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Photocatalytic Oxidation of Hydrocarbons by a Bis-iron(III)-μ-oxo Pacman Porphyrin Using O_2 and Visible Light

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Iron(III) porphyrin complexes can promote substrate oxidation by using molecular oxygen as the oxygen atom source.[1−3] Such systems become catalytic in the presence of an external co-reductant[4] such as borohydrides,[5] ascorbate,[6] or Zn metal.[7] We have recently shown that diiron bisporphyrin architectures can support similar catalysis without the need for the stoichiometric reductant.[8−10] The overall cycle for these systems relies on a photon to cleave the thermally inert Fe−O bonds of a diiron(III)-μ-oxo bisporphyrin to generate a geminal $PFe^{II}/PFe^{IV}{=}O$ pair (P = porphyrin).[11−13] The active catalyst, which is the ferryl ($PFe^{IV}{=}O$) complement of the pair, is capable of oxygenating substrates with the concomitant formation of two equivalents of reduced iron(II) porphyrin.[14] Reaction of the two separate ferrous porphyrin subunits with O_2 re-forms the diiron(III)-μ-oxo bisporphyrin complex for re-entry into a photocatalytic cycle.[15−17] We have extensively investigated various architectural designs of the bisporphyrin cofacial cleft[8−10] and found that diiron(III)-μ-oxo bisporphyrins juxtaposed by a single rigid pillar sterically direct substrate to the electronically preferred side-on approach to the metal−oxo bond.[18] Pacman architectures bearing a dibenzofuran (DPD) spacer, with its significant vertical flexibility, are especially effective at enhancing oxidation owing to greater substrate access to the photogenerated terminal $PFe^{IV}{=}O$.[19]

Photocatalytic oxidation cycles using Pacman systems have been turned over with easily oxidized organic substrates (i.e., phosphines and sulfides)[8,9] and, more recently, with olefins by using electron-deficient diiron(III)-μ-oxo bisporphyrins.[10] We sought to expand the scope of substrate oxidation and turned our attention to exploring the viability of photocatalytically oxidizing aliphatic C−H bonds. We now report that fluorinated Pacman bisporphyrins appended to the DPD scaffold promote the photocatalytic oxidation of hydrocarbons using visible light and O_2 as the terminal oxidant and oxygen atom source.

Fluorinated Pacman, $(DPDF)Fe_2O$ (Figure 1), is prepared by reaction of the corresponding free-base Pacman porphyrin with $FeBr_2$ and 2,6-lutidine followed by exposure to air and treatment with basic alumina.[10] $(DPDF)Fe_2O$ is thermally inert to typical hydrocarbons; however, irradiation ($\lambda_{exc} = 425$ nm) of anaerobic pyridine solutions of the complex in the presence of excess toluene (1.0 M) prompts the changes in the absorption spectrum shown in Figure 1. Similar spectral changes are observed for the photolysis of $(DPDF)Fe_2O$ in the presence of the other hydrocarbons listed in Tables 1 and 2. The organic oxidation products of Table 2 were characterized and quantified by GC/MS anayslsis (see Supporting Information). For all photoreactions, well-anchored isosbestic points are maintained throughout photolysis, attesting to a clean and quantitative process. With the appearance of the final absorption spectrum, no further spectral changes are observed upon continued irradiation. Furthermore, no photochemistry is observed upon irradiation of solutions containing only hydrocarbon or porphyrin. For each photolysis reaction, a single porphyrin product is isolated with an electronic absorption spectrum identical to that of the independently prepared iron(II) porphyrin complex, $(DPDF)Fe_2$, in pyridine. We suspect that the $(DPDF)Fe_2$ photoproduct is axially ligated by pyridine, though crystals of this complex have not been isolated.

