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Electrocatalytic Oxygen Reduction by Iron Tetra-arylporphyrins Bearing Pendant Proton Relays

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Ⓢ *Supporting Information*

ABSTRACT: Iron(III) *meso*-tetra(2-carboxyphenyl)-porphine chloride (**1**) was investigated as a soluble electrocatalyst for the oxygen reduction reaction (ORR) in acetonitrile with $[H(DMF)^+]OTf^-$. Rotating ring-disk voltammetry, spectroelectrochemistry, and independent reactions with hydrogen peroxide indicate that **1** has very high selectivity for reduction of O_2 to H_2O, without forming significant amounts of H_2O_2. Cyclic voltammetric measurements at high substrate/catalyst ratios (high oxygen pressure) allowed the estimation of a turnover frequency (TOF) of 200 s^{-1} at −0.4 V vs $Cp_2Fe^{+/0}$. This is, to our knowledge, the first reported TOF for a soluble ORR electrocatalyst under kinetically controlled conditions. The 4-carboxyphenyl isomer of **1**, in which the carboxylic acids point away from the iron center, is a much less selective catalyst. This comparison shows that carboxylate groups positioned to act as proton delivery relays can substantially enhance the selectivity of ORR catalysis.

The oxygen reduction reaction (ORR, eq 1) is a key component of many fuel cells, which promise excellent

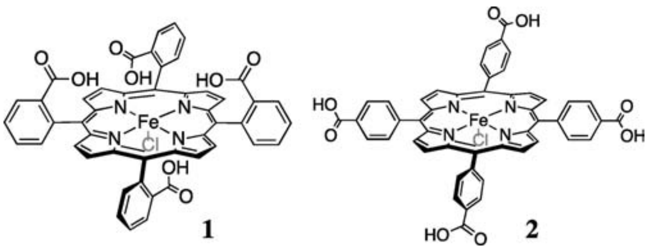
$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \tag{1}$$

efficiency in the conversion of chemical to electrical energy.[1] Current fuel cells use platinum as the electrocatalyst, but for reasons of cost and scarcity there is great interest in catalysts which do not require precious metals.[2] New catalysts should be rapid at moderate overpotentials and have high selectivity for $4e^-/4H^+$ reduction to H_2O. The alternative formation of H_2O_2 lowers the cell potential and causes oxidative damage. Studies of molecular ORR catalysts have in large part focused on the delivery of the four needed electrons but, as indicated by eq 1, it is equally important to arrange the delivery of the four protons. This report describes a dramatic effect of proton relays on the selectivity of iron porphyrin electrocatalysts for the ORR.

Proton relays are acid/base sites positioned in the second coordination sphere of a metal complex. Their value in electrocatalysis of proton-coupled electron transfer (PCET) reactions has been clearly shown in the DuBois group's very efficient nickel(II) bis(diphosphine) electrocatalysts for reduction of protons to dihydrogen.[3] Nocera et al. have developed "hangman" porphyrin and corrole catalysts in which a single carboxylic acid is poised over the central metal. A recent report describes an increase in selectivity to H_2O from 40 to 55% upon inclusion of the acid into cobalt corrole electrocatalysts supported on carbon nanotubes.[4] Yang and co-workers described more dramatic effects of proton relays using DuBois nickel-phosphine catalysts with amines in the second coordination sphere, but the ligands were rapidly oxidized under ORR conditions.[5] Borovik et al. recently reported catalytic O_2 reduction by a manganese complex that includes a coordinated carboxamide as a proton shuttle.[6] These studies with pendant acids are an extension of the many elegant examples of hydrogen-bonding groups in the second coordination sphere modulating the reactivity of intermediates from dioxygen adducts to oxo complexes.[7]

Iron(III) (*meso*-tetra(2-carboxyphenyl)porphine chloride (**1**, Chart 1)[8] was selected for investigation both because of the extensive interest in iron porphyrins for oxygen binding and reduction[9] and because the four carboxylic acid groups oriented toward the redox center could act as proton relays. The 4-carboxyphenyl isomer (**2**, Chart 1) provides a direct comparison with a very similar electrocatalyst in which the carboxylic acid groups point away from the metal and cannot easily act as proton relays. Compound **1** is isolated as a mixture of non-interconverting isomers with carboxylic acid groups on either side of the porphyrin plane (one isomer is drawn in Chart 1).

