Acid-Induced Mechanism Change and Overpotential Decrease in Dioxygen Reduction Catalysis with a Dinuclear Copper Complex

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Supporting Information

ABSTRACT: Catalytic four-electron reduction of O2 by ferrocene (Fc) and 1,1′-dimethylferrocene (Me2Fc) occurs efficiently with a dinuclear copper(II) complex [CuII2(XYLO)(OH)]2+ (1), where XYLO is a m-xylene-linked bis[(2-(2-pyridyl)ethyl)amine] dinucleating ligand with copper-bridging phenolate moiety, in the presence of perchloric acid (HClO4) in acetone at 298 K. The hydroxide and phenoxo group in [CuII2(XYLO)(OH)]2+ (1) undergo protonation with HClO4 to produce [CuII2(XYLO)]4+ (2) where the two copper centers become independent and the reduction potential shifts from −0.68 V vs SCE in the absence of HClO4 to 0.47 V; this makes possible the use of relatively weak one-electron reductants such as Fc and Me2Fc, significantly reducing the effective overpotential in the catalytic O2-reduction reaction. The mechanism of the reaction has been clarified on the basis of kinetic studies on the overall catalytic reaction as well as each step in the catalytic cycle and also by low-temperature detection of intermediates. The O2-binding to the fully reduced complex [CuII2(XYLOH)]2+ (3) results in the reversible formation of the hydroperoxo complex ([CuII2(XYLO)(OOH)]2+) (4), followed by proton-coupled electron-transfer (PCET) reduction to complete the overall O2-to-2H2O catalytic conversion.

INTRODUCTION

The heme/copper (heme a3/CuB) heterodinuclear center in cytochrome c oxidases (Cox) catalyzes the four-electron and four-proton reduction of dioxygen (O2) to water in the final stage of the respiratory chain (eq 1).1–4

\[
\text{O}_2 + 4e^- (\text{from cyt-c}_{\text{reduced}}) + 8H^+ (\text{from outside membrane}) \\
\rightarrow 2H_2O + 4H^+ (\text{membrane translocated}) + 4\text{cyt-c}_{\text{oxidized}} \tag{1}
\]

The catalytic four-electron reduction of O2 to water has attracted much interest because of the important role in respiration5 and also potential application in fuel cell technology.6 The four-electron reduction of O2 is catalyzed by platinum instilled in carbon at the cathode in fuel cells.7 To achieve substantial activity, high loadings of this precious metal are required which have prompted research efforts to develop catalysts based on nonprecious metals such as Co and Fe.8–9 Cu catalysts have also merited considerable interest,19–24 in relation with copper containing enzymes, the so-called multicopper oxidases (MCOs), which efficiently effect the four-electron four-proton reduction to water as part of their function.25–28

In contrast to such heterogeneous systems, investigations on the catalytic reduction of O2 by metal complexes in homogeneous systems have provided deeper insight into the catalytic mechanism of the two-electron and four-electron reduction of O2. Solution variable-temperature kinetic studies and detection of reactive metal–O2 intermediates reveal the controlling factors in the two- vs four-electron reduction of O2 with metal complexes.29–35 The key feature is the modification of supporting ligand environments which can allow for differing copper–dioxygen intermediates.

So far we found that two mononuclear copper complexes having tmpa (tmpa = tris(2-pyridylmethyl)amine) (A),36 bzpy1 = N,N-bis[2-(2-pyridyl)ethyl]benzylamine (B)37 and one dinuclear copper complex with N3 ligand (N3 = -(CH2)3-linked bis[(2-(2-pyridyl)ethyl)amine])37 (C) (Scheme 1) efficiently catalyze the four-electron reduction of dioxygen via the formation of [[(tmpa)CuII]2(μ-1,2-O22−)]2+ (A1), [CuIII(bzpy1)(μ-(O2−)]2+ (B1) and [CuIII(N3)(μ-η1:η2-O22−)]2+ (C1) intermediates, respectively, which were prone to proton-promoted reductive O–O cleavage to give water, in preference to simple protonation leading to H2O2.36,37 However, the dinuclear copper(II) complex [CuII2(XYLO)-(OH)]2+ (1) (Scheme 1), where XYLO is a m-xylene-linked bis[(2-(2-pyridyl)ethyl)amine] dinucleating ligand with copper-bridging phenolate moiety, catalyzes the two-electron reduction

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of O₂ to hydrogen peroxide in the presence of trifluoroacetic acid (HOTF) via the hydroperoxo intermediate (D1). In all cases, however, only a strong one-electron reductant such as decamethylferrocene (Fc*) could be used to reduce O₂ with the copper complexes. There has so far been no example for the catalytic reduction of O₂ by one-electron reductants weaker than Fc* with Cu complexes.

