Applied Catalysis A: General 464–465 (2013) 95–100

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Visible light-driven aerobic oxidation catalyzed by a diiron(IV) μ-oxo biscorrole complex

Rui Zhang*, Eric Vanover, Tse-Hong Chen, Helen Thompson

Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101-1079, USA

ARTICLE INFO

Article history:
Received 1 March 2013
Received in revised form 10 May 2013
Accepted 19 May 2013
Available online 29 May 2013

Keywords:
Iron corrole
Aerobic oxidation
Visible light
Photo-disproportionation

ABSTRACT

Under visible light irradiation, the diiron(IV) μ-oxo-bis(5,10,15-tripentafluorophenylcorrole) complex catalyzes the aerobic oxidations of hydrocarbons in sequences employing photo-disproportionation reactions. The active oxidant, highly reactive corrole-iron(V)-oxo species, can be detected in real time via laser flash photolysis methods.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Selective oxidation of organic compounds represents a leading technology for commodity chemical production [1]. Oxidation catalysis also plays an essential role in both energy production and energy conservation, as over 90% of all chemical processes are catalytic. However, oxidation is among the most problematic processes. Many stoichiometric oxidants with heavy metals are expensive and toxic, thus, economically and environmentally inviable. As the demand for "greener" processing increases, the ideal system for catalytic oxidation is the use of molecular oxygen or hydrogen peroxide as the primary oxygen source together with recyclable catalysts in nontoxic solvents [2,3]. In this context, many transition metal catalysts have been synthesized to mimic the predominant oxidation catalysts in Nature, namely the cytochrome P450 enzymes [4]. Most biological oxidations mediated by P450 enzymes are highly, often completely, stereoselective and ecologically sustainable. However, biological oxidations involve sophisticated electron and proton transfer steps to activate molecular oxygen and are currently difficult to implement with a synthetic catalyst [5]. In biomimetic catalytic oxidations, a transition metal catalyst is oxidized to a high-valent metal-oxo species [6] by a sacrificial oxidant, and then the activated transition metal-oxo intermediate oxidizes the substrate [7].

Photochemical reactions are intrinsically advantageous because activation is obtained by the absorption of a photon, which leaves no residue; whereas most chemical methods involve the use of toxic/polluting reagents [8]. To this end, we aim to use visible light (sunlight) to induce reversible redox processes of the metal center, avoiding all the disadvantages deriving from the use of chemical reagents. Notably, *trans*-dioxoruthenium(VI) porphyrins have been shown to catalyze the clean aerobic epoxidation of olefins in the absence of a reducing agent [9,10]. However, due to product inhibition, these reactions afforded only up to 50 turnovers and proceeded at relatively slow rates. The chemistry of cofacial bisporphyrins has also drawn increased attention owing to the ability of these systems to utilize molecular oxygen and visible light for organic oxidations [11,12]. One example is the catalytic aerobic oxidation by high-valent iron(IV)-oxo species in a process that involves photo-disproportionation of a diiron(III)-μ-oxo bisporphyrin complex [13,14]. The low reactivity of the formed iron(IV)-oxo oxidant and the poor quantum efficiency are serious obstacles that prohibit the use of iron porphyrins as practical photocatalysts. Recently, Nocera and co-workers have achieved a remarkable improvement of the catalytic efficiency of diiron(III)-μ-oxo bisporphyrin systems by employing "Pacman" ligand designs with organic spacer-hinges to preorganize two iron centers in a cofacial arrangement [15–18].

In catalytic macrocycle-iron-oxo chemistry, the transient with iron in the formal +5 oxidation state exists mainly as an iron(IV)-oxo complex with the ligand oxidized to a radical cation [19]. The well known porphyrin-manganese(V)-oxo complexes showed higher

---

Abbreviations: TPFC, 5,10,15-tripentafluorophenylcorrole trianion; TPC, 5,10,15-triphenylcorrole trianion; TMP, 5,10,15,20-tetramesitylporphyrin dianion; TPP, 5,10,15,20-tetraphenylporphyrin dianion; LFP, laser flash photolysis; n.d., not detected.

* Corresponding author at: Department of Chemistry, Western Kentucky University, 1906 College Heights Blvd. #11079, Bowling Green, KY 42101-1079, USA. Tel.: +1 270 745 3803; fax: +1 270 745 5361.
E-mail address: rui.zhang@wku.edu (R. Zhang).

0926-860X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.05.025

reactivity than the well known iron(IV)-oxo radical cation in the same ligand system [20–22]. A reported oxoiron(V)-oxo complex supported by a tetraanionic ligand showed truly unprecedented reactivity [23]. The porphyrin/corrole-iron(V)-oxo transients produced by laser flash photolysis (LFP) methods also displayed the appropriate high level of reactivity [24,25]. Due to recent progress in the methods for triarylcorrole synthesis [26,27], metallocorrole complexes have attracted considerable interest in view of their similarities to metalloporphyrins [28,29]. Corrole-metal-oxo complexes along with *meso-N*-substituted analogs, namely corrolazines, are inherently more stable than the corresponding porphyrin congeners [30]. The relatively stable manganese(V)-oxo corrole/corrolazine complexes were readily isolated and characterized by oxidation of the manganese(III) salt with chemical oxidants [31–33]. In a recent report, Goldberg and co-workers described the generation of new manganese(V)-oxo π-cation radical corrolazine that is more reactive oxidant than its one-electron-reduced analog [34].

