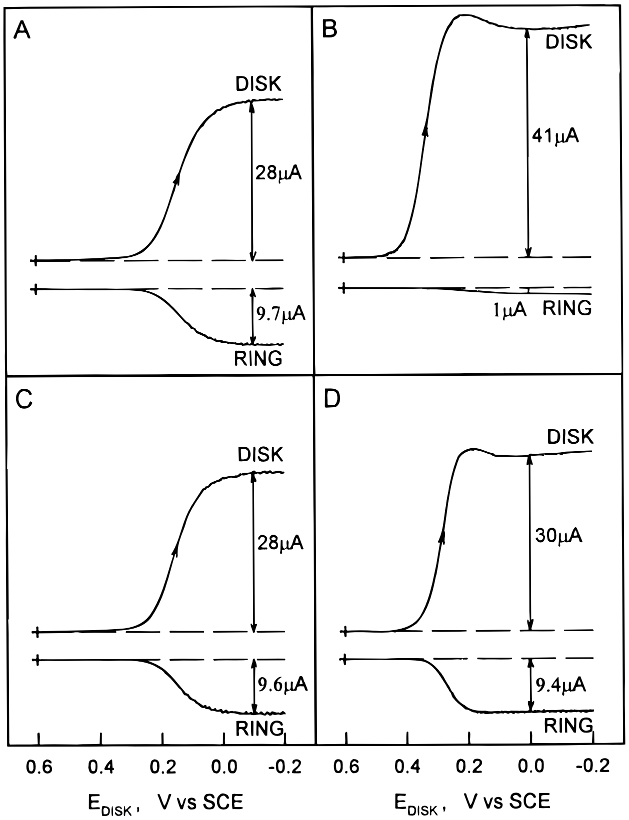

Figure 3. Reduction of O_2 at a rotating platinum ring−graphite disk electrode. The ring electrode was maintained at 1.0 V. The disk was coated with (A) 2.2 × 10^{-9} mol cm^{-2} of **I**, (B) 2.0 × 10^{-9} mol cm^{-2} of **III**, (C) 2.2 × 10^{-9} mol cm^{-2} of **II**, and (D) 2.2 × 10^{-9} mol cm^{-2} of **IV**. All of the coatings also contained 1.8 × 10^{-8} mol cm^{-2} of Nafion sulfonate groups. Supporting electrolyte: 0.5 M $HClO_4$−0.5 M NH_4PF_6 saturated with air. Electrode rotation rate: 100 rpm. The disk potential was scanned at 5 mV s^{-1}.

The results, shown in Figure 3, demonstrate that the unmethylated porphyrin, **III**, achieves an almost quantitative four-electron reduction of O_2 to H_2O (Figure 3B) while **I** and **II** yield only the two-electron reduction and **IV** appears to reduce about 93% of the O_2 by only two electrons. The broad peaks in the initial portions of the voltammetric response of the disk electrodes coated with **III** and **IV** (Figure 3B,D) arise from the reduction of the Ru(III) centers coordinated to the porphyrins.

Discussion

Comparison of the behaviors shown in the four panels of Figure 3 leads clearly to the conclusion that the presence of the two methyl groups in **IV** prevents the $Ru(NH_3)_5{}^{2+}$ complexes coordinated to the four pendant 4-cyanophenyl ligands from exerting their influence to direct the reaction along the pathway that leads to the electroreduction of O_2 by four electrons. It seems most reasonable to attribute the difference in the catalytic behaviors of **III** and **IV** to the diminished transfer to the porphyrin ring in **IV** of electron density generated by the π-back-bonding of the $Ru(NH_3)_5{}^{2+}$ complexes to the cyanophenyl ring. The dihedral angle between the porphyrin and phenyl rings of **IV** is expected to be larger than that of **III** because of the steric interaction between the two methyl groups of **IV** and the hydrogen atoms in the pyrrole β-positions of the porphyrin ring. The extent of π-back-bonding into the cyanophenyl rings of **III** and **IV** cannot be substantially different because the formal potentials of the Ru(III)/Ru(II) couples are essentially equal in **III** and **IV**. However, the extent to which the back-bonding electron density in the cyanophenyl rings of **III** and **IV** is

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[12] Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1976**, *15*, 1107.

transmitted to the catalytically important Co−O_2 adduct at the center of the porphyrin ring should be significantly greater for **III** than for **IV** because of the smaller dihedral angle between the rings of the former catalyst. The effects of ortho-methyl groups in altering electronic communication between a porphyrin and aryl substituents in the *meso* positions of the porphyrin ring were well documented in recent reports by Bocian and co-workers.[13] The reasons that better transmission of electron density from the Ru(II) complexes to the porphyrin ring leads to an enhancement in the catalysis of the four-electron reduction of O_2 have yet to be fully identified although some speculations were offered in our previous reports.[5,6]