We report herein that [Cu II₂(XYLO)(OH)]²⁺ (1) can instead act as an efficient catalyst for the four-electron reduction of O₂ by one-electron reductants weaker than Fc* such as ferrocene (Fc) and 1,1′-dimethylferrocene (Me₂Fc) in the presence of HClO₄ in acetone. The reasons why the same catalyst can act in either the two-electron or four-electron reduction of O₂ by Fc* and Fc in the presence of CF₃COOH and HClO₄, respectively, are elucidated on the basis of new kinetic studies on the overall catalytic reactions as well as each catalytic step and also by detection of copper dioxygen-derived intermediates which form during the catalytic cycle. The present study leads to successful achievement of two important features, which have never been previously observed:

- We have been able to effect catalytic O₂ reduction using significantly less overpotential with a dinuclear copper complex, which is of course more desirable and more energy efficient.
- We have been able to change the number of electrons in the catalytic reduction of O₂ from two electrons to four electrons by only increasing the acidity of the proton source employed.

The mechanistic insights obtained in this study should serve as useful and broadly applicable principles for future design of more efficient catalysts in fuel cells.

### RESULTS AND DISCUSSION

#### Catalytic Four-Electron Reduction of O₂ by Fc and Me₂Fc with 1 in the Presence of HClO₄.

The addition of a catalytic amount of 1 to an air-saturated acetone solution of Me₂Fc and perchloric acid (HClO₄) results in the efficient reduction of O₂ by Me₂Fc to afford the corresponding dimethylferrocenium cation (Me₂Fc⁺). The spectral changes for the catalytic reduction of O₂ by Me₂Fc with 1 in the presence of HClO₄ in acetone at 298 K are shown in Figure S1 (see Supporting Information [SI]). When more than 4 equiv of Me₂Fc relative to O₂ (limiting [O₂]) was employed, 4 equiv of Me₂Fc⁺ (λ max = 650 nm, ε = 360 M⁻¹ cm⁻¹) were formed in the presence of excess HClO₄ (Figure 1). From iodometric titration experiments, it was confirmed that no H₂O₂ had formed after completion of the reaction (Figure S2 in SI). Thus, the four-electron reduction of O₂ by Me₂Fc occurs efficiently with a catalytic amount of 1 in the presence of HClO₄ (eq 2).

\[
4\text{Me}_2\text{Fc} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Me}_2\text{Fc}^+ + 2\text{H}_2\text{O}
\] (2)
When Me2Fc was replaced by the weaker reductant, Fc, the four-electron reduction of O2 by Fc also occurred efficiently with 1 (Figure S3 in SI). The rate of formation of Me2Fc+ and Fc+ obeyed pseudo-first-order kinetics under the conditions that $[1] \ll [O_2] < [Me_2Fc] < [HClO_4]$ (Figure 1 inset). The time profiles of the absorbance at 650 nm due to Me2Fc+ and at 620 nm due to Fc+ and the first-order plots by varying HClO4, O2, and catalyst are shown in SI, Figures S4, S5, S6a, and Figure 2a, respectively. The pseudo-first-order rate constant ($k_{obs}$) increased linearly with increasing concentration of 1 (Figures 2b and S6b in SI). It should be noted that no oxidation of Me2Fc occurs by O2 in the presence of HClO4 without 1, under the present experimental conditions, even though ferrocene derivatives are known to be slowly oxidized by O2 in the presence of strong acids.39,40 It should also be noted that the use of a noncoordinating solvent (acetone) is essential for the four-electron reduction of O2 by Me2Fc and Fc with HClO4, because a coordinating solvent such as acetonitrile prohibits such chemistry. The two-step protonation in Scheme 2 was confirmed by the EPR titration with HClO4. The starting dinuclear copper(II) complex $[Cu^{II}(XYLO)(OH)]_2(PF_6)_2$ (1) is EPR silent because of antiferromagnetic coupling of the two Cu(II) ions (Figure 4a). It should be noted that, when the complex 1 was protonated with trifluoroacetic acid (HOTF), the protonated complex was EPR silent, indicating the two Cu(II) ions still maintain an electronic/magnetic interaction after the protonation of 1 with HOTF.38 In the presence of one equiv of HClO4, which can protonate the OH group to produce H2O, however, a typical axial Cu(II) EPR spectroscopic signal was observed, indicating that both the hydroxide and the phenoxo groups of the complex were EPR silent, indicating the two Cu(II) ions still maintain an electronic/magnetic interaction after the protonation of 1 with HOTF.38

