Homogenous Electrocatalytic Oxygen Reduction Rates Correlate with Reaction Overpotential in Acidic Organic Solutions

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ABSTRACT: Improved electrocatalysts for the oxygen reduction reaction (ORR) are critical for the advancement of fuel cell technologies. Herein, we report a series of 11 soluble iron porphyrin ORR electrocatalysts that possess turnover frequencies (TOFs) from 3 s⁻¹ to an unprecedented value of 2.2 × 10⁶ s⁻¹. These TOFs correlate with the ORR overpotential, which can be modulated by changing the E½ of the catalyst using different ancillary ligands, by changing the solvent and solution acidity, and by changing the catalyst’s protonation state. The overpotential is well-defined for these homogeneous electrocatalysts by the E½ of the catalyst and the proton activity of the solution. This is the first such correlation for homogeneous ORR electrocatalysis, and it demonstrates that the remarkably fast TOFs are a consequence of high overpotential. The correlation with overpotential is surprising since the turnover limiting steps involve oxygen binding and protonation, as opposed to turnover limiting electron transfer commonly found in Tafel analysis of heterogeneous ORR materials. Computational studies show that the free energies for oxygen binding to the catalyst and for protonation of the superoxide complex are in general linearly related to the catalyst E½, and that this is the origin of the overpotential correlations. This analysis thus provides detailed understanding of the ORR barriers. The best catalysts involve partial decoupling of the influence of the second coordination sphere from the properties of the metal center, which is suggested as new molecular design strategy to avoid the limitations of the traditional scaling relationships for these catalysts.

INTRODUCTION

Fuel cells offer clean and effective electrical power generation from chemical fuels for stationary, portable, and transport applications.¹ Widespread implementation of fuel cell technologies has been limited in large part by the inefficient oxygen reduction reaction (ORR) at the cathode, and by the typical requirement for large amounts of expensive platinum.²³ This motivates research in heterogeneous and homogeneous catalysts, from new platinum alloy nanocrystals supported on electrodes⁴ to novel earth-abundant carbonaceous materials⁵ to unique molecular structures and hybrid combinations.⁶⁷ Homogeneous electrocatalysts have yet to match heterogeneous materials in turnover frequencies (TOFs) per active site at modest overpotentials, but they permit facile development of important structure/activity and driving force/activation barrier relationships. Such atomic-level understanding is key to building better ORR electrocatalysts.

Iron and cobalt complexes with N₄-macrocyclic ligands have been extensively studied as ORR catalysts⁸⁹ and are models for promising but complex solid Fe/N/C ORR electrodes.¹⁰ Molecular ORR electrocatalysts are typically only soluble in organic solvents such as N,N′-dimethylformamide (DMF) or acetonitrile (ACN), making it difficult to directly compare and understand the effects of different design features. In addition, the standard potentials for O₂/H₂O in nonaqueous solvents were unknown until recently.¹¹¹² Therefore, previous studies have predominantly done aqueous measurements of molecular ORR electrocatalysts adsorbed on electrodes, often in complex pastes. In these situations, differing local environments complicate understanding,¹³ with some elegant exceptions.⁷⁸

Described here are studies on a series of 11 iron porphyrin ORR electrocatalysts ([FeIII(por)]OTf with OTf = trifluoromethanesulfonate, Figure 1A). Catalysts 1 and 8–11 were designed with pendant functionalities to serve as potential “proton relays”, with the aim of facilitating H⁺ delivery to the iron active site. This has been shown to be an effective strategy for other homogeneous electrocatalysts for H⁺ and CO₂
The electrochemistry of complexes 1–11 has been examined in DMF or ACN, with excess [DMF-H]OTf as the acid. Most catalysts could only be evaluated in one of these solvents, due to limited solubility. Cyclic voltammograms (CVs) of the complexes all showed a reversible Fe(III/II) redox couple in the absence of O2. Changing the substituents on the porphyrin scaffold allowed tuning of the Fe(III/II) reduction that initiates electrocatalysis (E_{Fe(III/II)}) over a significant range in ACN (~100 mV) and DMF (~270 mV). In the presence of excess acid and 1 atm of O2, CVs of 1–11 showed a substantial increase in current, indicative of ORR electrocatalysis (Figure 1B).

