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Production of a Putative Iron(V)−Oxocorrole Species by Photo-Disproportionation of a Bis-Corrole−Diiron(IV)−μ-Oxo Dimer: Implication for a Green Oxidation Catalyst

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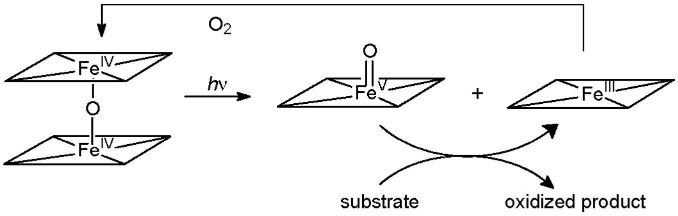
ABSTRACT



Photodisproportionation of a bis-corrole−diiron(IV)−μ-oxo dimer gave a corrole−iron(III) species and a corrole−iron(V)−oxo species that can be detected and studied in real time. Air oxidation of the corrole−iron(III) species regenerated the bis-corrole−diiron(IV)−μ-oxo dimer, allowing the development of a photocatalytic method for organic oxidations using molecular oxygen and visible light.

Catalytic oxidations of organic substrates by macrocycle−iron complexes have been objects of research interest for decades.[1−4] Porphyrin− and corrole−iron complexes are models for heme-containing enzymes and serve as efficient two-electron, oxo-transfer catalysts with peroxy compounds functioning as the terminal or sacrificial oxidants.[1−4] Most commonly, a macrocycle iron(III) species is oxidized to an iron−oxo species with a formal oxidation state on iron of +5, and the intermediate high-valent iron−oxo complex then oxidizes an organic substrate. Catalytic oxidations accomplished with iron in a formal +4 oxidation state, which might disproportionate to give a higher valent iron−oxo species,[5] are possible. In this regard, cofacial bis-porphyrin−diiron(III)−μ-oxo complexes[6,7] have drawn considerable attention because these systems can effect organic oxidations in catalytic cycles using molecular oxygen as a terminal oxidant and photodisproportionation of the μ-oxo dimer to give transient porphyrin−iron(IV)−oxo species.[8−11]

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(1) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411–1456.

(2) *Metalloporphyrins in Catalytic Oxidations*; Sheldon, R. A., Ed.; Marcel Dekker: New York, 1994.

(3) Gross, Z.; Gray, H. B. *Adv. Synth. Catal.* **2004**, *346*, 165–170.

(4) Aviv, I.; Gross, Z. *Chem. Commun.* **2007**, 1987–1999.

(5) Pan, Z. Z.; Newcomb, M. *Inorg. Chem.* **2007**, *46*, 6767–6774.

(6) Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1537–1554.

(7) Rosenthal, J.; Bachman, J.; Dempsey, J. L.; Esswein, A. J.; Gray, T. G.; Hodgkiss, J. M.; Manke, D. R.; Luckett, T. D.; Pistorio, B. J.; Veige, A. S.; Nocera, D. G. *Coord. Chem. Rev.* **2005**, *249*, 1316–1326.

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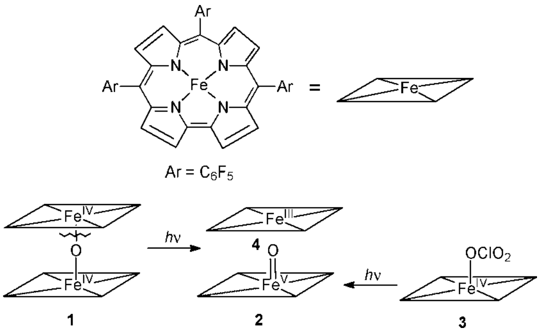
In catalytic porphyrin−iron−oxo chemistry, the transient with iron in the formal +5 oxidation state exists mainly as an iron(IV)−oxo complex with the porphyrin oxidized to a radical cation.[12−15] True metal(V)−oxo complexes, which are generally rare and elusive, are known to be more reactive than the metal(IV)−oxo ligand radical cation valence tautomers. For example, porphyrin−manganese(V)−oxo complexes display higher reactivity than the analogous iron(IV)−oxoporphyrin radical cation,[5,16−18] and a recently reported oxoiron(V) complex supported by a tetraanionic ligand showed unprecedented reactivity.[19] We reported photoinduced ligand cleavage reactions that generated highly reactive corrole− and porphyrin−iron−oxo intermediates that are best described as iron(V)−oxo species.[20−22] In this work, we report a catalytic oxidation system based on a cofacial bis-corrole−iron(IV)−μ-oxo complex, which employs a photodisproportionation reaction that gives an iron(III) and putative iron(V)−oxo species. The highly oxidized iron atoms in this system result in a more powerful oxidant than is formed in the cofacial bis-porphyrin systems.