The catalytic reduction of O2 by Me2Fc and Fc with 1 was made possible only by the presence of HClO4. The effect of protonation of 1 was first examined by the spectral titration of 1 with HClO4 (Figure 3). The absorption band at 378 nm
due to $[Cu^{II}(XYLO)(OH)]^{2+}$ decreased with increasing concentration of HClO4 and this was completely different from the spectral behavior of complex 1 with CF3COOH (HOTF), where the absorption band was shifted to 420 nm and a clean isosbestic point was observed at 430 nm.38 These spectral changes in the presence of HClO4 indicate that not only the hydroxide group but also the phenoxo group of $[Cu^{II}(XYLO)(OH)]^{2+}$ (1) are protonated with HClO4, a much stronger acid than CF3COOH, to produce $[Cu^{II}(XYLOH)]^{4+}$ (2) (Scheme 2).

The two-step protonation in Scheme 2 was confirmed by the EPR titration with HClO4. The starting dinuclear copper(II) complex $[Cu^{II}(XYLO)(OH)]_2(PF_6)_2$ (1) is EPR silent because of antiferromagnetic coupling of the two Cu(II) ions (Figure 4a). It should be noted that, when the complex 1 was protonated with trifluoroacetic acid (HOTF), the protonated complex was EPR silent, indicating the two Cu(II) ions still maintain an electronic/magnetic interaction after the protonation of 1 with HOTF.38 In the presence of one equiv of HClO4, which can protonate the OH group to produce H2O, afforded the EPR silent species. In the presence of excess HClO4 however, a typical axial Cu(II) EPR spectroscopic signal was observed, indicating that both the hydroxide and the...
oxidation potential of Me2Fc (peak is much more negative as compared to the one-electron oxidation potential of Fc to Cu II sites (Figure 4b).

Once the phenoxy group is protonated, the two Cu sites become independent and more electron deficient because of the lack of the coordination of the anionic phenoxy donor ligand. This was confirmed by the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements on 1 in the absence and presence of HClO4 in acetone as shown in Figure 5. An irreversible cathodic peak current was observed at Eox = 0.26 V vs SCE. Thus, electron transfer from Fc to Cu II sites (Figure 4b). This was confirmed by examination of electron transfer from Me2Fc or Fc to Cu II in the presence of excess HClO4 is twice that observed for complex 1 (0.10 mM). This result indicates that the two Cu sites of protonated 1 (Scheme 2) act independently without any interaction between them. The observed pseudo-first-order rate constant (kobs) increased linearly with increasing concentration of Me2Fc and Fc (Figure 6). The second-order rate constants (kcat) of electron transfer from Me2Fc and Fc to 1 at 298 K were determined to be 2.7 × 10^2 M^-1 s^-1 and 1.8 × 10^2 M^-1 s^-1 from the slopes of linear plots of kobs vs [Me2Fc] and [Fc], respectively. The kcat values are listed in Table S1 (SI) together with the kobs values.