Turnover frequencies (TOFs, s\(^{-1}\)) were quantified electrochemically using foot-of-the-wave analysis (FOWA; see Supporting Information). This TOF is defined by the rate law \(-d[O_2]/dt = \text{TOF}[Fe^3]\), as is common;\(^{16,17}\) it corresponds to the more electrochemically precise \(\text{TOF}_{\text{max}}\) recently introduced by Savéant et al.\(^{18,19}\) FOWA enables determination of TOFs for soluble electrocatalysts despite limitations such as substrate consumption and catalyst decomposition.\(^{18}\) The TOFs in the presence of 1 atm of O2 and 20 mM [DMF-H]OTf are given in Table 1. The TOFs in general increase linearly with increasing partial pressures of O2 and [DMF-H]OTf (Figures S1 and S20). The TOFs in the presence of 1 atm of O2 and 20 mM [DMF-H]OTf, 100 mV/s scan rate. The TOF (or \(\text{TOF}_{\text{max}}\)) values are well-defined properties of the molecular catalysts. For the catalysts studied here, the rate of O2 consumption near the electrode surface (and thus current, Figure 1B) reaches a plateau when \(E < E_{1/2}\), representing the maximum chemical rate under conditions where electron transfer from the electrode to the soluble catalyst is rapid and complete.\(^{18}\) This is in contrast to heterogeneous electrocatalysts where the current typically continues to increase exponentially with the applied potential.

The effective overpotential for different molecular electrocatalysts can then be defined by the potential of the catalysis-initiating redox couple (in this case the \(E_{1/2}\) of Fe(III/II), \(E_{Fe(III/II)}\)) and the ORR equilibrium potential under the relevant catalytic conditions (O2 pressure, proton and water activity).\(^{12}\) Catalyst selectivity was investigated by electrochemical detection of hydrogen peroxide using rotating ring disk voltammetry (RRDV, see Supporting Information for details). Under identical conditions, 1–11 produced minor amounts of hydrogen peroxide (~15% H2O2). The % H2O2 converts to an average number of electrons transferred per catalytic turnover (\(n_{cat} > 3.83\)), which has been included in the TOF calculations. Thus, these catalysts are quite selective for the direct reduction of O2 to H2O, as has been previously reported for iron porphyrin complexes under similar conditions.\(^{20,21}\)

The 2-carboxyphenyl catalyst (1) and its methyl ester (2) are both remarkably fast catalysts in ACN solution, with TOFs of \(2.2 \times 10^6\) s\(^{-1}\) for both systems under our standard conditions (Table 1). Contributions from adsorbed or heterogeneous catalysis on the electrode surface were found to be negligible through use of a rinse test (Figure S18). The catalytic rate of O2 reduction by 1 was also examined by a nonelectrochemical

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**Table 1. Catalyst Reduction Potentials (vs Ferrocene/Ferrocenium, \(Fc^{+/0}\)), ORR Overpotentials (See Text), and TOF from FOWA**

| catalyst | \(E_{Fe(III/II)}\) (V) | \(\eta_{Fe/ORR}\) (V) | TOF (s\(^{-1}\)) |
|----------|-----------------|-----------------|-----------------|
| 1\(^{ACN}\) | −0.375 | 1.21 | 2.2 \times 10^6 |
| 2\(^{ACN}\) | −0.390 | 1.24 | 2.2 \times 10^6 |
| 9\(^{ACN}\) | −0.326 | 1.15 | 6.5 \times 10^4 |
| 10\(^{ACN}\) | −0.296 | 1.13 | 2.2 \times 10^5 |
| 11\(^{ACN}\) | −0.280 | 1.11 | 2.2 \times 10^6 |
| 1\(^{DMF}\) | −0.630 | 1.18 | 2.0 \times 10^4 |
| 2\(^{DMF}\) | −0.611 | 1.16 | 2.5 \times 10^5 |
| 3\(^{DMF}\) | −0.547 | 1.10 | 1.6 \times 10^5 |
| 4\(^{DMF}\) | −0.536 | 1.09 | 1.8 \times 10^5 |
| 5\(^{DMF}\) | −0.530 | 1.08 | 2.7 \times 10^5 |
| 6\(^{DMF}\) | −0.491 | 1.04 | 5.0 \times 10^5 |
| 7\(^{DMF}\) | −0.486 | 1.04 | 1.5 \times 10^5 |
| 8\(^{DMF}\) | −0.362 | 0.91 | 3.0 \times 10^4 |

