ORGANIC LETTERS

2010
Vol. 12, No. 10
2246−2249

Photocatalytic Aerobic Oxidation by a Bis-porphyrin−Ruthenium(IV) μ-Oxo Dimer: Observation of a Putative Porphyrin−Ruthenium(V)−Oxo Intermediate

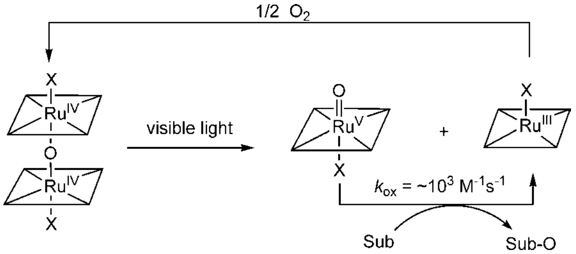
Eric Vanover,[†] Yan Huang,[†] Libin Xu,[‡,§] Martin Newcomb,[*,‡] and Rui Zhang[*,†]

Department of Chemistry, Western Kentucky University, 1906 College Heights Boulevard, Bowling Green, Kentucky 42101, and Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607

rui.zhang@wku.edu; men@uic.edu

Received March 11, 2010

ABSTRACT



The title complexes catalyze the aerobic oxidations of hydrocarbons using visible light and atmospheric oxygen as oxygen source in sequences employing photodisproportionation reactions. The putative oxidants, ruthenium(V)−oxo porphyrin species, can be detected and studied in real time via laser flash photolysis methods.

Selective oxidation is a key technology for the synthesis of high value chemicals in the pharmaceutical and petrochemical industries, but oxidations are among the most problematic processes to control.[1] Many stoichiometric oxidants with heavy metals are expensive and/or toxic and, thus, impractical. The ideal green catalytic oxidation process would use molecular oxygen or hydrogen peroxide as the primary oxygen source, recyclable catalysts in nontoxic solvents, and an inexpensive energy source.[2] In this context, we have an interest in photochemical generation of highly reactive metal−oxo intermediates which, upon oxidization of substrates, give low-valent metal complexes that can be recycled for catalytic oxidations. One example of a catalytic aerobic oxidation driven by a photodisproportionation reaction employed a diiron(III)−μ-oxo bisporphyrin complex[3] and photocatalytic oxidations of hydrocarbons using molecular oxygen as the oxygen source with no added reducing agent for the oxygen have been developed.[4] The low reactivity of the formed iron(IV)−oxo transients and poor quantum efficiency are serious obstacles that limit the use of iron porphyrins as practical photocatalysts, but the catalytic

---

[†] Western Kentucky University.
[‡] University of Illinois at Chicago.
[§] Current Address: Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235.

(1) Bäckvall, J. E. *Modern Oxidation Methods*; Wiley-VCH Verlag: Weinheim, 2004.

(2) Punniyamurthy, T.; Velusamy, S.; Iqbal, J. *Chem. Rev.* **2005**, *105*, 2329–2363.

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

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

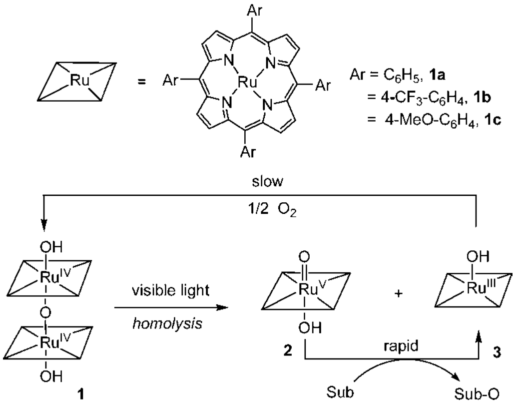
10.1021/ol1005938

efficiency of diiron(III)−μ-oxo bisporphyrin systems was improved by Nocera and co-workers who employed “Pacman” ligand designs with organic spacer hinges serving to preorganize two iron centers in a cofacial arrangement.[5–8]