Recently, we have reported that ruthenium(IV) μ-oxo bisporphyrins catalyze the aerobic oxidation of hydrocarbons through a ruthenium(V)-oxo species in a photo-disproportionation mechanism [35]. Another way to investigate the scope of the photo-disproportionation reactions could be the utilization of corrole complexes with iron metal. Our preliminary results have shown that the photochemistry of a fluorinated iron(IV) μ-oxo biscorrole appears to present a photo-disproportionation manifold similar to that of the iron porphyrin systems [36]. In this work, we report a visible-light driven aerobic oxidation of hydrocarbons catalyzed by a bis-corrole-iron(IV) μ-oxo complex using only molecular oxygen without the need for an external reducing reagent. The proposed catalytic sequence involves the following: (1) photo-disproportionation of the μ-oxo iron(IV) biscorrole to form iron(III) and iron(V)-oxo oxidizing species; (2) substrate oxidation by resulting reactive iron(V)-oxo species to give oxidized products and a second iron(III) species; (3) aerobic oxidation of iron(III) complex to regenerate the μ-oxo iron(IV) dimer. The suggested transient iron(V)-oxo species that are highly reactive oxidants for a wide range of oxidations can be detected and studied in real time via laser flash photolysis methods.

2. Experimental

2.1. Materials and instruments

Acetonitrile was obtained from Fisher Scientific and distilled over P_2O_5 prior to use. All reactive substrates for photocatalytic studies were the best available purity from Sigma–Aldrich Chemical Company and were purified by passing through a dry column of active alumina (Grade I) before use. Pyrrole (98%) and benzaldehyde from Sigma–Aldrich were distilled prior to use. Pentafluorobenzaldehyde, trifluoroacetic acid (TFA) (99%) and *N*,*N*-dimethylformamide (DMF) were purchased from Sigma–Aldrich and used as received. $[Fe^{III}(TPP)]_2O$ (TPP = *meso*-tetrakisphenylporphyrinato dianion) was obtained from Strem Chemical Company and used as received. $Ru^{VI}(TMP)O_2$ (TMP = *meso*-tetrakismesityl-porphyrinato dianion) was prepared according to the known procedure [37].

Corrole free ligands (**1**) employed in this study, 5,10,15-tripentafluorphenylcorrole (H_3TPFC) [27] and 5,10,15-triphenylcorrole (H_3TPC) [38], were prepared according to the literature procedures, and their characterization data (^1H NMR and UV/vis) were consistent with reported values. The corrole-iron(III) dietherate complexes (**2**) were prepared as previously described [39]. In a typical procedure, a solution of **1** (50 mg, 68 mmol) and a large excess of iron(II) chloride (127 mg, 680 mmol) in DMF was heated at reflux for 60 min. Evaporation of solvent followed by column chromatography on silica gel (diethyl ether), resulted in isolation of the desired $Fe^{III}(TPFC)(OEt)_2$ in >90% yield. Following the known procedure [39], the fluorinated diiron(IV) μ-oxo biscorrole (**3**), formulated as $[Fe^{IV}(TPFC)]_2O$, was prepared by aerobic oxidation of $Fe^{III}(TPFC)(OEt)_2$ in a solution of acetonitrile and cycloheptane. Complex **3** was characterized by UV–visible, IR and ^1H NMR spectra that matched those previously reported [39]. The UV–visible spectra of complex **3** and its corrole-iron(III) precursor **2** are shown in Fig. 1.

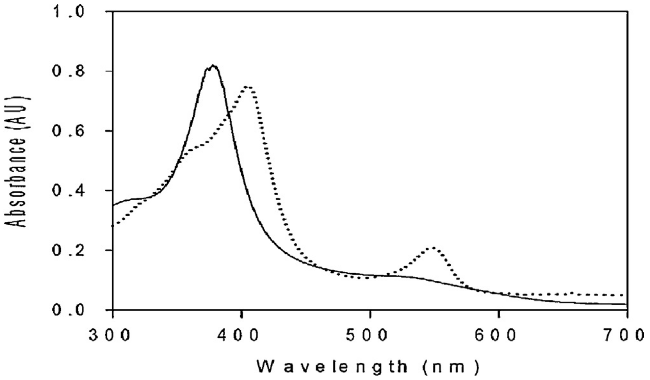


Fig. 1. UV–visible spectra of $[Fe^{IV}(TPFC)]_2O$ (solid lines) and $Fe^{III}(TPFC)(OEt)_2$ (dotted lines) in CH_3CN.

UV–vis spectra measurements were performed on an Agilent 8453 diode array spectrophotometer at room temperature. IR spectra were obtained on a Bio-Rad FT-IR spectrometer. ^1H NMR spectra were recorded on a JEOL ECA-500 MHz spectrometer at 298 K with tetramethylsilane (TMS) as internal standard. Chemical shifts (ppm) are reported relative to TMS.