The kcat values (2.7 × 10^2 M^-1 s^-1 and 1.8 × 10^2 M^-1 s^-1) of electron transfer from Me2Fc and Fc to 1 in the presence of 40 mM HClO4 are significantly larger than the corresponding kobs values (see eqs 3 and 4) values (42 M^-1 s^-1 in Figure 2b and 10 M^-1 s^-1 in Figure S6b [SI]) in the presence of 40 mM HClO4, respectively. Thus, the electron-transfer step is not the rate-determining step in the catalytic cycle. The electron transfer from Me2Fc and Fc to 1 in the presence of excess HClO4 without O2 results in formation of the protonated dinuclear Cu(I) complex, [CuII(2XYLOH)2+]2+ (Scheme 2), which can reduce O2. Next we examined the reaction of [CuII(2XYLOH)2+]2+ with O2 at low temperatures to detect any copper–dioxigen intermediate.

**Reversible Binding of O2 to [CuII(2XYLOH)2+]2+.** When O2 was bubbled into an acetone solution of separately synthesized dicopper(I) complex, [CuII(2XYLOH)2+]2+ at 193 K, the absorption band at 395 nm due to the hydroperoxocomplex, [CuII(2XYLOH)2+](OH)2]2+ shifted immediately as shown in Figure 7 and Scheme 4. The yield of hydroperoxocomplex, [CuII(2XYLOH)2+](OH)2]2+ was determined to be 100% at
193 K. As the temperature increased, the absorption band at 395 nm due to \([\text{Cu}^{II}_{2}(XYLO)(OOH)]^{2+}\) decreased. This process was reversible at low temperatures up to 223 K (Figure 8a). The temperature dependence of \(K_{eq}\) was examined (Figure S9 in SI), and the van’t Hoff plot (Figure 8b) afforded \(\Delta H = -31 \text{ kJ mol}^{-1}\) and \(\Delta S = -86 \text{ J K}^{-1} \text{ mol}^{-1}\). The equilibrium constant at 298 K was estimated to be 11 M\(^{-1}\) from the extrapolation of the van’t Hoff plot. The equilibrium lies to the reactant side at 298 K when only a small portion of \([\text{Cu}^{II}_{2}(XYLO)(OOH)]^{2+}\) is converted to \([\text{Cu}^{II}_{2}(XYLO)(OOH)]^{2+}\) (~10%).

This intermediate was further reduced by decamethylferrocene (Fc\(^*\)) in the presence of HClO\(_4\) at 193 K (Scheme 5, Figure 9). Fc\(^*\) was used because the reactions with Me\(_2\)Fc and Fc were too slow to be followed at 193 K.

An alternate reaction pathway that may contribute in a small way to the overall chemistry and catalytic cycle comes about if the hydroperoxo complex \([\text{Cu}^{II}_{2}(XYLO)(OOH)]^{2+}\) (4) is protonated in the presence of HClO\(_4\) to yield hydrogen peroxide and protonated dicopper(II) complex, \([\text{Cu}^{II}_{2}(XYLOH)]^{4+}\) (2) (Scheme 6a). This was separately demonstrated using excess HClO\(_4\) (10 equiv) (Figure S10 in SI). However, we find that if hydrogen peroxide forms in this manner, it would be readily reduced to H\(_2\)O by the dicopper(I) complex \([\text{Cu}^{I}_{2}(XYLOH)]^{2+}\) (3) (Scheme 6b and Figure 10; see also Figure S11 in SI). Although H\(_2\)O\(_2\) and Cu(II)-H\(_2\)O\(_2\) adducts have been previously reported to react directly with acetone,\(^43,44\) clean and fast conversion of 3 with H\(_2\)O\(_2\) to 1 in Figure 10 suggests the reaction of H\(_2\)O\(_2\) and the Cu complex with acetone may be negligible under the present reaction conditions. The observed first-order rate constant \((k_{obs})\) increased linearly with increasing concentration of H\(_2\)O\(_2\) (Figure 10b). The second-order rate constant \((k_2)\) was determined to be 2.5 × 10\(^3\) M\(^{-1}\) s\(^{-1}\) at 298 K, which is much larger than the \(k_{obs}/[1]\) values (vide supra). Thus, under the catalytic conditions, the H\(_2\)O\(_2\) produced, if any, is rapidly reduced by \([\text{Cu}^{II}_{2}(XYLOH)]^{2+}\), contributing to the overall four-electron four-proton reduction of O\(_2\).