Among the high-valent metal−oxo species, metal(V)−oxo complexes deserve special attention because they are highly reactive, although rare and elusive. The known porphyrin manganese(V)−oxo complexes showed higher reactivity than well-studied iron(IV)−oxo porphyrin radical cation analogues.[9,10] A recent paper by Collins et al. reported spectroscopic evidence for an oxoiron(V) complex supported by a tetraanionic ligand that showed unprecedented reactivity.[11] Putative porphyrin− and corrole−iron(V)−oxo transients produced by laser flash photolysis methods displayed the appropriate high levels of reactivity expected for iron(V)−oxo species,[12,13] and we recently reported a photodisproportionation of a bis-corrole−iron(IV) μ-oxo dimer that apparently gave the same type of corrole−iron(V)−oxo transient in a system that has potential for light-driven oxidation catalysis.[14]

Porphyrin−ruthenium(V)−oxo transients[15,16] are attractive candidates for oxidations, and these species are proposed intermediates in very efficient catalytic processes,[17] although not yet observed directly; computational studies suggest that they are stable with respect to ruthenium(IV)−oxo porphyrin radical cations.[18] In this study, we explore the applicability of ruthenium porphyrins, which are known to display good oxidative robustness,[19] in a light-driven catalytic process. We report that ruthenium(IV) μ-oxo bisporphyrin complexes catalyze the aerobic oxidation of hydrocarbons using visible light and atmospheric oxygen as oxygen source in sequences employing photodisproportionation reactions to give putative ruthenium(V)−oxo species as shown in Scheme 1.

Scheme 1



The diruthenium(IV)−μ-oxo-bis[5,10,15,20-tetraphenylporphyrin] precursor **1a** was synthesized according to reported methods.[20] The hydroxyl axial ligands were readily replaced with chloride anions to give a μ-oxo complex formulated as $[Ru^{IV}(TPP)Cl]_2O$ (Supporting Information, Figure S1). Two other dimer complexes, $[Ru^{IV}(4\text{-}CF_3\text{-}TPP)OH]_2O$ **(1b)** and $[(Ru^{IV}(4\text{-}MeOTPP)OH]_2O$ (**1c**), were prepared in a similar manner. The complexes were characterized by UV−visible, ^1H NMR, and IR spectra that matched those reported.[20] When dissolved in acetonitrile solution, complexes **1** were thermally stable to hydrocarbons, but irradiation with light (λ_{max} = 420 nm) of anaerobic solutions of complexes **1** in the presence of excess triphenylphosphine (50 mM) resulted in changes in the absorption spectra with isosbestic points (Figure 1). Similar spectral changes were previously observed upon the photolyses of diiron(III)-μ-oxo bisporphyrin complexes in the presence of Ph_3P.[21] According to previous studies by Collman and co-workers,[22] the product formed with λ_{max} at 430 nm was assigned as $Ru^{II}(TPP)(PPh_3)_2$. The spectral signature of $Ru^{II}(TPP)(PPh_3)_2$ was further confirmed by production of the same species in the known experiment of the Ru^{VI}-$(TPP)O_2$ with Ph_3P.[23]

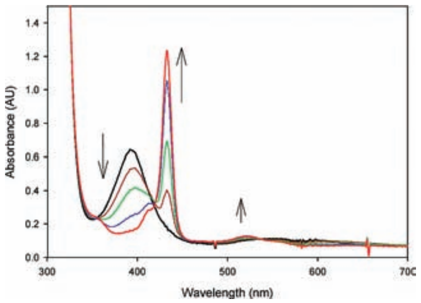


Figure 1. UV−vis spectral change of **1a** (6×10^{-6} M) in the presence of excess Ph_3P (50 mM) upon irradiation with a 300-W visible lamp (λ_{max} = 420 nm) in anaerobic CH_3CN solution. The spectra were recorded at t = 0, 2, 4, 6, and 10 min.

---

(5) Chang, C. J.; Baker, E. A.; Pistorio, B. J.; Deng, Y.; Loh, Z.-H.; Miller, S. E.; Carpenter, S. D.; Nocera, D. G. *Inorg. Chem.* **2002**, *41*, 3102–3109.

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

(7) Rosenthal, J.; Pistorio, B. J.; Chng, L. L.; Nocera, D. G. *J. Org. Chem.* **2005**, *70*, 1885–1888.

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

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

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

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

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

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

(14) Harischandra, D. N.; Lowery, G.; Zhang, R.; Newcomb, M. *Org. Lett.* **2009**, *11*, 2089–2092.