2.2. General procedure for photocatalytic aerobic oxidations

A Rayonet photoreactor (RPR-100) with a wavelength range of 400–500 nm ($\lambda_{max} = 420$ nm) from 300 W mercury lamps (RPR-4190×12) was used for the photocatalytic reactions. The photochemical reactions typically consisted of 1.0–1.5 mg of $[Fe(TPFC)]_2O$ (approximate 0.5–1 μmol) in 5 mL of acetonitrile containing over 4 mmol of organic substrates. Dry oxygen gas was bubbled through the solution as it was irradiated. Aliquots of the reaction solution at constant time interval were analyzed by GC/MS spectrometer (Agilent GC6890/MS5973) to determine the formed products and yields with an internal standard (1,2,4-trichlorobenzene). The trend in the product yields roughly parallels irradiation time. Monitoring reaction by UV–vis spectroscopy indicated that no significant degradation of catalyst **3** was found after 24 h photolysis

2.3. Lash flash photolysis studies

Laser flash photolysis (LFP) experiments were conducted at ambient temperature (22 ± 1 °C) on an Applied Photophysics LKS-60 kinetic spectrometer equipped with an SX-18MV stopped-flow mixing unit. Oversampling (64:1) was employed in all cases to improve the signal-to-noise. In experiments with the diiron(IV) μ-oxo biscorrole **3**, 100 μL of a CH_3CN solution of freshly prepared dimer **3** (ca. 2.0×10^{-5} M) was mixed in a 2 mm × 10 mm optical cell with an equal volume of acetonitrile (for self decay studies) or acetonitrile containing a reactive substrate, and the solution was irradiated with a ca. 5 mJ of 355 nm light from a Nd-YAG laser (ca. 7 ns pulse). The signal was monitored at fixed wavelengths with 3–20 nm steps to produce a time resolved spectrum.

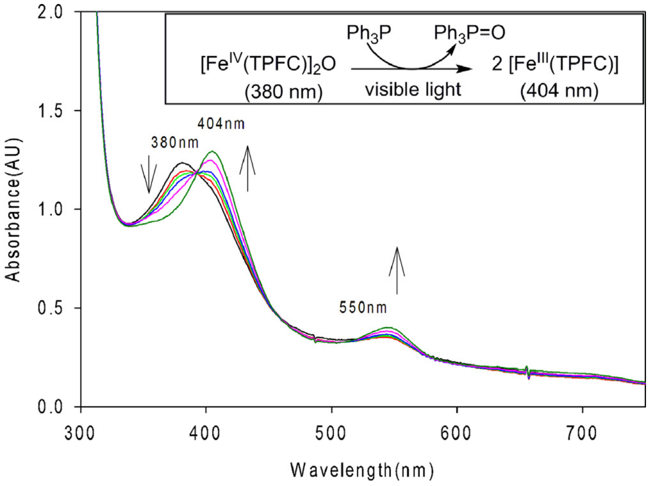


Fig. 2. UV–visible spectral change of $[Fe^{IV}(TPFC)]_2O$ (**3**) in the presence of Ph_3P (4 mM) upon irradiation with a visible lamp (λ_{max} = 420 nm) in anaerobic CH_3CN solution over a span of 15 min at 2 min intervals.

3. Results and discussions

3.1. *Synthesis and photochemical behavior of the diiron(IV) μ-oxo biscorrole*

Our study started with the preparation of corrole-iron(III) complexes which were obtained by metalation of free corrole ligand (H_3TPFC or H_3TPC) in hot DMF with $FeCl_2$ as the metal source (Scheme 1). According to the procedure described by Gross et al. [39] diiron(IV)-μ-oxo-bis(5,10,15-tripentafluorocorrole) catalyst (**3**) was readily prepared by aerobic oxidation of the monomeric precursor Fe^{III}(TPFC) (**2**) in oxygen-saturated acetonitrile and heptanes solution. The diiron(IV) μ-oxo-bis(5,10,15-tripentafluorocorrole) precursor (**3**) with λ_{max} at 380 nm was characterized by UV–vis, ^1H NMR and IR spectra, matching those reported [39]. It is worth mentioning, that electron-withdrawing substituents such as F on corrole ligand are necessary for μ-oxo dimer formation and using the same procedure by reacting the iron(III) complex with a non-halogenated 5,10,15-triphenylcorrole; i.e. Fe^{III}(TPC) in air did not give the corresponding μ-oxo products. Presumably, the electron-withdrawing subsitutents would stabilize the iron(IV) complex in a dimeric form by reducing the electron density of metal atoms. In our recent study, we also found the marked dependence of formation of ruthenium(IV) μ-oxo bisporphyrins on the electron-withdrawing substituents on phenyl ring [40].

Similar to the well established photo-disproportionation of diiron(III)-μ-oxo bisporphyrin complexes [13], irradiation of the thermally stable complex **3** with visible light in the presence of excess triphenylphosphine (4 mM) converted to iron(III) corrole monomer **2** with well-anchored isosbestic points (Fig. 2). The reactants and products of the overall photoreaction (depicted in the inset) are matched to their respective absorption profiles [41]. This photochemical observation of a clean reduction of $[Fe^{IV}(TPFC)]_2O$ to Fe^{III}(TPFC) supports a photo-disproportionation pathway that allows for the generation of the iron(V)-oxo oxidant. Similar spectral changes were also observed upon the photolyses of diruthenium(IV)-μ-oxo bisporphyrin complexes in the presence of excess Ph_3P [35].