The overall catalytic cycle is summarized in Scheme 7. The protonation of \([\text{Cu}^{II}_{2}(XYLO)(OH)]^{2+}\) (1) results in formation...
of \([\text{Cu}^{II}(\text{XYLO})]^{4+}\) (2), which can be reduced by two equiv of Fe and Me₂Fc to produce fully reduced dicopper(1) complex \([\text{Cu}^{III}(\text{XYLO})]^{2+}\) (3). The O₂-binding to (3) to produce hydroperoxo complex \([\text{Cu}^{II}(\text{XYLO})(\text{OOH})]^{2+}\) (4) is an equilibrium process. At 298 K, only a small portion of \([\text{Cu}^{II}(\text{XYLO})]^{2+}\) is converted to \([\text{Cu}^{II}(\text{XYLO})(\text{OOH})]^{2+}\), the concentration of which is proportional to the O₂ concentration. \([\text{Cu}^{II}(\text{XYLO})(\text{OOH})]^{2+}\) that is formed undergoes further reduction by PCET from Fe and Me₂Fc, leading to the four-electron reduction of O₂. In this final two-electron peroxide reduction, the first PCET reduction may be the rate-determining step followed by the much faster second PCET reduction to produce H₂O. In such a case, the overall catalytic rate is proportional to concentrations of 1, O₂, HClO₄, and electron donors (Fe and Me₂Fc) as observed in Figure 2 and Figures S4–S6 in SI. The PCET reduction of \([\text{Cu}^{II}(\text{XYLO})(\text{OOH})]^{2+}\) may compete with the protonation of \([\text{Cu}^{II}(\text{XYLO})(\text{OOH})]^{2+}\) (4) to generate H₂O₂ (Scheme 6); however, H₂O₂ thus produced is rapidly reduced to H₂O by \([\text{Cu}^{II}(\text{XYLO})]^{2+}\) (vide supra).

According to Scheme 7, the equilibrium between \([\text{Cu}^{II}(\text{XYLO})]^{2+}\) (3) with O₂ and \([\text{Cu}^{II}(\text{XYLO})(\text{OOH})]^{2+}\) (4) at 298 K lies to the side of \([\text{Cu}^{II}(\text{XYLO})]^{2+}\) (vide infra), the \([\text{Cu}^{II}(\text{XYLO})]^{4+}\) complex is being converted to \([\text{Cu}^{II}(\text{XYLO})]^{2+}\) during the catalytic reaction but \([\text{Cu}^{II}(\text{XYLO})]^{4+}\) (2) may be regenerated after the completion of the catalytic reaction when all ferrocenes were consumed. This was confirmed as the change in the EPR spectra as shown in Figure 11, where the EPR signal due to \([\text{Cu}^{II}(\text{XYLO})]^{4+}\) (2) observed before the reaction disappeared during the catalytic reaction but reappeared after completion of the reaction without exhibiting any decomposition.

The kinetic results (as described by eqs 3 and 4) and the absence of the EPR signal due to 2 during the catalytic reaction indicate that the reaction of 3 with O₂, Me₂Fc and H⁺ involves all of these species in the rate-determining step. As described above, we have also separately shown that 4 is formed by the reaction of 2 and O₂ at 193 K (Figure 7). At 298 K, the equilibrium for the formation of 4 lies to 2 (vide supra), when the concentration of 4 may be proportional to \([\text{O}_2]^{4-}\). Then, the PCET reduction of 4 by Me₂Fc may compete with the formation of H₂O₂ by the protonation of 4. At 193 K, the protonation of 4 to produce H₂O₂ may be the major pathway as indicated by the results in Figure 9. At 298 K, however, the PCET reduction of 4 by Me₂Fc may be the major pathway when the rate of formation of Me₂Fc⁺ is derived as given by eq S, where \(k_{\text{PCET}}\) is the rate constant of PCET reduction of 4.