\(^{ACN}\) in ACN (superscript "ACN") or DMF (superscript "DMF"), 0.1 M [Bu4N][PF6], 1 atm of O2, 20 mM [DMF-H]OTf, 100 mV/s scan rate. Experimental uncertainties are ±5 mV for \(E_{Fe(III/II)}\) ±20 mV for overpotentials, and ±15% for TOFs.

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**Figure 1.** (A) Iron(III) 5,10,15,20-tetraarylporphyrin electrocatalysts 1–11. (B) CV of 1 in ACN under 1 atm of N2 (blue) or O2 (red), 20 mM [DMF-H]OTf, 100 mV/s scan rate; the inset shows the electrocatalytic onset (foot-of-the-wave) region.
stopped-flow kinetics study (see Supporting Information). Following our earlier methodology, an ACN solution of 3 μM 1, 8 mM Cp₅Fe (Cp₅ = pentamethylcyclopentadienyl), and 2.2 mM [DMF-H][OTf]/2.2 mM DMF was mixed with an air-saturated O₂ solution. The appearance of [Cp₅Fe]⁺ was complete within 200 ms (Figure S46). Converting the derived third order rate constant to a TOF under the electrochemical conditions gives TOF = 1.1 × 10⁶ s⁻¹. Thus, spectrochemical kinetic measurements are consistent with the electrochemical results and provide confirmation of the remarkably high catalytic activities observed.

The TOFs for 1 and 2 in ACN are, to our knowledge, the fastest TOFs ever reported for homogeneous ORR electrocatalysts. Furthermore, the TOFs for 1 and 9 increase linearly with [DMF-H]+ until saturation kinetics are observed at higher acid concentrations and the TOFs become independent of [DMF-H]+. The maximum TOFs are 3 × 10⁶ s⁻¹ and 2.5 × 10⁶ s⁻¹ for 1 and 9, respectively. Based on the catalytic mechanism in Figure 2A, when the rate becomes independent of acid concentration, the TOF is limited by O₂ binding (see Supporting Information, page 5). Using TOF = k₂[O₂] and [O₂] = 8 mM in ACN under 1 atm of O₂, the saturation TOFs correspond to second order rate constants for O₂ binding, k₂[O₂] = 4 × 10⁹ M⁻¹ s⁻¹ (1) and 3 × 10⁹ M⁻¹ s⁻¹ (9). These are in the range of typical k₂ for ferrous porphyrins. Thus, these catalysts approach the fastest possible rate, being only ~10⁵ below the rate constant for diffusive encounter of O₂ and the catalyst.

The 2-pyridyl substituted complex 8, unique among the catalysts in the series, displays an inverse dependence on the concentration of acid. Increasing the concentration of [DMF-H][OTf] causes the TOF for 8 to decrease, and also shifts the E₁/₂ of the catalyst (see Supporting Information, page 5). We therefore define a characteristic overpotential under these conditions, η₈/ Orr = E₁/₂,O₂ - E₁/₂,air. This η₈/ Orr is the characteristic value within the general definition of overpotential as the difference between E₁/₂,O₂ and the applied potential E. We
emphasize that $\eta_{Fe/ORR}$ is a well-defined single value for a molecular electrocatalyst, because the current density (and thus reaction rate) are constant at overpotentials beyond $E_{Fe(III/II)}$.\textsuperscript{24} This contrasts with the situation for heterogeneous electrocatalysts, where the current density increases exponentially with $\eta$.