Table 1
Photocatalytic aerobic oxidation of *cis*-cyclooctene by a diiron(IV) μ-oxo biscorrole.[a]

Entry	Catalyst	Solvent	T (day)	TON[b,c]
1	$[Fe^{IV}(TPFC)]_2O$	CH_3CN	1	90 ± 10
			2	200 ± 12
			3	320 ± 30
			4	540 ± 40
2		$CHCl_3$	1	34 ± 5
3		C_6H_6	1	60 ± 10
4		THF	1	70 ± 9
5[d]		CH_3CN	1	<10
6[e]		CH_3CN	1	140 ± 16
7[f]		CH_3CN	1	81 ± 10
8	$[Fe^{III}(TPFC)]\cdot Et_2O$	CH_3CN	1	85 ± 5
9[e]		CH_3CN	1	154 ± 26
10	$[Fe^{III}(TPC)]\cdot Et_2O$	CH_3CN	1	n.d.
11[g]	$[Fe^{III}(TPP)]_2O$	CH_3CN	1	40 ± 5
12	$Ru(TMP)O_2$	CH_3CN	1	18 ± 2

[a] The reaction was carried out in a Rayonet reactor, with ca. 0.5 μmol of catalyst in 5 mL of solvent containing 4 mmol of *cis*-cyclooctene. Oxygen-saturated solutions were irradiated with visible light (λ_{max} = 420 nm) or otherwise noted. Products were analyzed on an HP 6890 GC with a DB-5 capillary column employing an internal standard (1,2,4-trichlorobenzene).

[b] TON represents the total number of moles of product produced per mole of catalyst. All reactions were run 2–3 times, and the data reported are the averages with standard deviation (1σ). Note the product yields in our catalytic studies are not given because we typically have large excesses of substrates to catalyst (>8000:1).

[c] The major product was *cis*-cyclooctene oxide, detected in >95% yield.

[d] UV light (λ_{max} = 350 nm).

[e] 5 mg of anthracene was added.

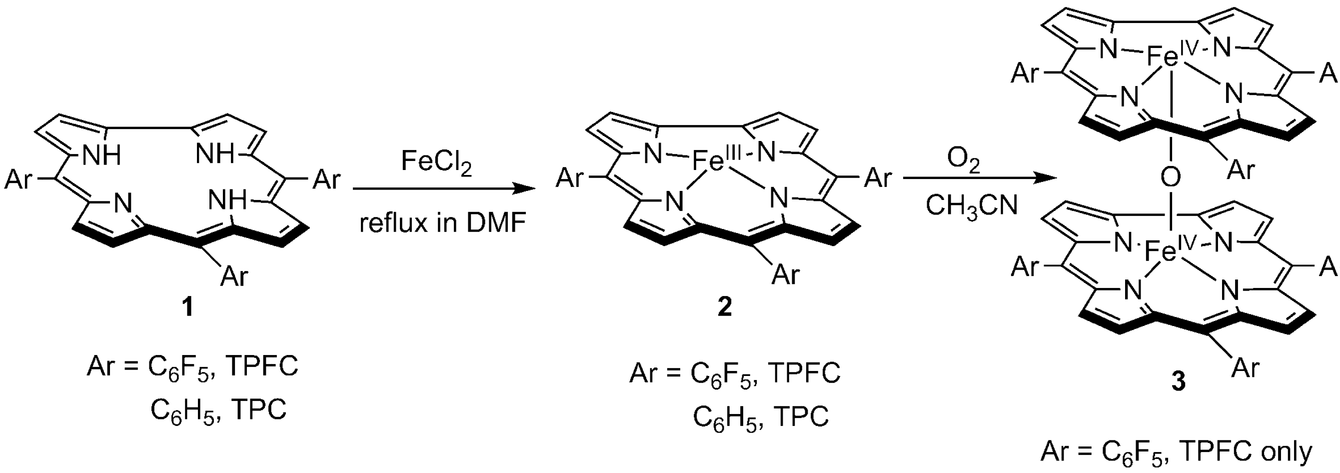
[f] 5 mg of *N-tert*-butyl-phenylnitrone (radical inhibitor) was added.

[g] Enone formation (~20%) was detected.