Chart 1. Structures of Electrocatalysts 1 (One Isomer) and 2



The electrochemical properties of **1** and **2** have been examined in acetonitrile in the presence or absence of O_2 and strong acid ($[H(DMF)^+][OTf^-]^{10}$), using 0.1 M $[^nBu_4N][PF_6]$ electrolyte and a glassy carbon working electrode. The compounds have very limited solubility in dry acetonitrile in the absence of acid, so 1% water was typically added to obtain cyclic voltammograms (CVs) under N_2. CVs of **1** show broad, overlapping peaks at ca. −290 and −550 mV (Figure 1 inset; all

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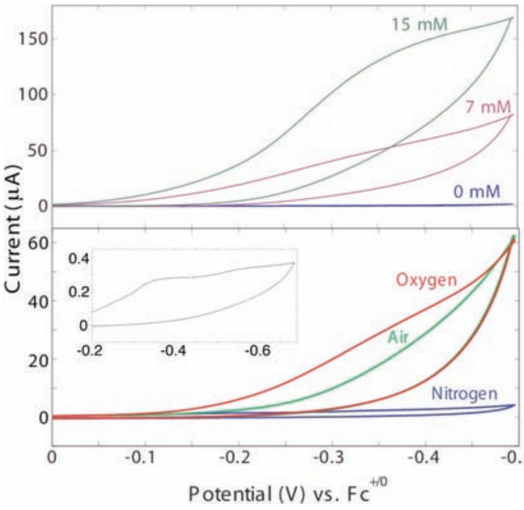

Figure 1. (Top) CVs of 0.2 mM **1** in MeCN under 1 atm O_2 ($[O_2]$ = 8 mM)[13] and $[H(DMF)^+]$ = 0, 7, and 15 mM. (Bottom) CVs 0.2 mM **1** in MeCN with $[H(DMF)^+]$ = 10 mM under 1 atm of N_2, air, and O_2. Inset: CV of 2.5 mM **1** with no added acid under pure N_2. All scans were collected at 100 mV s^{-1} using a glassy carbon working electrode with an area of 0.9 cm^2.

potentials are reported versus ferrocene, $Fc^{+/0}$). The peaks are attributed to the $Fe^{III/II}$ couples of the various species present under these conditions, likely containing different axial ligands, based on studies of related compounds.[11] In the presence of dioxygen, no anodic current is observed, indicating that the electrogenerated Fe^{II} complexes react rapidly with O_2. When both O_2 and $[H(DMF)^+][OTf^-]$ are present, the CVs show a significant increase in the current at approximately the onset of the Fe^{III} reduction (Figure 1). For instance, the cathodic current at −0.35 V for solutions of 0.2 mM **1** and 10 mM $H(DMF)^+$ is 13 times larger under 1 atm of O_2 vs 1 atm N_2. The observed increase in current is indicative of electrocatalysis. Similar electrocatalytic CVs are observed for **2**.

Compound **1** was also found to catalyze the chemical reduction of O_2 using ferrocene (Fc) as the reductant. With 0.1 mM **1**, 32 mM Fc, 16 mM $H(DMF)^+$, and 4 mM O_2 in MeCN, >10 equiv of Fc^+ (1 mM) was observed within 1 s by stopped-flow kinetics and UV/vis spectroscopy (Figures S18 and S19).[12] While some oxidation of Fc is observed under these conditions in the absence of a catalyst, the acceleration by **1** is at least 10^5 (Figure S20). This rapid oxidation of Fc occurs even though the $Fc^{+/0}$ couple (0 V) is quite positive of the onset of electrocatalysis (Figure 1).

The selectivity of the ORR by **1** and **2** was measured by rotating ring-disk voltammetry (RRDV, Figure 2). These experiments used 0.2 mM solutions of **1** or **2** with 1 atm O_2 and 18 mM $[(DMF)H]^+[OTf]^-$ in 99:1 MeCN:H_2O.[14] The rotation rate was 1250 rpm, and the platinum ring was poised at +1016 mV to oxidize any H_2O_2 hydrodynamically swept over it (added H_2O_2 was readily detected in this manner in the absence of **1** or **2**). When the disk potential was scanned from 0 to −500 mV, substantial cathodic currents were observed at the disk, consistent with the CVs in Figure 1. Solutions of **2** showed a small amount of anodic current at the ring, with $i_{disk}/i_{ring} \approx 80$ at −400 mV. The shape of the ring current scan mirrors that of the disk current (Figure 2, bottom), indicating that a species formed at the disk is responsible for the ring current, presumably H_2O_2 as in related experiments.[9] This i_{disk}/i_{ring} and the measured ring-disk collection efficiency of 26% imply that 3.8 electrons were consumed per O_2 reduced, and that ~9% H_2O_2 was formed.[12−16,15] The ring currents were substantially smaller for solutions of **1** ($i_{disk}/i_{ring} \approx 300$ at −400 mV) and did not mirror the shape of the disk current. Control experiments suggest that this very small ring current is the result of the uncatalyzed reduction of O_2 to H_2O_2 at the disk in the presence of acid,[16] so the amount of H_2O_2 formed is likely much less than indicated by the i_{disk}/i_{ring} (≪2%).