\[
d[\text{Me}_2\text{Fc}^+]/dt = k_{\text{PCET}} K[\text{Me}_2\text{Fc}][\text{O}_2][\text{H}^+] \tag{5}
\]

and \(K\) is the equilibrium constant of formation of 4 with O₂ from 3. The derived kinetic equation (eq 5) agrees with the experimental observations in eqs 3 and 4. If the protonation of 4 to produce H₂O₂ was the major pathway at 298 K, the rate would not be dependent on Me₂Fc because electron transfer from Me₂Fc to 2 was shown to be too fast to be involved in the rate-determining step. Because the rate is proportional to [Me₂Fc], the rate-determining step must be the PCET reduction of 4 by Me₂Fc. It should be noted that the protonation of 1 is completed in the presence of HClO₄ (>10 mM) as shown in Figure 2, when the linear dependence of the rate on concentration of HClO₄ (>10 mM) in Figure 2c results from the rate-determining PCET reduction of 4.

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Figure 10. (a) UV–vis spectral changes observed in the reaction of H₂O₂ (0.033 mM) with \([\text{Cu}^{II}(\text{XYLO})]^{2+}\) (0.025 mM) in acetonitrile at 298 K. Inset shows the time profile monitored at 378 nm due to the formation of \([\text{Cu}^{II}(\text{XYLO})(\text{OOH})]^{2+}\). (b) Plot of \(k_{\text{obs}}\) vs [H₂O₂] in the reaction of H₂O₂ with \([\text{Cu}^{II}(\text{XYLO})]^{2+}\) (0.025 mM) in acetonitrile at 298 K.

Figure 11. EPR spectra of (a) \([\text{Cu}^{II}(\text{XYLO})(\text{OH})](\text{PF}_6)_2\) (1) (0.040 mM) with HClO₄ (40 mM) and (b, c) the reaction solution of 1 (0.040 mM) with Me₂Fc (10 mM) in the presence of HClO₄ (40 mM) in O₂-saturated acetonitrile at 298 K [(b) during the reaction and (c) after completion of the reaction]. Spectra were recorded at 20 K. The experimental parameters: microwave frequency = 9.654 GHz, microwave power = 1.0 mW, and modulation frequency = 100 kHz.
A dinuclear copper(II) complex ([CuII\textsubscript{2}(XYLO)(OH)]\textsuperscript{2+}) acts as an efficient catalyst for the four-electron reduction of O\textsubscript{2} by Me\textsubscript{2}Fc and Fc with HClO\textsubscript{4} in acetone as shown in Scheme 7. The hydroxide group as well as the phenoxo group of [CuII\textsubscript{2}(XYLO)(OH)]\textsuperscript{2+} (1) were protonated with HClO\textsubscript{4} to produce [CuII\textsubscript{2}(XYLOH)]\textsuperscript{4+} (2) which can be reduced by Me\textsubscript{2}Fc and Fc to produce [CuII\textsubscript{2}(XYLOH)]\textsuperscript{2+} (3). The dinuclear Cu(I) complex [CuI\textsubscript{2}(XYLOH)]\textsuperscript{2+} (3) reacts with O\textsubscript{2} to produce the hydroperoxo complex ([CuII\textsubscript{2}(XYLO)-(OOH)]\textsuperscript{+} (4)), and this is followed by PCET reduction, leading to the catalytic four-electron reduction of O\textsubscript{2} by Fc and Me\textsubscript{2}Fc.

It is instructive to compare and contrast the chemistry described here with that previously reported, both with exactly the same catalyst, [CuII\textsubscript{2}(XYLO)(OH)]\textsuperscript{2+} (1) (Schemes 1 and 8) but having very differing behaviors. As indicated in the summary in Scheme 8, 1 is quite difficult to reduce, but in the presence of HClO\textsubscript{4}, the bridging hydroxide ligand is displaced (as H\textsubscript{2}O) and now, reduction to a dicopper(I) (or a mixed-valent form, [CuI\textsubscript{2}Cu(XYLO)]\textsuperscript{2+})\textsuperscript{38} is possible; it is this/these forms which are required for O\textsubscript{2}-binding and initial reduction to the peroxide level.