3.2. *Screening catalytic oxidations of cis-cyclooctene*

As shown in the Fig. 2, the photo-disproportionation reaction of diiron(IV)-μ-oxo biscorrole (**3**) becomes catalytic in the presence of O_2. First the efficacy of photo-disproportionation of μ-oxo iron(IV) biscorrole **3** for a light-driven oxidation catalysis was evaluated in the aerobic oxidation of *cis*-cyclooctene (Table 1). Our immediate goal in this section was to identify the most efficient systems and optimal conditions from the screening reactions. After 24 h of photolysis with visible light (λ_{max} = 420 nm), *cis*-cyclooctene oxide was obtained as the only identifiable oxidation product (>95% by GC) with ca. 90 turnovers (abbreviated as TON representing moles of product/moles of catalyst) of catalyst **3** (entry 1). The trend in the TONs roughly paralleled irradiation times and up to 540 TONs was obtained after four day irradiation. Control experiments showed 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 [42]. The use of other solvents instead of CH_3CN resulted in reduced TONs (entries 2–4), presumably due to a slower formation of the dimeric precursor **3**. It is known that the transformation of **2** to its μ-oxo dimer **3** has a very large solvent effect [41]. Catalyst degradation was a serious problem with higher-energy light and the use of UV irradiation (λ_{max} = 350 nm) shut down the catalytic activity completely (entry 5). Monitoring reaction by UV–vis spectroscopy indicated that the corrole catalyst was completely degraded only after 30 min photolysis of UV light.

In order to gain insight into the possible contribution of the radical autooxidation to the observed photocatalytic process, the experiment was also carried out in the presence of radical scavenger. Of note is the well known radical scavenger *N-tert*-butyl-phenylnitrone had almost no effect on cyclooctene expoxide formation (entry 7), which implies a non-radical oxidation process. It is interesting to note that the catalytic activity was enhanced by adding small amount of anthracene (entries 6 and 9), which could act as a photosensitizer. Similar enhancement effect was observed in the ruthenium(IV) μ-oxo bisporphyrins system [35]. In addition, the monomeric iron corrole Fe^{III}(TPFC) was tested as photocatalyst, which is capable of in situ formation of the μ-oxo dimer, giving comparable activity (entries 8 and 9). Instead, non-halogenated Fe^{III}(TPC) did not show appreciable catalytic activity



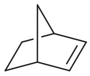
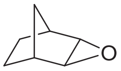
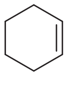
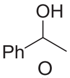
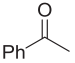
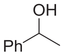
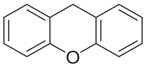
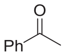
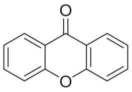
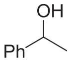
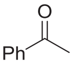
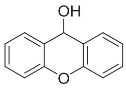
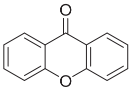
Scheme 1. Synthesis of the corrole-iron(III) and diiron(IV) μ-oxo complexes.

under identical conditions (entry 10). Clearly, the formation of μ-oxo dimer by molecular oxygen is essential for reactivity in the photocatalytic epoxidation of *cis*-cyclooctene. For the purpose of comparison, the well-known diiron(III) μ-oxo bisporphyrin complex $[Fe^{III}(TPP)]_2O$ and *trans*-dioxoruthenium(VI) tetramesitylporphyrin, i.e. $Ru^{VI}(TMP)O_2$, were also evaluated under identical conditions, giving comparatively low activities (entries 12 and 13).

3.3. Photocatalytic aerobic oxidation of alkenes and activated hydrocarbons

To further explore the substrate scope of the diiron(IV) μ-oxo corrole catalyst, the photocatalytic oxidations of a variety of organic substrates were examined under visible light and optimized conditions. Table 2 lists the oxidized products and corresponding TONs using the **3** as the photocatalyst. The trend in the TONs roughly parallels the substrate reactivity and significant activity was observed with up to 1580 TON. Similar to *cis*-cyclooctene, norborbene was oxidized to corresponding epoxide (*exo* mainly) with 72 TON after 24 h photolysis (entry 1). Cyclohexene, in contrast, which is susceptible to the allylic oxidation, gave primarily 2-cyclohexenol and 2-cyclohexenone along with minor expoxide (entry 2). This product distribution is no different than those typically obtained from cofacial iron and ruthenium porphyrin photocatalysts [17]. Activated hydrocarbons including triphenylmethane, diphenylmethane, ethylbenzene and xanthenes were

Table 2
Turnover numbers of photocatalyst **3** for alkenes and benzylic C-H oxidations.[a]

Entry	Substrate	Product	TON[b]
1[c]			72 ± 6
2		Cyclohexene oxide 2-Cyclohexenol 2-Cyclohexenone	40 ± 4 230 ± 24 102 ± 16
3[d]	Ph_3CH	Ph_3COH	380 ± 40
4	Ph_2CH_2	 	706 ± 60 220 ± 20
5	$PhCH_2CH_3$	 	80 ± 5 10 ± 2
6			1235 ± 120
7			1300 ± 140
8			1580 ± 175

[a] Typically with 0.5 μmol of **3** in 5 mL of CH_3CN containing 4–8 mmol of substrate and 5 mg anthracene.

[b] Determined for a 24 h photolysis (λ_{max} = 420 nm). The values (1σ) reported are the averages of 2–3 runs.

[c] >90% *exo* isomer.

[d] A minor product was detected by GC but not identified.