Back-Bonding vs Net Intramolecular Electron Transfer. The argument favoring π-back-bonding over net intramolecular electron transfer from Ru(II) to a Co(II)−O_2 adduct as the key to the enhanced four-electron catalytic activity of **III** (and its previously described analogs[1−6]) can be buttressed by considering the results of some previous studies by Taube[7] and Haim.[8] In those studies, rate constants were measured for what were unambiguously intramolecular electron-transfer reactions between reductants and oxidants coordinated to the same bridging ligands. Of particular relevance to the present study were results obtained with the complexes $[\mathrm{Ru^{II}(NH_3)_4(OH_2)L{-}LCo^{III}(NH_3)_5}]$[7] and $[\mathrm{Fe^{II}(CN)_5L{-}LCo^{III}(NH_3)_5}]$[8] with L−L = 1,2-bis(4-pyridyl)ethylene or 3,3′-dimethyl-4,4′-bipyridine. The rates of intramolecular electron transfer from the reductant (Ru(II) or Fe(II)) to the oxidant (Co(III)) were shown to be rather insensitive to the presence or absence of the two methyl groups despite the fact that when they are present the two pyridine rings are forced to lie nearly perpendicular to each other while they are expected to be coplanar with the unmethylated bridging bipyridine ligand.[7] There is no doubt that resonance interactions (e.g., π-back-bonding) between the adjacent rings in both of these L−L-bridged complexes and in porphyrins **III** and **IV** should be strongly diminished as the rings become less coplanar.[14] The observed lack of sensitivity of the rates of intramolecular electron transfer to the loss of ring coplanarity with the L−L-bridged complexes suggests that the same would be true for **III** and **IV**. Since the rate of the reduction of O_2 to H_2O is large enough for this process to become the dominant reaction only with the unmethylated porphyrin catalyst (Figure 3B), it follows that intramolecular electron transfer is not important in the catalytic mechanism that produces the four-electron electroreduction of O_2. Thus, the $Ru(NH_3)_5$ complexes coordinated to the cyanophenyl ligands of the porphyrin ring remain in their reduced, Ru(II) state throughout the catalytic cycle. All four of the electrons involved in the reduction of O_2 are supplied by the graphite electrode on which the porphyrin catalyst resides. The coordinated $Ru(NH_3)_5^{2+}$ groups play the role of a cocatalyst.

An additional recent result that supports the importance of π-back-bonding in converting cobalt porphyrins into four-electron catalysts for the electroreduction of O_2 involves the coordination of $Os(NH_3)_5^{3+/2+}$ complexes directly to the ring of a cobalt porphyrin.[15] The resulting osmiumated porphyrin provides substantial four-electron electroreduction of O_2 at electrode potentials that are too positive for $Os(NH_3)_5^{2+}$ to be present on the electrode surface. Thus, even when intramolecular electron transfer from Os(II) to a Co(II)−O_2 adduct is precluded, back-bonding from the $Os(NH_3)_5^{3+}$ group[16,17] is apparently sufficient to open the mechanistic pathway for the electroreduction of O_2 to H_2O.

Studies are continuing in an effort to identify more definitively the mechanisms by which coordination of back-bonding metals to the periphery of cobalt porphyrins converts them from two- to four-electron electrocatalysts for the reduction of O_2.

Experimental Section

Materials. Porphyrin I (Figure 1) was available from previous studies.[5] The synthesis of metal-free **II** was described in ref 18. The preparations of **III** and **IV** will be described elsewhere.[11] $[\mathrm{Ru(NH_3)_5(3,5\text{-}dimethylbenzonitrile)}](ClO_4)_2$ was prepared by following the procedure of Clarke and Ford[19] except that the product was not recrystallized because attempts to do so appeared to lead to its decomposition. 1,2-Dimethoxyethane (Aldrich, anhydrous), *N*,*N*-dimethylacetamide (Aldrich, anhydrous), MeOH (EM Science, OmniSolv), Al_2O_3 (Aldrich, activated, basic, Brockman I), and 3,5-dimethylbenzonitrile (Trans World Chemicals, 98%) were obtained from the commercial sources indicated. Other chemicals and materials were obtained and treated as previously described.[5] Stock solutions of the porphyrins in Figure 1 were prepared according to the following procedure: A 1.1 mg sample of **I** or 1.25 mg of **II** was dissolved in 8 mL of DME that had been freshly passed through a column of Al_2O_3. Brief sonication of the mixture at room temperature helped to dissolve the porphyrin. A 3.9 mg sample of **III** or 4.0 mg of **IV** as the trifluoromethanesulfonate salt was dissolved in 8 mL of MeOH that had been presaturated with dry argon. All stock solutions were protected from light.

Preparation of Catalyst Coatings. As in our previous study, the stability of catalyst coatings on edge plane pyrolytic graphite (EPG) electrodes (polished as previously described) was found to be improved by adding small quantities of Nafion to the coatings. Typically, 100 μL of a porphyrin stock solution was mixed with 40 μL of a 0.5 wt % Nafion solution in MeOH, 5.6 μL of the resulting solution was transferred to the surface of the freshly polished EPG electrode (0.32 cm^2), and the solvent was allowed to evaporate in air at room temperature. In some cases, better performance of the catalyst coatings was obtained by transferring to the electrode surface 5.6 μL of a solution prepared by adding 40 μL of a 0.5 wt % Nafion solution in MeOH to 100 μL of DME followed by 4 μL of the porphyrin stock solution. Proportionately smaller aliquots were used to coat the smaller (0.2 cm^2) disk of the platinum ring−graphite disk electrode which had a collection efficiency of 0.36 as measured using the $Fe(CN)_6^{3-/4-}$ couple.

The electrochemical apparatus and procedures matched those described previously.[5] Potentials are quoted with respect to the saturated calomel electrode (SCE).

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