The target oxidant in this study was the corrole−iron−oxo transient **2**, which was expected to be formed by photodisproportionation, or homolytic cleavage of an iron−oxygen bond,[23] of the bis-corrole−diiron(IV)−μ-oxo dimer **1** (Scheme 1). Irradiation of the corrole−iron(IV) chlorate **3** was found to give a highly reactive oxidant that was tentatively assigned the iron(V)−oxo structure **2** based on its unique UV−vis spectrum and its very high reactivity.[20] As discussed below, the same transient was formed by photolysis of dimer **1**, as determined by its spectral and kinetic behavior. The result supports the original assignment of the structure of the oxidant as an iron(V)−oxo species,[20] but it is the oxidizing properties of the intermediate and not its detailed structure that is most important.

Scheme 1



The bis-corrole−diiron(IV)−μ-oxo complex **1** was reported in 2001 by Simkhovich et al.[24] It was prepared by the reported method from the corresponding corrole by metal insertion to give the corrole−iron(III) dietherate complex initially followed by recrystallization from aerobic solutions of acetonitrile and cycloheptane to give **1**. Complex **1** was characterized by UV−vis, ^{1}H NMR, and ^{19}F NMR spectra that matched those previously reported.[24] The UV−vis spectra of complex **1** and its corrole−iron(III) precursor are shown in Figure 1A.

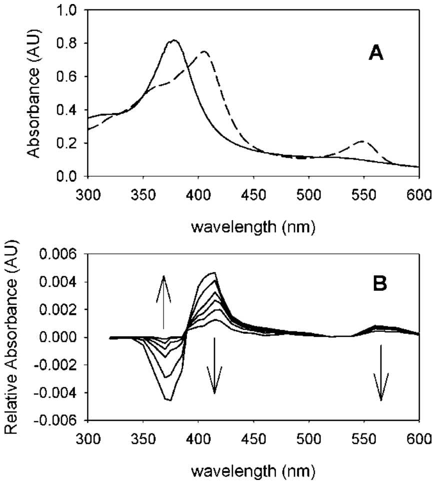


Figure 1. (A) Spectra of dimer **1** (solid line) and its iron(III) precursor (dashed line). (B) Difference spectra at 1, 2, 3, 4, 5, and 10 ms of the reaction after the laser pulse; difference spectrum = spectrum (t = 0) − spectrum (t = time).

When complex **1** was dissolved in acetonitrile solution and irradiated with 355 nm laser light, a short-lived transient **2** was formed. Figure 1B shows a time-resolved UV−vis spectrum of transient **2** acquired at ambient temperature over 10 ms following 355 nm laser irradiation of **1**. In a time-resolved difference spectrum, the only observable species are those that increase or decrease in concentration on the

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(8) Peterson, M. W.; Rivers, D. S.; Richman, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 2907–2915.

(9) Wasser, I. M.; Fry, H. C.; Hoertz, P. G.; Meyer, G. J.; Karlin, K. D. *Inorg. Chem.* **2004**, *43*, 8272–8281.

(10) Pistorio, B. J.; Chang, C. J.; Nocera, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 7884–7885.

(11) Rosenthal, J.; Luckett, T. D.; Hodgkiss, J. M.; Nocera, D. G. *J. Am. Chem. Soc.* **2006**, *128*, 6546–6547.

(12) Weiss, R.; Bulach, V.; Gold, A.; Terner, J.; Trautwein, A. X. *J. Biol. Inorg. Chem.* **2001**, *6*, 831–845.

(13) Ogliaro, F.; de Visser, S. P.; Groves, J. T.; Shaik, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2874–2878.

(14) Dey, A.; Ghosh, A. *J. Am. Chem. Soc.* **2002**, *124*, 3206–3207.

(15) Wasbotten, I.; Ghosh, A. *Inorg. Chem.* **2006**, *45*, 4910–4913.

(16) Groves, J. T.; Lee, J. B.; Marla, S. S. *J. Am. Chem. Soc.* **1997**, *119*, 6269–6273.

(17) Zhang, R.; Newcomb, M. *J. Am. Chem. Soc.* **2003**, *125*, 12418–12419.

(18) Zhang, R.; Horner, J. H.; Newcomb, M. *J. Am. Chem. Soc.* **2005**, *127*, 6573–6582.

(19) de Oliveira, F. T.; Chanda, A.; Banerjee, D.; Shan, X. P.; Mondal, S.; Que, L.; Bominaar, E. L.; Munck, E.; Collins, T. J. *Science* **2007**, *315*, 835–838.

(20) Harischandra, D. N.; Zhang, R.; Newcomb, M. *J. Am. Chem. Soc.* **2005**, *127*, 13776–13777.