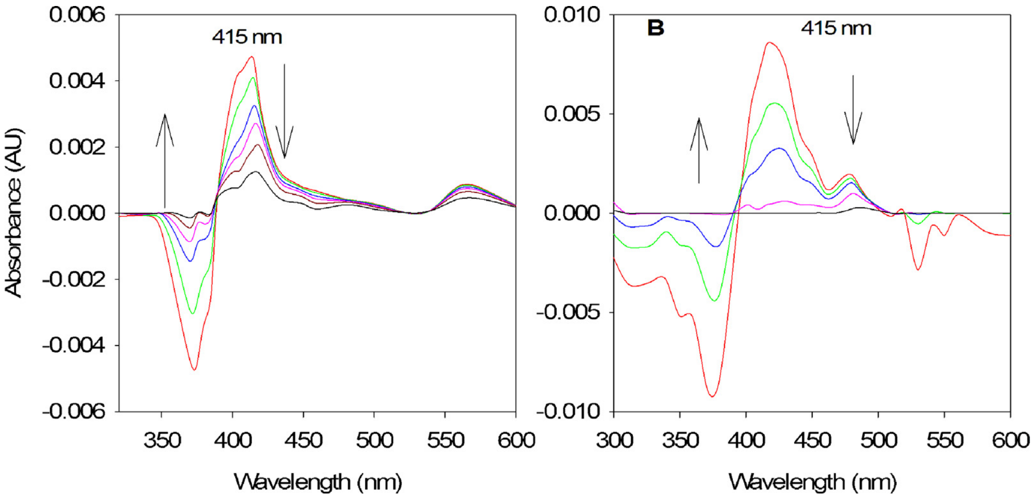
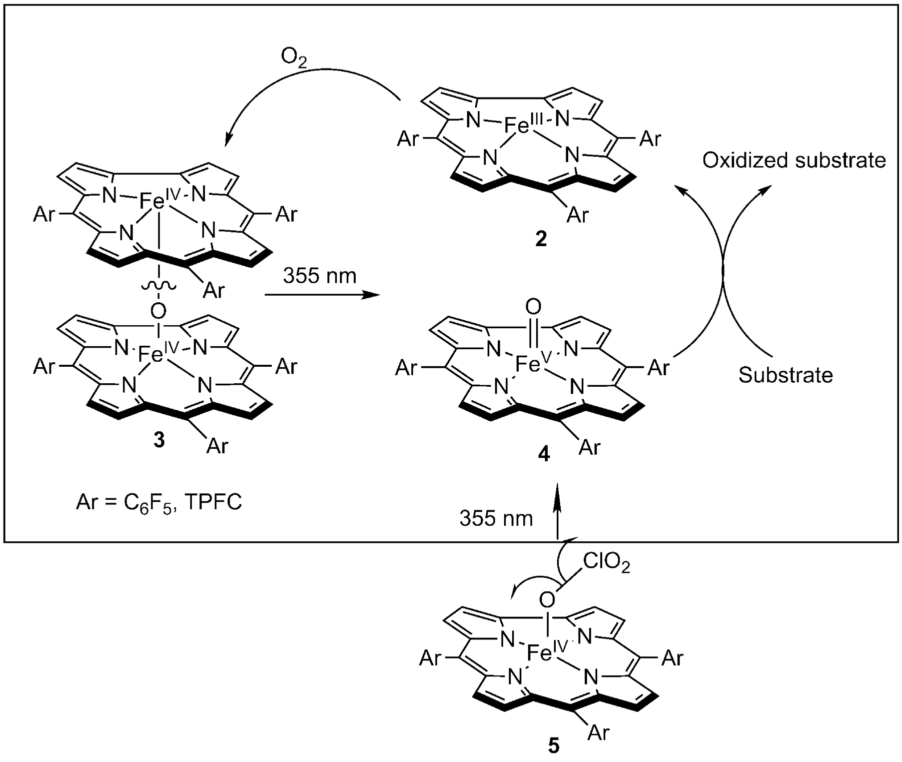


Fig. 3. (A) Time-resolved *difference* spectrum at 1, 2, 3, 4, 5, and 10 ms of the irradiation of **3** after the laser pulse in CH_3CN, difference spectrum = spectrum (t) – spectrum (0). (B) Time-resolved spectrum over 10 ms following 355 nm irradiation of $Fe^{IV}(ClO_3)$TPFC (**5**) in CH_3CN at 25 °C.

oxidized to the corresponding alcohols and/or ketones from overoxidation with total TONs ranging from 80 to 1200 (entries 3–6). As is evident from Table 2, the oxidation of secondary benzylic alcohols gave the highest catalytic activities (entries 7 and 8).

3.4. *Mechanistic studies of transient oxidizing species*

To probe the nature of the transient oxidizing species, we conducted laser flash photolysis (LFP) studies similar to those previously described for iron, manganese complexes [43] and bisporphyrin diruthenium(IV)-μ-oxo complexes [35]. When biscorrole-diiron(IV)-μ-oxo complex **3** was dissolved in acetonitrile solution and irradiated with 355 nm laser light, a short-lived transient **4** was formed. Fig. 3A shows a time-resolved UV–visible spectrum of transient **4** acquired at ambient temperature over 10 ms following 355 nm laser irradiation of **3**. Species **4** with a Soret band at $\lambda_{max} \approx 415$ nm decays in about 10 ms to give a product with a Soret band at $\lambda_{max} \approx 380$ nm. In view of its unique transient absorption spectrum and very high reactivity, transient **4** was tentatively assigned the corrole-iron(V)-oxo structure. We