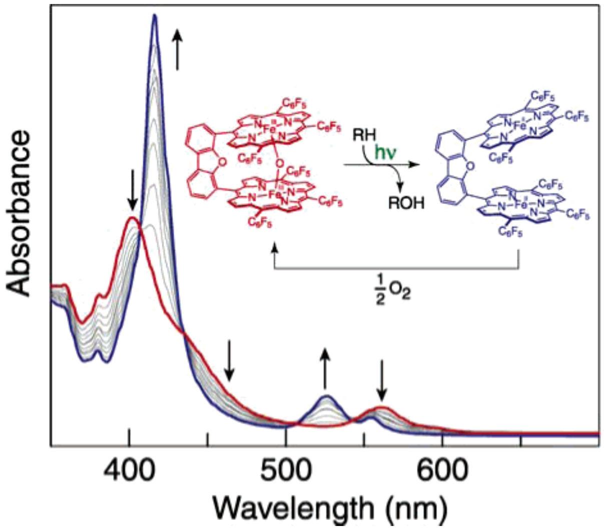

Figure 1. Time course of the changes in the absorption profile accompanying the photoconversion ($\lambda_{exc} = 425$ nm) of anaerobic pyridine solutions of $(DPDF)Fe_2O$ (7×10^{-6} M) in the presence of toluene (1.0 M) at 298 K. The reactants and products of the overall photoreaction (depicted in the inset) are matched by color to their respective absorption profiles. Spectra were recorded over the span of 4 h at 20 min intervals. As emphasized in the inset, this photoreaction becomes catalytic in the presence of O_2.

Table 1. Summary of Kinetic Data for Reaction of Various Hydrocarbons with $(DPDF)Fe_2O$ ($\lambda_{exc} = 425$ nm)[a]

substrate	BDE_{C-H} (kcal/mol)	IE (eV)	Φ_p	k_{ox} ($M^{-1}\ s^{-1}$)
fluorene	80	7.91	1.52×10^{-2}	1.36×10^{7}
diphenylmethane	84.5	8.73	2.76×10^{-3}	2.41×10^{6}
cumene	84.8	8.8	1.99×10^{-3}	1.74×10^{6}
toluene	90	8.83	1.51×10^{-3}	1.32×10^{6}
toluene-d_8	90	8.83	9.79×10^{-4}	8.53×10^{5}

[a] All IE values obtained from NIST (http://webbook.nist.gov/chemistry/); BDEs were taken from ref 20.

Table 1 lists the product appearance quantum yields (Φ_p) for the photoreactions of $(DPDF)Fe_2O$ with hydrocarbon substrates. The photoefficiencies for the stoichiometric oxidation span roughly 1 order of magnitude. As we have shown previously[19] and describe in the Supporting Information, the magnitude of Φ_p is related directly to the competition between the rate of substrate oxidation (k_{ox}) vs Pacman reclamping ($k_{reclamp}$). By using time-resolved transient spectroscopy to measure $k_{reclamp}$, together with Φ_p, the k_{ox} values listed in Table 1 can be calculated. There is a linear correlation between $\log(k_{ox})$ and the C−H bond dissociation energy

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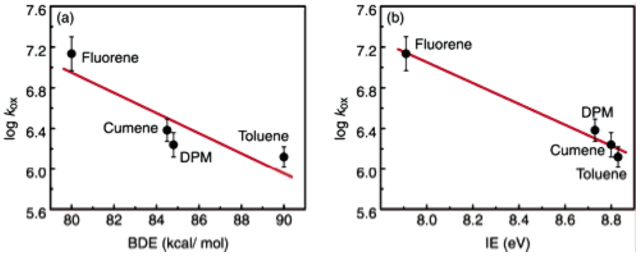

Figure 2. Correlation between the rate constant for the photooxidation of the hydrocarbons (1.0 M in pyridine) listed in Table 2 by (DPDF)Fe_2O (7×10^{-6} M) and (a) the C−H bond dissociation energy and (b) ionization energy of the substrate. The C−H bonds of hydrocarbons are oxidized catalytically by the electron-deficient Pacman porphyrin, (DPDF)Fe_2O, using visible light and molecular oxygen as the terminal oxidant and oxygen atom source. The photocatalytic reactions proceed under mild conditions (ambient temperature and pressure) without the need for an external co-reductant.