(15) Groves, J. T.; Bonchio, M.; Carofiglio, T.; Shalyaev, K. *J. Am. Chem. Soc.* **1996**, *118*, 8961–8962.

(16) Wang, C.; Shalyaev, K. V.; Bonchio, M.; Carofiglio, T.; Groves, J. T. *Inorg. Chem.* **2006**, *45*, 4769–4782.

(17) Ohtake, H.; Higuchi, T.; Hirobe, M. *Heterocycles* **1995**, *40*, 867–903.

A series of ruthenium(IV)−μ-oxo bisporphyrins was evaluated in the aerobic oxidation of *cis*-cyclooctene (Table 1). The reactions were carried out with 0.5 μmol of catalyst in 5 mL of oxygen-saturated solution containing 4 mmol of *cis*-cyclooctene. 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. 220 turnovers (abbreviated as TON representing moles of product/mol of catalyst) of catalyst **1a** (entry 1). The trend in the TONs roughly paralleled irradiation times. 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.[24] The use of other solvents instead of CH_3CN, or air as oxygen source (data not shown), resulted in reduced TONs (entries 2−4). Catalyst degradation was a problem with higher-energy light, but the use of UV irradiation increased catalytic activity (entry 5). It is interesting to note that the catalytic activity was enhanced by adding small amounts of anthracene (entries 6 and 9). Quite surprisingly, the axial ligand on the metal had a significant effect, and the $[Ru^{IV}(TPP)Cl]_2O$ (entry 7) gave reduced activity compared to $[Ru^{IV}(TPP)OH]_2O$. The substituent in the porphyrin ligand gave a noticeable effect on the catalytic activity (entries 1, 8, and 10), with the most electron-demanding system, namely $[Ru^{IV}(4\text{-}CF_3\text{-}TPP)OH]_2O$, being the most efficient catalyst.

Table 1. Aerobic Photocatalytic Oxidation of *cis*-Cyclooctene with Diruthenium(IV) μ-Oxo Porphyrins[a]

entry	catalyst	solvent	t/day	TON[b,c]
1	$[Ru^{IV}(TPP)OH]_2O$ **1a**	CH_3CN	1	220 ± 16
			2	460 ± 40
			3	640 ± 65
2		$CHCl_3$	1	110 ± 18
3		C_6H_6	1	140 ± 6
4		THF	1	190 ± 10
5[d]		CH_3CN	1	340 ± 8
6[e]		CH_3CN	1	300 ± 35
7	$[Ru^{IV}(TPP)Cl]_2O$	CH_3CN	1	70 ± 5
8	$[Ru^{IV}(4\text{-}CF_3\text{-}TPP)OH]_2O$ **1b**	CH_3CN	1	250 ± 21
9[e]		CH_3CN	1	340 ± 9
10	$[Ru^{IV}(4\text{-}MeOTPP)OH]_2O$ **1c**	CH_3CN	1	190 ± 23

[a] The reaction was carried out in a Rayonet reactor, with 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 5890 GC with a DB-5 capillary column employing an internal standard. [b] TON represents the total number of moles of product produced per mole of catalyst. All reactions were run three times, and the data reported are the averages with standard deviation (1σ). [c] The major product was *cis*-cyclooctene oxide, detected in >95% yield. [d] UV−vis light (λ_{max} = 350 nm). [e] 5 mg of anthracene was added.