Scheme 2. A proposed catalytic cycle for the photocatalytic aerobic oxidations by the diiron(IV) μ-oxo biscorrole. The scheme also shows formation of the oxidizing corrole-iron(V)-oxo species (**4**) by photolysis of iron(IV) chlorate monomer (**5**).

have found that the oxidizing species **4** generated from hemolytic photocleavage of the Fe-O bond of **3** is spectroscopically and kinetically indistinguishable from the species formed by photolysis of the corresponding corrole-iron(IV) chlorate complex (Fig. 3B) [24]. Regardless of the fact that iron(V)-oxo species are generally rare and elusive, Goldberg and coworkers have recently reported the spectroscopic evidence for a high-valnet corrolazine-iron-oxo intermediate at the iron(V) oxidation level [44,45].

On the basis of the present experimental facts, a catalytic cycle is proposed in Scheme 2. First, photo-disproportionation of μ-oxo **3** gives one molecule of a corrole-iron(III) species **2** in addition to the highly reactive iron(V)-oxo transient **4**. Subsequently, oxidation of an organic substrate by the resulting **4** gives a second molecule of **2**. After the oxygen transfer, autooxidation of the corrole-iron(III) complex **2** then regenerates the *bis*-corrole-diiron(IV) μ-oxo complex **3** (Scheme 2). The pivotal role of the μ-oxo dimer reformation was unequivocally confirmed when the non-halogenated Fe^{III}(TPC) was employed as catalyst. The notable absence of catalytic activity in the case of Fe^{III}(TPC) compared to Fe^{III}(TPFC) for the epoxidation of *cis*-cyclooctene illustrates that the formation of μ-oxo dimer **3** by aerobic oxidation of **2** is essential to effect the photocatalytic oxidation. Although the oxidation of **2** by O_2 to form **3** has been known for some time, the detailed mechanism has hitherto apparently not been fully disclosed. In this process, four electrons are needed to reduce O_2 and produce **3**. We speculate that the reaction could start with diiron(IV) peroxo-bridged complex to give two iron(V)-oxo intermediates, then dimerize to generate the diiron(IV)-μ-oxo biscorrole **3** with loss of a H_2O, which is similar to the well-known process described by Bach and co-workers for diiron(III)-μ-oxo bisporphyrin complexes [46].

4. Conclusions

In conclusion, we have shown that a fluorinated diiron(IV)-μ-oxo biscorrole catalyzed aerobic oxidation of alkenes and activated hydrocarbons under visible light irradiation. The observed photocatalytic oxidation is ascribed to a photo-disproportionation mechanism to afford a highly reactive corrole-iron(V)-oxo species that can be directly observed by laser flash photolysis methods. It is noteworthy that the use of visible light (solar light) for activation of atmospheric oxygen without the consumption of a reducing agent in aforementioned photocatalysis is particularly relevant to realizing innovative and economically advantageous processes for conversion of hydrocarbons into oxygenates. Further studies to define synthetic applications and characterize the proposed iron(V)-oxo transients more fully are ongoing in our laboratory.

Acknowledgments

This work was supported by the NSF grant (CHE-1213971) and an internal grant from WKU Office of Research (RCAP). We thank Dr. Martin Newcomb at UIC (University of Illinois at Chicago) for help with the LFP experiments and Dr. Eric Conte at WKU for the assistance of GC analysis.