(21) Pan, Z.; Zhang, R.; Fung, L. W. M.; Newcomb, M. *Inorg. Chem.* **2007**, *46*, 1517–1519.

(22) Pan, Z.; Wang, Q.; Sheng, X.; Horner, J. H.; Newcomb, M. *J. Am. Chem. Soc.* **2009**, *131*, 2621–2628.

(23) Suslick, K. S.; Watson, R. A. *New J. Chem.* **1992**, *16*, 633–642.

(24) Simkhovich, L.; Mahammed, A.; Goldberg, I.; Gross, Z. *Chem.—Eur. J.* **2001**, *7*, 1041–1055.

time-scale of the measurements, 10 ms in this case. Positive peaks are from species decaying with time, and negative peaks are from species forming with time. Thus, Figure 1B shows that species **2** with a Soret band at $\lambda_{max} \approx 415$ nm decays in about 10 ms to give a product with a Soret band at $\lambda_{max} \approx 370$ nm. This time-resolved spectrum for **2** and the rate of decay are essentially indistinguishable from those for the putative iron(V)−oxocorrole species formed by photolysis of chlorate complex **3**.[20] The photolysis of **1** had a quantum yield of 4×10^{-4} (see the Supporting Information for details), which is similar to that reported for the photolysis of a bis-porphyrin−diiron(III)−μ-oxo complex.[8]

Kinetic studies were accomplished by generating transient **2** in the presence of organic substrates at high concentrations and measuring the rates of reactions under pseudo-first-order conditions. The pseudo-first-order rate constants obtained are listed in Table S1 in the Supporting Information. The kinetics are described by eq 1, where k_{obs} is the observed pseudo-first-order rate constant, k_0 is the background rate constant for decay in the absence of substrate, k_{ox} is the second-order rate constant, and [substrate] is the concentration of substrate. As shown in Figure 2, plots of k_{obs} versus the concentrations of substrate were linear. Values for the second-order rate constants solved according to eq 1 are collected in Table 1. The rate constants for decay in acetonitrile and for reactions with cis-cyclooctene and ethylbenzene were the same when **2** was produced from both precursors, confirming that the same oxidizing species was produced from both routes.

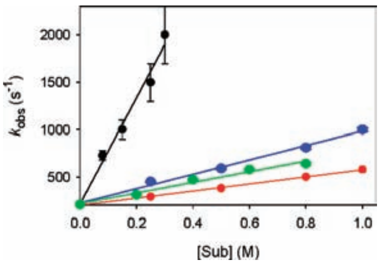


Figure 2. Observed rate constants for reactions of **2** with *cis*-cyclooctene (black), cumene (blue), ethylbenzene (green), and toluene (red).

Table 1. Second-Order Rate Constants for Reactions of **2**[a]

source	substrate	k_{ox} (M^{-1} s^{-1})
1	none	208 s^{-1}[b]
	cis-cyclooctene	$(5.4 \pm 0.3) \times 10^3$
	dihydroanthracene	$(4.9 \pm 0.2) \times 10^3$
	cumene	$(7.7 \pm 0.5) \times 10^2$
	ethylbenzene	$(5.8 \pm 0.4) \times 10^2$
	toluene	$(4.0 \pm 0.1) \times 10^2$
3[c]	none	200 s^{-1}[b]
	cyclohexene	$(7.4 \pm 0.3) \times 10^3$
	cis-cyclooctene	$(5.9 \pm 0.2) \times 10^3$
	ethylbenzene	$(5.7 \pm 0.3) \times 10^2$
	ethylbenzene-d_{10}	$(1.6 \pm 0.2) \times 10^2$

[a] Reactions at 22 °C in acetonitrile. [b] Pseudo-first-order decay rate constant in the absence of substrate. [c] Preliminary results from **3** were reported in ref 20.

$$k_{obs} = k_0 + k_{ox}[\text{substrate}] \tag{1}$$

Comparison of the kinetics of reactions of the corrole−iron−oxo species **2** to those of various porphyrin−metal−oxo complexes (Table 2) suggests that it is a true iron(V)−oxo species.[14] Corrole and corrolazine[25] macrocycles are trianionic, whereas porphyrins are dianionic, and iron(V)−oxocorrole complexes will be less unstable than iron(V)−oxoporphyrin complexes but still high in reactivity.[15] The 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin−manganese(V)−oxo complex[17,18] and putative 5,10,15,20-tetraphenylporphyrin−iron(V)−oxo complex[22] are 2 orders of magnitude more reactive in ethylbenzene oxidations than **2**, but complex **2** is 100 times more reactive than an iron(IV)−oxoporphyrin radical cation.[26] Importantly, transient **2** is much more reactive than the corresponding porphyrin−iron(IV)−oxo species.[5] The high potential energy of complex **2** is indicated by the small kinetic isotope effect for oxidation of ethylbenzene and ethylbenzene-d_{10} ($k_H/k_D = 3.6$), which is consistent with a highly exothermic reaction, and by the small slope in the correlation of the logarithms of the rate constants for oxidations of a series of arene C−H bonds with the bond dissociation energies (Figure 3), which is similar to that found