In a fashion similar to that described for *cis*-cyclooctene epoxidation, the photocatalytic oxidations of a variety of organic substrates were examined. Table 2 lists the oxidized products and corresponding TONs using the $[Ru^{IV}(4\text{-}CF_3\text{-}TPP)OH]_2O$ (**1b**) as the photocatalyst. The trend in the TONs roughly parallels the substrate reactivity, and significant activity was observed with up to 3900 TON. After 24 h photolysis, norbornene was oxidized to norbornene oxide (*exo* mainly) with 200 TON (entry 1). Cyclohexene, in contrast, is susceptible to the allylic oxidation that gave primarily 2-cyclohexenone and 2-cyclohexenol along with minor epoxide (entry 2). This product distribution is no different than those typically obtained from cofacial iron porphyrin photocatalysts.[7] Activated hydrocarbons including triphenylmethane, diphenylmethane, ethylbenzene, and xanthenes were oxidized to the corresponding alcohols and/or ketones from overoxidation with total TONs ranging from 560 to 2900 (entries 3−6). Noticeably, the oxidation of secondary benzylic alcohols gave the highest catalytic activities (entries 7 and 8). Competitive catalytic oxidation of ethylbenzene and ethlybenzene-d_{10} revealed a kinetic isotope effect (KIE) of $k_H/k_D = 4.8 \pm 0.2$ at 298 K, similar to the KIE reported for the reaction of ethylbenzene with an electron-deficient iron(IV)−oxo porphyrin radical cation species.[25] The observed KIE is larger than those observed in autoxidation processes,[26] suggesting a nonradical mechanism that involves the intermediacy of ruthenium(V)−oxo species as postulated in Scheme 1.

Table 2. Turnover Numbers for Alkenes and Benzylic C−H Oxidations Using **1b** as the Photocatalyst[a]

entry	substrate	product	TON[b]
1	norbornene	norbornene oxide[c]	200 ± 40
2	cyclohexene	2-cyclohexenol	160 ± 14
		2-cyclohexenone	350 ± 31
		cyclohexe oxide	30 ± 3
3	triphenylmethane	triphenylmethanol	1120 ± 48
4	diphenylmethane	diphenylmethanol	820 ± 102
		benzophenone	140 ± 18
5	ethylbenzene	1-phenylethanol	380 ± 41
		acetophenone	180 ± 19
6[d]	xanthene	9-xanthone	2900 ± 140
7	1-phenylethanol	acetophenone	3300 ± 240
8[e]	9-xanthenol	9-xanthone	3900 ± 280

[a] Typically with 0.25 μmol of **1b** in 5 mL of CH_3CN containing 2−4 mmol of substrate and 5 mg of anthracene. [b] Determined for a 24 h photolysis (λ_{max} = 420 nm). The values reported are the averages of 2−3 runs (1σ deviation). [c] >90% *exo* isomer. [d] One minor product was detected by GC but not identified. [e] 48% product yield.

---

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

(19) Che, C.-M.; Huang, J.-S. *Chem. Commun.* **2009**, 3996–4015.

(20) Sugimoto, H.; Higashi, T.; Mori, M.; Nagano, M.; Yoshida, Z.; Ogoshi, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 822–828.

(21) Richman, R. M.; Peterson, M. *J. Am. Chem. Soc.* **1982**, *104*, 5795–5796.

(22) Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151–5163.

(23) Che, C.-M.; Zhang, J.-L.; Zhang, R.; Huang, J.-S.; Lai, T.-S.; Tsui, W.-M.; Zhou, X.-G.; Zhou, Z.-Y.; Zhu, N.; Chang, C. K. *Chem.—Eur. J.* **2005**, *11*, 7040–7053.

(24) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395–427.

(25) Pan, Z.; Zhang, R.; Newcomb, M. *J. Inorg. Biochem.* **2006**, *100*, 524–532.

(26) Sawyer, D. T.; Kang, C.; Llobet, A.; Redman, C. *J. Am. Chem. Soc.* **1993**, *115*, 5817–5818.

To probe the nature of the transient oxidizing species, we conducted laser flash photolysis (LFP) studies similar to those previously described for iron and manganese complexes.[27] As shown in Figure 2A, the photodisproportionation of the bisporphyrin diruthenium(IV)−μ-oxo complexes exhibited a fast decay followed by a slow growth that were observed in different time scales (Figure 2A). Figure 2B shows a time-resolved *difference* spectrum for a 50 ms time scale, where the only observable transients are those that increase or decrease in concentration on the short time scale, **2a** and **3a** in this case. Irradiation of the complex $[Ru^{IV}(TPP)OH]_2O$ **1a** with 355 nm laser light at ambient temperature in CH_3CN solution instantly produced a highly reactive transient **2a** displaying a strong Soret band at 390 nm, which rapidly decayed to form a compound (**3a**) with Soret band at 410 nm and Q-band at 530 nm (Figure 2B). The spectrum of **3a** was essentially identical to that of $Ru^{III}(OMe)TPP$, which was independently prepared from a reported method.[15] Accordingly, we assigned the structure of **2a** as $[Ru^{V}(O)(TPP)(OH)]$ and that of **3a** as $Ru^{III}(TPP)OH$. It is noteworthy that the photolysis efficiency could be enhanced by adding benzophenone or anthracene, which presumably acts as a photosensitizer. In the presence of anthracene (10 mM), the photolysis of **1a** had a quantum yield of 1.1×10^{-3} (see the Supporting Information for details), which is 10 times greater than that reported for the photolysis of a bis-porphyrin diiron(III) μ-oxo complex.[3] In a slower subsequent phase of the reaction (Figure S2 in the Supporting Information), exposing photoproduct **3a** to oxygen led to regeneration of the dimetal(IV)-μ-oxo complex **1a** through an autoxidation pathway.[22]