With HOTF, however, the phenoxo O-atom still bridges the Cu(II) ions, leaving the redox potential negative enough to require stronger reductants such as Me\textsubscript{2}Fc or Fc*. A key coordination chemistry aspect is that HClO\textsubscript{4} as proton source is strong enough to break the phenoxo bridge between copper ions, allowing facile reduction of the Cu(II) ions with Me\textsubscript{2}Fc or even Fc itself; the complex produced, [CuII\textsubscript{2}(XYLOH)]\textsuperscript{4+} (2), now has Cu(II) ions possessing only N\textsubscript{3}-bis[(2-(2-pyridyl)ethyl)amino] chelation (Scheme 8). Thus, the change to perchloric acid facilitates a drop in effective overpotential of \(-0.30\) V, or more (Scheme 8).

Perchloric acid effects another dramatic change; the reaction mechanism switches from the catalytic two-electron two-proton reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2} with HOTF, to the catalytic four-electron four-proton reduction of O\textsubscript{2} to water with HClO\textsubscript{4}. First, with HClO\textsubscript{4}, PCET reduction/protonation of [CuII\textsubscript{2}(XYLO)(OOH)]\textsuperscript{2+} (4) is the rate-determining step. Second, note that in both systems, the hydroperoxo complex 4 is the key oxygen intermediate which is formed. HOTF readily protonates off the bound \(\text{OOH}^+\) ligand giving H\textsubscript{2}O\textsubscript{2}, but it is not strong enough to allow PCET hydroperoxide reduction to water. Perchloric acid does facilitate the latter hydroperoxide reductive cleavage to water, accounting for the differing stoichiometries of catalytic O\textsubscript{2}-reduction chemistry.

Although the mechanism of the PCET reduction of 4 by Me\textsubscript{2}Fc has yet to be clarified, the chemistry described here provides the first example of four-electron reduction of O\textsubscript{2} by one-electron reductants weaker than Fc* such as Fc and Me\textsubscript{2}Fc in the presence of HClO\textsubscript{4} in acetone by a copper complex acting as a catalyst. The present study opens a new approach to achieve less overpotential which is more desirable and more energy efficient for the catalytic four-electron reduction of O\textsubscript{2} using copper complexes.

### EXPERIMENTAL SECTION

**Materials.** Grade-quality solvents and chemicals were obtained commercially and used without further purification unless otherwise noted. Decamethylferrocene (Fc\textsuperscript{+}), 1,1’-dimethylferrocene (Me\textsubscript{2}Fc), ferrocene (Fc), hydrogen peroxide (30%), and HClO\textsubscript{4} (70%) were purchased from Aldrich Co., U.S., and NaI (99.5%) was from Junsei Chemical Co., Japan. Acetone was purchased from JT Baker, U.S., and used either without further purification for nonair-sensitive experiments or dried and distilled under argon and then deoxygenated by bubbling with argon for 30–45 min and kept over activated molecular sieve (4 Å) for air-sensitive experiments.\textsuperscript{45}

Preparation and handling of air-sensitive compounds were performed under Ar atmosphere (<1 ppm O\textsubscript{2} and <1 ppm H\textsubscript{2}O) in a glovebox (Korea Kiyon Co., Ltd.). The copper complexes, [Cu\textsubscript{II}(XYLH)-(CH\textsubscript{3}CN)\textsubscript{2}]\textsuperscript{2+} (XYLH = m-xylene-linked bis[(2-(2-pyridyl)ethyl)amine])\textsuperscript{\textsuperscript{46}} which is a precursor complex, [Cu\textsubscript{II}(XYLO)(OH)]\textsuperscript{2+} (1), and [Cu\textsubscript{II}(XYLH)]\textsuperscript{2+} were prepared according to the literature procedures.\textsuperscript{47}