Table 2. Rate Constants for Reactions with Ethylbenzene[a]

oxidant[b]	k_{ox} (M^{-1} s^{-1})	ref
(TPFPP)Mn^{V}O(X)	1.3×10^5	18
(TPP)Fe^{V}O(ClO$_4$)	8×10^4	22
2	600	this work
(TPFPP)$^{\bullet +}$Fe^{IV}O(ClO$_4$)	6	26
(TPFPP)Fe^{IV}O	<0.01[c]	5

[a] Second-order rate constants at ambient temperature. [b] TPFPP = 5,10,15,20-tetrakis-(perfluorophenyl)porphyrin; TPP = 5,10,15,20-tetraphenylporphyrin. [c] Too slow to measure.

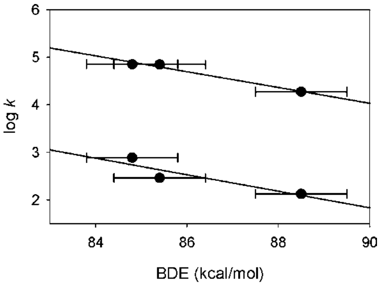
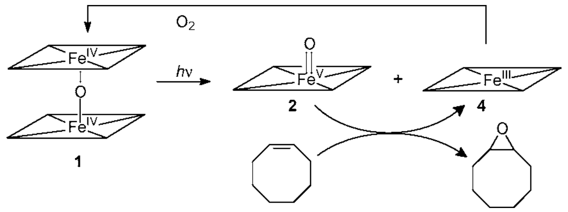


Figure 3. Correlations of logarithms of statistically corrected rate constants for oxidations of cumene, ethylbenzene, and toluene with C−H bond dissociation energies (BDE) of the substrates. The lower set of data is for corrole−iron−oxo complex **2**, and the upper set is for the putative tetramesitylporphyrin−iron(V)−oxo complex (ref 22).

for oxidations by a putative porphyrin−iron(V)−oxo complex.[22]

The elements of a highly reactive, yet economical and green, catalytic oxidation system exist in the reactions discussed above. A proposed catalytic mechanism is shown in Scheme 2. Photodisproportionation of complex **1** gives one molecule of a corrole−iron(III) species **4** in addition to the highly reactive iron−oxo transient **2**. Oxidation of an organic substrate by **2** gives a second molecule of **4**. Autoxidation of the corrole−iron(III) complex **4** then returns the bis-corrole−diiron(IV)−μ-oxo complex **1** (Scheme 2).

Scheme 2



The potential for a catalytic system was evaluated in the aerobic oxidation of *cis*-cyclooctene (Scheme 2). The reaction system consisted of 1 μmol of **1** in 5 mL of acetonitrile containing 5 mmol of cyclooctene. Dry air was bubbled through the solution as it was irradiated with 400−500 nm light. After 48 h of photolysis, *cis*-cyclooctene oxide was obtained as the only identifiable oxidation product (>95% by GC) with ca. 200 turnovers of catalyst. The catalyst was unchanged as evaluated by UV−vis spectroscopy. Control experiments demonstrated that no epoxide was formed in the absence of either the catalyst or light. The results cannot be ascribed to the chemistry of singlet oxygen, which is characterized by efficient “ene” reactions of alkenes.[27] Further investigations of substrate scope, optimization of reaction conditions, and mechanisms of the oxidation reaction are currently underway.

In summary, photocleavage of a bis-corrole−iron(IV)−μ-oxo dimer proceeds by homolysis of an Fe−O bond to give an iron−oxo transient that is spectroscopically and kinetically indistinguishable from the species formed by photolysis of the corresponding corrole−iron(IV) chlorate complex. This transient is most likely a corrole−iron(V)−oxo species as judged by its high reactivity in comparison to porphyrin−iron−oxo complexes. The autoxidation of corrole−iron(III) species in aerobic solutions to give the bis-corrole−iron(IV)−μ-oxo dimer combined with the photochemical homolytic cleavage of the dimer represents an attractive green catalytic cycle.

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Supporting Information Available: Detailed kinetic results and experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Goldberg, D. P. *Acc. Chem. Res.* **2007**, *40*, 626–634.
(26) Pan, Z.; Zhang, R.; Newcomb, M. *J. Inorg. Biochem.* **2006**, *100*, 524–532.
(27) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395–427.