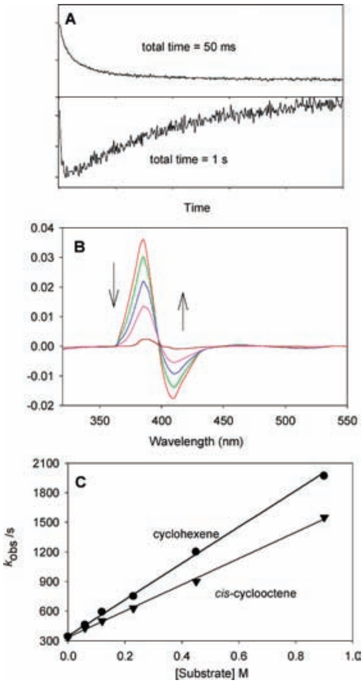


Figure 2. (A) Kinetic trace at λ_{max} (390 nm) showing a rapid decay followed by a slow growing process after laser pulse. (B) Time-resolved *difference* spectrum at 0.2, 1, 2, 5, 8, and 10 ms, following 355 nm irradiation of $[Ru^{IV}(TPP)OH]_2O$ (**1a**) in the presence of benzophenone (10 mM) in CH_3CN at 25 °C; difference spectrum = spectrum (t) − spectrum (final = 50 ms). In this representation, decaying peaks have positive absorbances, whereas growing peaks have negative absorbances. (C) Observed pseudo-first-order rate constants for reactions of **2a** with cyclohexene (circles) and *cis*-cyclooctene (triangles) in CH_3CN.

Kinetic studies were accomplished by generating transient **2a** in the presence of organic substrates at varying high concentrations under pseudo-first-order conditions. 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.

$$k_{obs} = k_0 + k_{ox}[\text{substrate}] \qquad (1)$$

The results from reactions of **2a** formed by photolysis of **1a** are shown graphically in Figure 2C, where plots of k_{obs} versus the concentrations of cyclohexene and *cis*-cyclooctene were linear, and the rate constants (k_{ox}) for their reactions with **2a** are 1.8×10^3 and 1.3×10^3 M^{-1} s^{-1}, respectively. Second-order rate constants with other substrates are collected in Table S1 (Supporting Information). Remarkably, the observed rate constants for reactions of the putative ruthenium(V)−oxo species **2a** with alkenes are 5−6 orders of magnitude greater than those for similar reactions of the well-characterized *trans*-dioxoruthenium(VI) porphyrins.[23]

In summary, we have demonstrated that the ruthenium(IV)−μ-oxo bisporphyrins catalyzed efficient aerobic oxidation of alkenes and activated hydrocarbons using visible light and atmospheric oxygen. The observed photocatalytic oxidation is ascribed to a photodisproportionation mechanism to afford a putative porphyrin−ruthenium(V)−oxo species that can be directly observed and kinetically studied by laser flash photolysis methods. Further studies to characterize the observed transients more fully and to define synthetic applications are ongoing in our laboratory.

Acknowledgment. This work was supported by PRF (48764-GB4) and Kentucky EPSCoR (REG 2008) grants to R.Z. and by NIH (GM48722) and NSF (CHE-0601857) grants to M.N. We thank Dr. Eric Conte for assistance with the GC analysis.

Supporting Information Available: Figures S1−2 and Table S1 and experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

OL1005938

---

(27) Zhang, R.; Newcomb, M. *Acc. Chem. Res.* **2008**, *41*, 468–477.