**Instrumentation.** UV–vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments Cryostat USP-203A for low-temperature experiments or a UNISOKU RSP-601 stopped-flow spectrometer equipped with a MOS-type highly sensitive photodiode array. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed on an ALS 630B electrochemical analyzer, and voltammograms were measured in deaerated chemical analyzer, and voltammograms were measured in deaerated solution containing 0.20 M TBAPF\textsubscript{6} as a supporting electrolyte at room temperature. A conventional three-electrode cell was used with a gold working electrode (surface area of 0.3 mm\textsuperscript{2}), and a platinum wire was the counter electrode. The gold working electrode was routinely polished with BAS polishing alumina suspension and rinsed with acetone before use. The potentials were measured with respect to the Ag/AgNO\textsubscript{3} (10 mM) reference electrode and were converted to values vs SCE by adding 0.29 V.\textsuperscript{48} All electrochemical measurements were carried out under an atmospheric pressure of nitrogen. X-band EPR spectra were recorded at 5 or 20 K using an X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM). Low temperature was achieved and controlled with an Oxford Instruments ESR900 liquid helium quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. The experimental parameters for EPR spectra were as follows: microwave frequency = 9.646 GHz at 5 K and 9.654 GHz at 20 K, microwave power = 1.0 mW, modulation amplitude = 10 G, gain = 5 × 10\textsuperscript{5}, modulation frequency = 100 kHz, time constant = 81.92 ms, and conversion time = 81.00 ms.

**Kinetic Measurements.** The UV–vis spectral changes were recorded on a Hewlett-Packard 8453 diode array spectrophotometer equipped with Unisoku thermostatted cell holder for low-temperature experiments. Rate constants in the oxidation reaction of ferrocene derivatives by O\textsubscript{2} in the presence of catalytic amount of 1 and excess amount of perchloric acid (HClO\textsubscript{4}) in acetone at 298 K were determined by monitoring the appearance of the absorption band due to the corresponding ferrocenium ions (Fc*: \(\lambda_{\text{max}} = 620\) nm, \(\varepsilon_{\text{max}} = 430\) M\textsuperscript{-1} cm\textsuperscript{-1}; Me\textsubscript{2}Fc*: \(\lambda_{\text{max}} = 650\) nm; \(\varepsilon_{\text{max}} = 360\) M\textsuperscript{-1} cm\textsuperscript{-1}; Fc*\textsuperscript{2+}: \(\lambda_{\text{max}} = 9.646\) GHz at 5 K and 9.654 GHz at 20 K, microwave power = 1.0 mW, modulation amplitude = 10 G, gain = 5 × 10\textsuperscript{5}, modulation frequency = 100 kHz, time constant = 81.92 ms, and conversion time = 81.00 ms.
Spectroscopic Measurements. The amount of H$_2$O$_2$ was determined by titration with iodide ion. The diluted acetone solution of the reduced product of O$_2$ was treated with an excess of NaI. The amount of I$_2$ formed was then quantified using its visible spectrum ($\lambda_{\text{max}} = 361$ nm; $\epsilon = 2.5 \times 10^3$ M$^{-1}$ cm$^{-1}$).

Low-Temperature Experiments Concerning the Generation of [Cu$_2$(XYLO)(OOH)]$^2+$ (4). Under an argon atmosphere within a glovebox, [Cu$_2$(XYLO)(PF$_6$)$_2$] (0.11 mM) was dissolved in 3.0 mL of O$_2$-free acetone. The cuvette was fully sealed with a septum and quickly removed from the glovebox and cooled to ~80 °C in the UV–vis spectrophotometer equipped with a thermostat cell holder. O$_2$ was gently bubbled through the reaction solution, and the formation of the hydroperoxo species was followed by change in the absorbance at 395 nm.

ASSOCIATED CONTENT

Supporting Information
Figures S1–S11 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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The ox values of ferrocene derivatives in acetone are virtually the same as those in MeCN; see: Noviandri, I.; Brown, K. N.; Fleming, D. S.; Gulyas, P. T.; Lay, P. A.; Masters, A. F.; Phillips, L. J. Phys. Chem. B 1999, 103, 6713. Further, we checked to see if the $E^{\text{ox}}$ values of ferrocene derivatives remain the same in the presence of HClO$_4$, and in fact they do (see Figure S7 in SI).

At higher temperature, however, $[\text{Cu}^{\text{II}}(\text{XYLO})(\text{OOH})]^{2+}$ started to decompose.

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42 At higher temperature, however, $[\text{Cu}^{\text{II}}(\text{XYLO})(\text{OOH})]^{2+}$ started to decompose.