Correlating log(TOF) with $\eta_{Fe/ORR}$ for the 11 catalysts analyzed in different conditions shows that all of the results fall on two parallel lines (Figure 2C). The simple relationship between TOF and $\eta_{Fe/ORR}$ has been independently observed in three different ways: (i) changing the catalyst, which changes $E_{Fe(III/II)}$; (ii) changing the solvent, which alters $E_{O_2/H_2O}$; and (iii) changing the [DMF-H]$^+$, which shifts $E_{O_2/H_2O}$ in a Nernstian fashion. Catalyst 8 is unique since both i and iii occur upon changing the [DMF-H]$^+$. Considering both changes for 8 in Figure 2C places all of its values on a LFER of similar slope to catalysts 1–7 in DMF. This analysis allows, for the first time, the direct comparison of homogeneous ORR electrocatalysts in different solvents and with different acid concentrations. Thus, catalysts 1, 2, 9, and 10 in ACN and 8 in DMF are clearly better catalysts than the other, because they lie on a line that is above and to the left. At a given $\eta_{Fe/ORR}$, the catalyst systems on the left line have higher TOFs, or stated another way, these catalysts require a lower $\eta_{Fe/ORR}$ to reach the same TOF.

Dissecting the TOF/$\eta_{Fe/ORR}$ correlations provides additional understanding. The log(TOF) vs $\eta_{Fe/ORR}$ lines in Figure 2C have inverse slopes of 57 and 54 mV per decade in TOF for the left and right correlations, respectively. This is (by coincidence we believe) remarkably close to the Nernstian slope of 59 mV per decade in concentration. We emphasize that this plot is distinct from the Tafel plot analysis of a single electrocatalyst at different applied potentials (molecular or heterogeneous). Figure 2C relates the properties of different catalysts under different conditions. Fundamentally, these correlations show how the barrier height of turnover limiting step(s) changes as a function of overall driving force, varied via $E_{O_2/H_2O}$, $E_{Fe(III/II)}$, or both for 8.

The presence of these correlations is remarkable. For these catalysts, the measured TOF is limited by the $O_2$ binding equilibrium and the rate of protonation of the superoxide intermediate, as shown in the mechanism in Figure 2A. The TOFs are not determined by any electrochemical step. The correlations indicate that electronic modifications of the catalysts linearly tune the free energies of the relevant intermediates and reaction steps of the catalytic cycle.

This tuning is revealed by density functional theory (DFT) calculations of the reduction potentials $E_{Fe(III/II)}$, $O_2$ binding equilibrium constants $pK_{O2}$ and the $pK_s$ of the protonated superoxide intermediate ([Fe$^{III}$(por)($O_2$)$_2$]$^+$). All of the catalysts were calculated except for 1, 2, and 8, for which many rotamers exist in solution. The $pK_s$ of the protonated superoxide intermediate ([Fe$^{III}$(por)($O_2$)$_2$]$^+$) is directly related to the free energy of protonation of the superoxide, the rate-determining step. The calculations show clear correlations among the computed catalyst $E_{Fe(III/II)}$, the $pK_{O2}$, and the $pK_s$ (Figure 3). Electron donating substituents that shift $E_{Fe(III/II)}$ to more negative values increase the $O_2$ affinity and the superoxide basicity, increasing the TOF. Quantitatively, using simple transition state theory and Bell–Polanyi–Evans (BPE) arguments, it is possible to show that log(TOF) = $-pK_{O2} + a\cdot pK_s + C$. Taking $a = 1/2$ (see Supporting Information), the computations predict a LFER of 43 mV/decade in TOF, in good agreement with the experimental value.\textsuperscript{25} For $a = 0.23$, computations and experiments match exactly.