References

[1] J.E. Baeckvall, Modern Oxidation Methods, Wiley-VCH Verlag, Weinheim, 2004.
[2] R. Noyori, M. Aoki, K. Sato, Chem. Commun. (2003) 1977–1986.
[3] T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329–2363.
[4] P.R. Ortiz de Montellano (Ed.), Cytochrome P450 Structure, Mechanism, and Biochemistry, 3rd ed., Kluwer Academic/Plenum, New York, 2005.
[5] I.G. Denisov, T.M. Makris, S.G. Sligar, I. Schlichting, Chem. Rev. 105 (2005) 2253–2277.
[6] B. Meunier (Ed.), Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations, Springer-Verlag, Berlin, 2000.
[7] B. Meunier, Chem. Rev. 92 (1992) 1411–1456.
[8] A. Maldotti, A. Molinari, R. Amadelli, Chem. Rev. 102 (2002) 3811–3836.
[9] J.T. Groves, R. Quinn, J. Am. Chem. Soc. 107 (1985) 5790–5792.
[10] T.-S. Lai, R. Zhang, K.-K. Cheung, C.-M. Che, H.-L. Kwong, Chem. Commun. (1998) 1583–1584.
[11] J.P. Collman, P.S. Wagenknecht, J.E. Hutchison, Angew. Chem. 106 (1994) 1620–1639.
[12] J. Rosenthal, J. Bachman, J.L. Dempsey, A.J. Esswein, T.G. Gray, J.M. Hodgkiss, D.R. Manke, T.D. Luckett, B.J. Pistorio, A.S. Veige, D.G. Nocera, Coord. Chem. Rev. 249 (2005) 1316–1326.
[13] M.W. Peterson, D.S. Rivers, R.M. Richman, J. Am. Chem. Soc. 107 (1985) 2907–2915.
[14] I.M. Wasser, H.C. Fry, P.G. Hoertz, G.J. Meyer, K.D. Karlin, Inorg. Chem. 43 (2004) 8272–8281.
[15] C.J. Chang, E.A. Baker, B.J. Pistorio, Y. Deng, Z.-H. Loh, S.E. Miller, S.D. Carpenter, D.G. Nocera, Inorg. Chem. 41 (2002) 3102–3109.
[16] B.J. Pistorio, C.J. Chang, D.G. Nocera, J. Am. Chem. Soc. 124 (2002) 7884–7885.
[17] J. Rosenthal, B.J. Pistorio, L.L. Chng, D.G. Nocera, J. Org. Chem. 70 (2005) 1885–1888.
[18] J. Rosenthal, T.D. Luckett, J.M. Hodgkiss, D.G. Nocera, J. Am. Chem. Soc. 128 (2006) 6546–6547.
[19] F. Ogliaro, S.P. de Visser, J.T. Groves, S. Shaik, Angew. Chem. Int. Ed. 40 (2001) 2874–2878.
[20] J.T. Groves, J. Lee, S.S. Marla, J. Am. Chem. Soc. 119 (1997) 6269–6273.
[21] R. Zhang, M. Newcomb, J. Am. Chem. Soc. 125 (2003) 12418–12419.
[22] R. Zhang, J.H. Horner, M. Newcomb, J. Am. Chem. Soc. 127 (2005) 6573–6582.
[23] F. Tiago de Oliveira, A. Chanda, D. Banerjee, X. Shan, S. Mondal, L. Que, E.L. Bominaar Jr., E. Muenck, T.J. Collins, Science 315 (2007) 835–838.
[24] D.N. Harischandra, R. Zhang, M. Newcomb, J. Am. Chem. Soc. 127 (2005) 13776–13777.
[25] Z. Pan, R. Zhang, L.W.M. Fung, M. Newcomb, Inorg. Chem. 46 (2007) 1517–1519.
[26] Z. Gross, N. Galili, Angew. Chem. Int. Ed. Engl. 38 (1999) 2366–2369.
[27] Z. Gross, N. Galili, L. Simkhovich, I. Saltsman, M. Botoshansky, D. Blaeser, R. Boese, I. Goldberg, Org. Lett. 1 (1999) 599–602.
[28] Z. Gross, H.B. Gray, Adv. Synth. Catal. 346 (2004) 165–170.
[29] I. Aviv, Z. Gross, Chem. Commun. (2007) 1987–1999.
[30] A.J. McGown, Y.M. Badiei, P. Leeladee, K. Prokop, S. Debeer, D.P. Goldberg, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), Handbook of Porphyrin Science, World Scientific Press, Singapore, 2011.
[31] Z. Gross, G. Golubkov, L. Simkhovich, Angew. Chem. Int. Ed. Engl. 39 (2000) 4045–4047.
[32] B.S. Mandimutsira, B. Ramdhanie, R.C. Todd, H.L. Wang, A.A. Zareba, R.S. Czernuszewicz, D.P. Goldberg, J. Am. Chem. Soc. 124 (2002) 15170–15171.
[33] K.A. Prokop, D.P. Goldberg, J. Am. Chem. Soc. 134 (2012) 8014–8017.
[34] K.A. Prokop, H.M. Neu, S.P. de Visser, D.P. Goldberg, J. Am. Chem. Soc. 133 (2011) 15874–15877.
[35] E. Vanover, Y. Huang, L. Xu, M. Newcomb, R. Zhang, Org. Lett. 12 (2010) 2246–2249.
[36] D.N. Harischandra, G. Lowery, R. Zhang, M. Newcomb, Org. Lett. 11 (2009) 2089–2092.
[37] J.T. Groves, R. Quinn, Inorg. Chem. 23 (1984) 3844–3846.
[38] B. Koszarna, D.T. Gryko, J. Org. Chem. 71 (2006) 3707–3717.
[39] L. Simkhovich, A. Mahammed, I. Goldberg, Z. Gross, Chem. Eur. J. 7 (2001) 1041–1055.
[40] R. Zhang, Y. Huang, C. Abebrese, H. Thompson, E. Vanover, C. Webb, Inorg. Chim. Acta 372 (2011) 152–157.
[41] L. Simkhovich, I. Goldberg, Z. Gross, Inorg. Chem. 41 (2002) 5433–5439.
[42] D.R. Kearns, Chem. Rev. 71 (1971) 395–427.
[43] R. Zhang, M. Newcomb, Acc. Chem. Res. 41 (2008) 468–477.
[44] A.J. McGown, W.D. Kerber, H. Fujii, D.P. Goldberg, Am. Chem. Soc. 131 (2009) 8040–8048.
[45] K. Cho, P. Leeladee, A.J. McGown, S. DeBeer, D.P. Goldberg, J. Am. Chem. Soc. 134 (2012) 7392–7399.
[46] D.-H. Chin, G.N. Lama, A.L. Balch, J. Am. Chem. Soc. 102 (1980) 5945–5947.