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Photochemical Generation of a Highly Reactive Iron−Oxo Intermediate. A True Iron(V)−Oxo Species?

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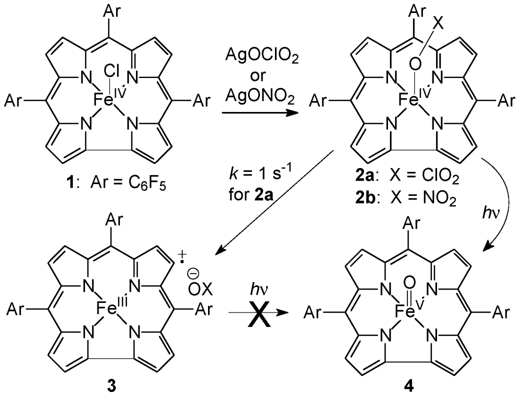
High-valent metal−oxo transients are active intermediates in many catalytic oxidation processes in nature and in the laboratory.[1] Iron is one of the most common metals in the catalysts, especially the catalysts in nature, where it is found in the form of porphyrin−iron, mononuclear non-heme iron, and diiron assemblies.[2] The readily accessible high oxidation state of iron is +4. Porphyrin−iron(IV)−oxo species are well-known, and two-electron oxo transfer oxidation of porphyrin−iron(III) salts gives observable iron(IV)−oxo porphyrin radical cations in enzymes (Compound I) and in models.[3] Species with more highly oxidized iron atoms are rare.[4] The active oxidizing species from an iron catalyst is usually ascribed to an iron(IV)−oxo ligand radical cation, but paradoxically, independently generated iron(IV)−oxo porphyrin radical cations do not exhibit the high reactivity necessary for hydrocarbon oxidation reactions.[5]

We recently introduced laser flash photolysis (LFP)-induced ligand cleavage reactions that generate ligand−manganese(V)−oxo derivatives that can be studied in real time.[6] Herein, we report extension of the methods to production of a highly reactive high-valent iron−oxo transient that we tentatively identify as a corrole−iron(V)−oxo species.[7] The results indicate that isomerization of a ligand−iron(V)−oxo species to the isomeric iron(IV)−oxo ligand radical cation can be slow, permitting substrate oxidation by the highly reactive iron(V)−oxo species.

Air oxidation of 5,10,15-tris(pentafluorophenyl)corrole−iron(III) in the presence of HCl gave the known corrole−iron(IV) chloride salt **1**,[8] which was allowed to react with $Ag(ClO_3)$ or with $Ag(NO_3)$ in acetonitrile (Scheme 1). The reaction of **1** with $Ag(ClO_3)$ gave an intermediate (**2a**) that reacted rapidly ($\tau = 1$ s) to give a stable product (**3a**). The reaction of **1** with $Ag(NO_3)$ gave a species (**2b**) that was spectroscopically similar to **2a** and considerably more stable with $\tau > 100$ s. From the UV−visible and ESR spectra, we assign the structures of compounds **2** as corrole−iron(IV) chlorate and nitrate, respectively, and compound **3a** as an iron(III) corrole radical cation.[9]

Scheme 1



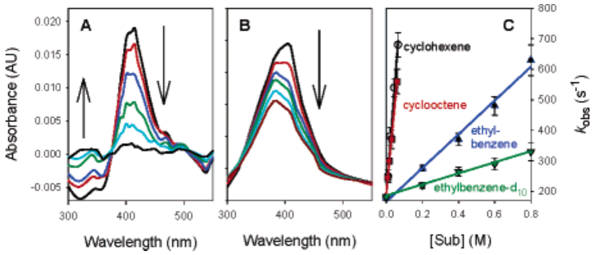


Figure 1. (A) Time-resolved spectrum for transient **4** (22 °C, CH_3CN) at 0.5, 2, 4, 8, 12, and 20 ms after formation. (B) Time-resolved decay spectrum from reaction of neutral iron(III)−corrole with mCPBA (22 °C, CH_3CN) over 20 ms. (C) Observed rate constants for reactions of **4**.

LFP of **2a** in CH_3CN with 355 nm light gave a new reactive transient (**4**) with a strong, sharp Soret band that decayed rapidly (Figure 1A). LFP of nitrate **2b** gave the same transient, albeit with lower efficiency. The same species apparently also was formed as a short-lived transient when the neutral corrole−iron(III) species was mixed with excess mCPBA (Figure 1B); the rate constants for decay of these species were the same ($\tau \approx 0.005$ s; see Supporting Information). The photochemical reaction was specific for **2**; 355 nm photolysis of **3a** did not result in a noticeable reaction. We tentatively assign the structure of **4** as the corrole−iron(V)−oxo species shown in Scheme 1 on the basis of its UV−visible spectrum, its high reactivity (see below), and analogy to the photochemical reactions of corrole−manganese(IV) chlorates, which give corrole−manganese(V)−oxo species (e.g., **5**) upon 355 nm irradiation.[6c]

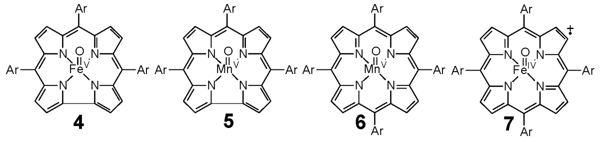
Transient **4** was shown to be a reactive iron−oxo intermediate in a preparative reaction. Nitrate precursor **2b** was prepared by mixing **1** with 1 equiv of $Ag(NO_3)$ in CH_3CN; under these conditions, the yield of **2b** determined by UV−visible spectroscopy was ca. 90%. An excess of *cis*-cyclooctene was added, and the mixture was photolyzed with 350 nm light. Following product workup, quantitative GC analysis showed the presence of *cis*-cyclooctene oxide in 50% yield based on precursor **2b**. No reaction of **2b** with cyclooctene was observed without light.