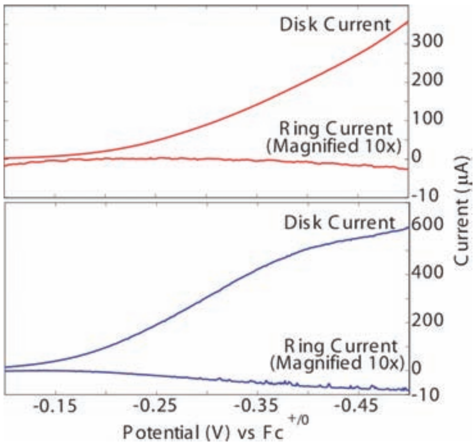

Figure 2. Rotating ring-disk voltammograms of **1** and **2** (top and bottom, respectively; 0.2 mM) + [H(DMF)]OTf (18 mM) under 1 atm O_2 in 99:1 MeCN:H_2O at 1250 rpm. The disk was scanned from 0 to −500 mV while the ring electrode was held at 1016 mV. Ring currents are magnified by a factor of 10.

The stability of **1** and **2** under ORR conditions provided a more sensitive test for the production of H_2O_2. Both **1** and **2** are rapidly decomposed by added H_2O_2. For instance, stopped-flow kinetic experiments showed that 15 μM solutions of **1** decayed with a half-life of 12 s upon addition of 150 μM urea–hydrogen peroxide,[17] as indicated by bleaching of the Soret band (Figure S17). Such bleaching of the Soret band is typical for iron porphyrin compounds upon addition of H_2O_2 and under ORR conditions.[9] However, spectroelectrochemical measurements using a transparent ITO working electrode show that **1** is remarkably stable under ORR conditions, with very little decay over 3600 s (Figures S14 and S15). This indicates that very little H_2O_2 is generated during catalysis. In contrast, parallel experiments with solutions of **2** show a half-life for decay of that electrocatalyst of <150 s under ORR conditions (Figure S12). Substantial decay was also observed in analogous spectroelectrochemical studies of O_2 reduction by iron(III) (*meso*-tetraphenyl)porphine chloride (Fe[TPP]Cl), a catalyst that has no relays (Figure S13). Decomposition of **1** was only observed at potentials sufficiently negative for the non-catalyzed reduction of O_2 to superoxide or H_2O_2 at the glassy carbon working electrode.[16] In sum, the decay of **1** is a very sensitive test for the production of H_2O_2, and the stability of **1** under ORR conditions indicates that it is very selective catalyst for the $4e^-/4H^+$ reduction to H_2O.[18] This high selectivity contrasts with the behavior of related catalysts that lack positioned proton relays.

Under 1 atm of oxygen, the catalytic CV current at −320 mV rises with increasing acid concentrations, up to $[H(DMF)^+]$ of at least ~15 mM.[16] A similar dependence on the concentration of O_2 was observed: at 20 mM concentration of acid, the catalytic current i_c at −320 mV is ~3 times larger under 1 atm

O_2 vs 1 atm of air (8 vs 1.7 mM O_2 in MeCN). The dependences of i_c on $[H^+]$ and $[O_2]$ indicate that the catalytic turnover is limited in part by the substrate concentrations and therefore likely limited in part by their diffusion to the electrode surface. To reach purely kinetic conditions where the electrocatalytic turnover is limited only by chemical steps and not by diffusion, high substrate-to-catalyst ratios and low scan rates are needed.[19] Under these specific conditions, the apparent catalytic rate constant k_{obs} for a soluble electrocatalyst is related to the ratio of catalytic current to the peak current in the absence of catalysis (i_c/i_p) by eq 2.[19] For the reactions

$$\frac{i_c}{i_p} = \frac{n_c}{0.447 n_p^{3/2}} \sqrt{\frac{RTk_{obs}}{F\nu}} \qquad (2)$$

discussed here, the number of electrons transferred in the non-catalytic wave (n_p) is 1, and the number of electrons transferred in the catalytic wave (n_c) is 4;[20] ν is the scan rate in V s^{-1}.

In order to reach the pure kinetic zone[19a] for ORR by **1**, CVs were obtained inside a pressure vessel at 17 atm of O_2 ($[O_2]$ in MeCN = 140 mM)[13] and $[H(DMF)^+]$ = 225 mM. Under these conditions, the catalytic current i_c at −400 mV is roughly independent of scan rate between ν = 25 and 250 mV s^{-1} with [**1**] = 0.030 mM, and between ν = 25 and 100 mV s^{-1} with [**1**] = 0.15 mM, (Figure 3, Figures S9−S11). This is a key indication that the kinetic zone has been reached.[21] At faster scan rates (250−1000 mV s^{-1}), i_c exhibits the usual linear relationship with $\nu^{1/2}$. At higher catalyst concentrations, the scan-rate-independent region is not evident, consistent with the interpretation of these changes being due to kinetic vs diffusive effects on the CVs.