The correlations and calculated energetics of elementary steps demonstrate that installing pendant protic or hydrogen bond donor/acceptor functionalities in the second coordination sphere (i.e., 1, 8–11) in most cases has a negligible effect on the TOFs for the ORR. The 2-carboxylic acid catalyst 1$^{DMF}$ has
a higher TOF than the isomeric 4-carboxylic acid isomer \( \gamma^\text{DMF} \) (2040 s\(^{-1}\) vs 15 s\(^{-1}\) in DMF) simply because 1 has the more negative reduction potential. Catalyst 1 and its methyl ester 2 have \( E_{Fe(III/II)} \) values within 19 mV and very close TOFs (within 20%), in both ACN and DMF, even though only 1 would appear to have proton relays. The presence of potential proton relays does not displace the pK\(_a\) and the pK\(_{\alpha}\) of the catalyst from the correlation lines. This conclusion contrasts with the great value of such “proton relays” in electrocatalysts for \text{H}^+ and \text{CO}_2 reduction\(^{15,16}\) and shows that the observation of improved rates for catalysts containing potential relays does not demonstrate a relay effect.

The lack of a “relay effect” arises from a thermodynamic mismatch; the pendant proton donors (PyH\(^+\), PhCO\(_2\)H) are not strong enough to protonate \([\text{Fe}^{III}(\text{por})\text{(O}_2\text{H})^+\])\(^{10}\). Using extrapolated values from Figure 3A for catalysts containing potential relays does not displace the pK\(_a\) units. The proton must be delivered from the much stronger \([\text{DMF-H}^+]\) acid in solution, which is the proton source in both DMF and ACN solvents. While there is no definitive evidence for intramolecular proton transfer in these systems, the second coordination sphere may play a noninnocent role in defining the TOF/\(\eta\) correlations. Such is the case for catalysts 9–11. Despite all having identical orthoamide NH groups\(^{26}\) that are highly pK\(_{\alpha}\)-mismatched with the external acid, catalysts 9 and 10 fall upon a more efficient TOF/\(\eta\) correlation than 11, discussed below.

Figure 2C shows two LFER lines of nearly identical slope for this set of catalysts and conditions. The lower \(\eta\) line (to the left) primarily has the systems in ACN, suggesting that this is the better solvent for ORR in general, but 8 \(^\text{DMF}\) falls on that line and 11 \(^\text{ACN}\) falls on the higher \(\eta\) line with most of the systems in DMF. As emphasized above, the TOFs are limited by O\(_2\) binding and the subsequent superoxide ligand protonation. Computationally, there is a single correlation between pK\(_{\alpha}\) and \(E_{Fe(III/II)}\), that includes all of the catalysts in both solvents (slope \(\sim100\) mV/unit pK\(_{\alpha}\), Figure 3A, left). Therefore, this is not the origin of the better catalysis by 9 and 10. Their advantage originates solely from their better proton transfer thermodynamics, as their protonated superoxide complexes have higher pK\(_{\alpha}\) values than would be expected from their \(E_{Fe(III/II)}\) (Figure 3A, right). Indeed, 9 and 10 have the most favorable \(\Delta G^o\) for proton transfer (\(-3.5\) and \(-1.8\) kcal/mol, respectively) of all catalysts analyzed. They are easier to protonate and have higher TOFs. We suspect that similar issues explain why 1, 2, and 8 fall on the better correlation line, but their complicated mixture of rotamers precluded computational analysis, as noted above. The related CF\(_3\)-substituted amide catalyst 11 does not have this elevated pK\(_{\alpha}\) and does not have the elevated TOF (it falls on the LFER line to the right).