Species **4** reacted rapidly when produced in CH_3CN solutions. In the absence of an organic reductant, the pseudo-first-order decay rate constant was $k = 200\ s^{-1}$. In the presence of organic reductants, the pseudo-first-order decay rate constants increased linearly with substrate concentration (Figure 1C). The kinetic data were solved via eq 1, where k_{obs} is the observed rate constant, k_0 is the background rate constant, k_{ox} is the second-order rate constant for oxidation of substrate, and [Sub] is the concentration of substrate. The second-order rate constants were $k_{ox} = (7.4 \pm 0.3) \times 10^3\ M^{-1}\ s^{-1}$ (cyclohexene), $k_{ox} = (5.9 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1}$ (*cis*-cyclooctene), $k_{ox} = (5.7 \pm 0.3) \times 10^2\ M^{-1}\ s^{-1}$ (ethylbenzene), and $k_{ox} = (1.6 \pm 0.2) \times 10^2\ M^{-1}\ s^{-1}$ (ethylbenzene-d_{10}).

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

10.1021/ja0542439 CCC: $30.25

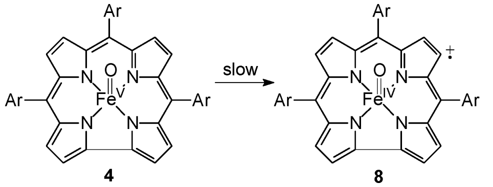
Table 1. Second-Order Rate Constants at Ambient Temperature for Oxidations of *cis*-Cyclooctene and Ethylbenzene[a]



	4	5	6	7
cyclooctene	5900	4	600000	50
$PhCH_2CH_3$	570	n.d.	130000	4

[a] In units of M^{-1} s^{-1}. Ar = (C_6F_5). Data for **5**, **6**, and **7** are from refs 5 and 6; n.d. = not determined.

Scheme 2



The assignment of an iron(V)−oxo structure to transient **4**, as opposed to an iron(IV)−oxo corrole radical cation, should be considered tentative until the species can be prepared in high conversion under conditions that permit more complete characterization. Nonetheless, the UV−visible spectrum and especially the reactivity of **4** suggest the iron(V)−oxo structure. For example, consider the rate constants shown in Table 1. Transient **4** is about 3 orders of magnitude more reactive than the analogous corrole−manganese(V)−oxo species **5**. In the related series of porphyrins, the porphyrin−manganese(V)−oxo cation **6** reacts more than 4 orders of magnitude faster than the iron(IV)−oxo porphyrin radical cation **7**. Remarkably, the neutral transient **4** is 100 times *more reactive* than the positively charged iron(IV)−oxo porphyrin radical cation **7**. If the new transient were the iron(IV)−oxo corrole radical cation (**8** in Scheme 2), one would expect the reactivity at ambient temperature to be at least 6 orders of magnitude smaller than observed.[10]

The corrole−iron(V)−oxo structure **4** is not necessarily the low-energy electronic configuration of the system. By analogy to porphyrin−iron−oxo species,[11] the isomeric iron(IV)−oxo corrole radical cation **8** (Scheme 2) should be a lower-energy species than **4**. If an intrinsic barrier for the electron transfer isomerization exists, structures **4** and **8** will be distinct isomers and not resonance forms. Such a barrier might result from a large degree of structural reorganization in the macrocycle upon oxidation and the attendant loss of delocalization energy. A barrier for electron transfer isomerization of **4** to **8** can function to trap high reactivity in the iron(V)−oxo species **4**, which would be expected to oxidize substrates rapidly, whereas the lower-energy isomer **8** would be expected to react sluggishly.

The possibility that a ligand−iron(V)−oxo species can convert relatively slowly to its iron(IV)−oxo ligand radical cation isomer might be an important feature for understanding catalytic oxidations by porphyrin−iron complexes in the laboratory and in nature. Under catalytic turnover conditions, a porphyrin−iron catalyst will oxidize cyclohexane,[12] and cytochrome P450$_{cam}$ hydroxylates an unactivated C−H bond in camphor so fast that the oxidant cannot be detected even in low-temperature studies.[13] The putative oxidants in both cases are iron(IV)−oxo porphyrin radical cations, that is, Compound I analogues. Authentic Compound I analogues do not hydroxylate unactivated C−H bonds rapidly, however.[5] Both in nature and in the laboratory, oxidation of the porphyrin−iron(III) species will give a porphyrin−iron(V)−oxo derivative as the first-formed intermediate, and it is possible that undetected iron(V)−oxo species hydroxylate unactivated C−H bonds in substrates faster than they isomerize to Compound I analogues.

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Supporting Information Available: UV−visible spectra, ESR spectra, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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