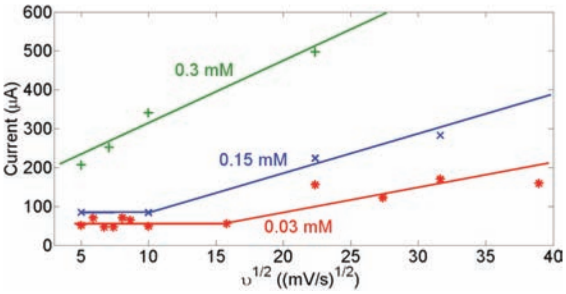

Figure 3. Cathodic current i_c at −400 mV of acetonitrile solutions containing **1** (indicated concentrations), O_2 (17 atm, 140 mM), and $H(DMF)^+$ (225 mM) plotted vs square root of scan rate, $\nu^{1/2}$.

Determination of the turnover frequency (TOF, k_{obs}) via eq 2 requires the ratio i_c/i_p, but the peak current in the absence of catalysis i_p cannot be measured directly at these very low catalyst loadings. Extrapolation from higher concentrations and comparisons with related compounds yield an estimate of i_p at [**1**] = 0.15 mM and ν = 100 mV s^{-1} of 1 µA.[22] (The i_c values measured in the pressure vessel with [**1**] = 0.15 mM are viewed as more reliable than those at 0.03 mM due to the presence of small background currents that have not been corrected for.) With i_c = 85 µA and $i_p \cong 1$ µA at 100 mV s^{-1}, eq 2 indicates that $k_{obs} \cong 200$ s^{-1}. Qualitatively, a high rate constant is implied by the 85 µA catalytic current even at the low catalyst loading of 0.15 mM. That **1** is a fast catalyst is also indicated by the rapid catalysis of aerobic Fc oxidation by **1**, even though the half-wave potential of Fc is 290 mV more positive of that of **1**. The high TOF is achieved under the relatively forcing conditions of 17 atm O_2, 225 mM $H(DMF)^+$, and −400 mV vs Fc. The thermodynamic potential for the ORR (eq 1) is not known under these conditions in MeCN, but −400 mV is certainly a high overpotential.

In summary, the efficacy of **1** as an electrocatalyst for the reduction of dioxygen to water in acetonitrile has been demonstrated. At low catalyst concentrations, high O_2 pressure (17 atm) and high acid concentration (225 mM $H(DMF)^+$), cyclic voltammetric studies indicate that catalysis is in a kinetic region where the current is limited only by catalyst turnover. Under these conditions, a high TOF for O_2 reduction is estimated, 200 s^{-1}. To the best of our knowledge this is the only report of the TOF for the ORR by a soluble electrocatalyst under limiting kinetic conditions, not limited by substrate diffusion.[19] Electrocatalysis by **1** is indicated to be highly selective for the $4e^-/4H^+$ reduction of O_2 to H_2O, since a combination of rotating ring-disk voltammetry, bulk electrolysis, and catalyst stability studies show that very little H_2O_2 is formed. The proton relays in the second coordination sphere appear to be very important to the high selectivity based on a comparison to the analogous 4-carboxy-substituted catalyst **2** in which the relays are pointed away from the redox center and which forms substantial H_2O_2. A possible explanation of this effect is that the relays preferentially deliver protons to the distal oxygen of a κ^1-$Fe(O_2)$ intermediate and thereby promote O−O bond cleavage over the loss of H_2O_2. This would be analogous to the selectivity-determining role of proton delivery in O_2 activation at the heme center in cytochrome P450 enzymes.[23] This and other issues are being probed with ongoing experimental and computational studies, both of this system and related catalysts with different proton relays.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details including synthetic methods, CV, RRDV, spectroelectrochemical, rapid scanning UV/vis, and NMR results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(20) The stoichiometric factor n_c refers to the number of electron-transfer steps to convert O_2 to H_2O; see ref 19c.

(21) The kinetic zone is also usually indicated by an *S*-shaped rather than peaked CV.[19] However, overlap of the more negative portion of the catalytic wave with the direct reduction of O_2 at the electrode under these conditions (Figures S10−S12)[16] distorts the wave shape, so the dependence of i_c on ν is more indicative in this case.

(22) This estimate is obtained by extrapolating from higher concentrations, using the sum of the currents observed in the multiple waves for **1** (Figure 1 inset) or using values for **2** (cf. Figure S6).

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