To further understand the origin of the distinct pK\(_{\alpha}\) values for the amide catalysts 9–11, we compared the optimized structures of the relevant intermediates. There is a hydrogen bond from the amide NH groups in the second coordination sphere to the distal O (O\(_{d}\)) of the O\(_2\)-derived ligand (Figure 3C). In principle, the hydrogen bonds should be strongest—greatest stabilization by the second coordination sphere—for the more electron rich intermediates. Indeed, for the protonated superoxide complexes \([\text{Fe}^{III}(\text{por})(\text{O}_2\text{H})^+\])\(^9\), the calculations show that the intermediate from 9 has the shortest NH–O distance, nearly 0.1 Å shorter than that in 11: d(NH–O\(_d\)) = 2.864 Å, 2.907 Å, and 2.966 Å for 9–11, respectively. However, the trend is the opposite when comparing the NH–O distances of the \([\text{Fe}^{III}(\text{por})(\text{O}_2\text{H})^+\]) intermediates, where the NH–O distances are 2.379 Å, 2.361 Å, and 2.296 Å for 9–11, respectively (see Figure S72). Therefore, proton transfer to form \([\text{Fe}^{III}(\text{por})(\text{O}_2\text{H})^+\])\(^9\) requires the largest changes in the NH–O distance for 11 (0.670 Å) when compared to 10 and 9 (0.546 and 0.485 Å). Given that the majority of the other bond lengths and angles are quite similar for 9–11, the NH–O hydrogen bond appears to play an important role in modulating the E\(_{1/2}\) to pK\(_{\alpha}\) and thus TOF relations. The stronger H-bonding interaction for the protonated superoxide complexes 9 and 10 allow for a more exergonic proton transfer, resulting in TOFs roughly 2 orders of magnitude larger than 11 under identical conditions (after correcting for the difference in overpotentials). This H-bonding effect of the “relay” was unexpected since the proton is delivered from the exogenous donor, \([\text{DMF-H}^+]\). Differences in proton transfer energetics may also be the reason for 1 and 2 behaving so much better in ACN than DMF, and also for 8 compared to 1–7. Understanding the better catalysis by these complexes is challenging because of the presence of multiple conformations and/or protonation states. The selective stabilization of one intermediate over another for 9 and 10 is an effect of the second coordination sphere groups, due to hydrogen bonding rather than proton delivery. The occurrence of this effect for complexes 9 and 10 but not for 11 shows the subtle interplay of factors contributing to such second coordination sphere effects.

The combined experimental and theoretical studies reported herein provide a detailed look at the factors that underlie molecular ORR electrocatalysis. Changing substituents on the aryl rings of these metallorporphyrin catalysts changes their \(E_{Fe(III/II)}\) and all of the key parameters change in parallel for most of the catalysts. This approach of finding linear free energy relationships is the same principle that has become a primary way to analyze sets of heterogeneous catalysts, including electrocatalysts.\(^{27}\) The widely used “volcano plots” and “scaling relationships” correlate catalyst activity with a single descriptor such as a surface–substrate binding energy or the d-band center, and the relationships hold when the free energies of the different catalytic steps scale linearly with the descriptor. A recent computational study of iron porphyrin ORR catalysts showed the presence of scaling relations for the binding of OH, O\(_2\), and OOH, but did not consider separate electron or proton transfer steps.\(^{28}\) The combined experimental and computational study reported here provides more detailed analysis and shows one way to overcome the scaling relationships. Further studies are in progress to design improved catalysts by further decoupling the properties of the second coordination sphere from those of the first. This is a new design principle for catalysis of multielectron/multiple proton reactions.

The results and analysis developed here allow, for the first time, comparisons of molecular \text{O}_2 reduction electrocatalysts under diverse conditions. The correlations observed in this study show that the ORR activities for catalysts 1–11 correlate with the well-defined overpotentials (\(\eta\)) for these molecular catalysts under a range of conditions, on two parallel linear free energy relationships. The correlations hold for a variety of electrocatalysts and media across 6 orders of magnitude in TOF, and show that the extraordinarily high TOFs for 1 and 2, close to the diffusion limit for the 4e\(^-/-4H^+\) ORR reaction, are mostly due to their high \(\eta\). These correlations are shown computationally to stem from the chemical steps of \text{O}_2 binding and proton transfer. The origin of the improved behavior of some of the electrocatalysts is shown to derive from deviations...
in the correlation of catalyst properties \( (E^\circ, K_{298}) \) with the basicity of the superoxide intermediate \( \left[ \text{Fe(por-O)}_2\text{O}^+ \right] \). This concept of decoupling the thermochemical properties of the first and second coordination spheres is a new approach to catalyst design.

**ASSOCIATED CONTENT**

* Supporting Information

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Synthesis procedures, characterization, and calculations (PDF)

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**Notes**

The authors declare no competing financial interest.

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