(BDE_{C-H}). Such correlations have been taken as evidence of concerted hydrogen atom transfer (HAT) reactions.[21] However, we note that an even stronger correlation exists between log(k_{ox}) and substrate ionization energy (IE). This result points to a mechanism where $H^{\bullet}$ abstraction occurs via an asynchronous proton-coupled electron transfer (PCET) to the ferryl. Indeed, oxidations ascribed to HAT, based on a correlation between log k and BDE, are generally fit equally well to a correlation of log k with IE, and in some cases, outliers of the BDE treatment are better fit to those that relate IE.[22]

Comparison of the kinetics for hydrogen atom abstraction from toluene-d_8 with the protio substrate reveals a kinetic isotope effect (k_H/k_D) of 1.55 at 298 K. The existence of even a small isotope effect at room temperature for hydrogen atom abstraction by the photogenerated $PFe^{IV}{=}O$ species speaks to coupling between the proton and electron coordinates[23] during hydrocarbon oxidation. The isotope effect observed for the Pacman $PFe^{IV}{=}O$ oxidant is significantly smaller than those observed for the oxidation of ethylbenzene by a series of non-heme $Fe^{IV}{=}O$ species, in which hydrogen tunneling mechanisms have been suggested to be involved in the C−H bond activation process.[24] The small kinetic isotope effect for the Pacman system suggests that substrate oxidation proceeds by an asynchronous PCET mechanism.[23] The correlation between log(k_{ox}) vs IE shown in Figure 2 is consistent with this contention.

Hydrocarbon photo-oxidation becomes catalytic when (DPDF)Fe_2O and substrate are irradiated in the presence of 1 atm of O_2 under conditions similar to those employed for the stoichiometric photoreaction. No photo-oxidation occurs upon irradiation under O_2 in the absence (DPDF)Fe_2O, and thermal reactions are negligible under these conditions. Table 2 lists the substrate turnover numbers (TONs) and selectivities for the substrate oxidation products. The trend in the TONs roughly parallels the substrate reactivity (lower IE correlates with higher TON). Competitive catalytic oxidation of toluene and toluene-d_8 (1.0 M) results in a benzaldehyde product that shows no isotopic scrambling. This result suggests that autoxidation processes do not contribute to the observed catalytic photo-oxidation chemistry. The product distributions we obtain are nearly identical to those observed for the stoichiometric oxidation of hydrocarbon substrates by non-heme $Fe^{IV}{=}O$ systems, which are generated thermally by Fe^{II} reactants that consume PhIO as the terminal oxidant.[24] The Pacman photocatalyst described here is distinguished from other C−H oxidants because it (1) catalytically oxidizes C−H bonds (2) with oxygen as the terminal oxidant and oxygen atom source and (3) without the need for a co-reductant. Hence, a catalytic cycle for C−H oxidation may be constructed with oxygen as the only reactant.

Table 2. Turnover Numbers and Conversion Yields for Hydrocarbon Oxidation by (DPDF)Fe_2O^a

substrate	product	TON^b
fluorene	fluorenone	287 ± 34 (100%)
dihydroanthracene	anthracene	235 ± 37 (100%)
diphenylmethane	benzophenone	160 ± 25 (100%)
cumene	acetophenone	143 ± 10 (55%)
	cumyl alcohol	116 ± 14 (45%)
toluene	benzaldehyde	76 ± 11 (100%)

[a] Determined for an 18 h photolysis ($\lambda_{exc} > 425$ nm) of solutions under 1 atm of O_2 (298 K) but otherwise of the same composition as those used in stoichiometric photolysis experiments. [b] TON represents the total number of moles of product produced per mole of catalyst. Value in parentheses represents the product distribution for the catalytic oxidation reactions.

In summary, Pacman platforms allow for the generation of a highly oxidizing ferryl intermediate using light in the visible region to drive the oxidative catalysis of a broad range of organic substrates, including phosphines, sulfides, olefins, and now hydrocarbons. Current studies are aimed at driving the quantum yields for substrate photo-oxidation to unity by hindering the reclamping of the photogenerated $PFe^{II}/PFe^{IV}{=}O$ pair. Pacman architectural design will prove to be crucial in this regard.

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

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