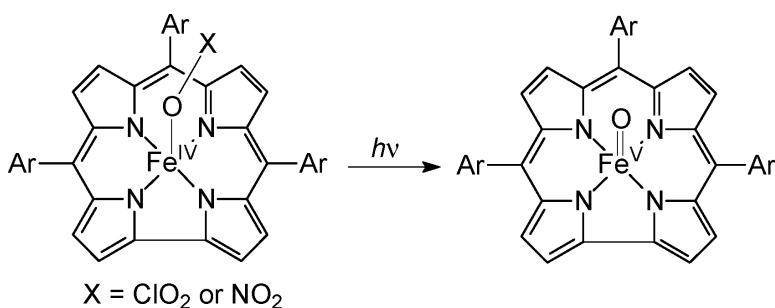


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Photochemical Generation of a Highly Reactive Iron–Oxo Intermediate. A True Iron(V)–Oxo Species?

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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(ClO₃) or with Ag(NO₃) in acetonitrile (Scheme 1). The reaction of **1** with Ag(ClO₃) gave an intermediate (**2a**) that reacted rapidly ($\tau = 1$ s) to give a stable product (**3a**). The reaction of **1** with Ag(NO₃) 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

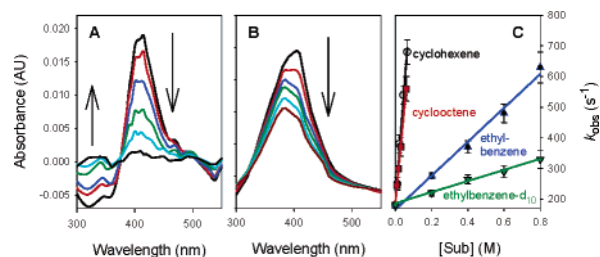
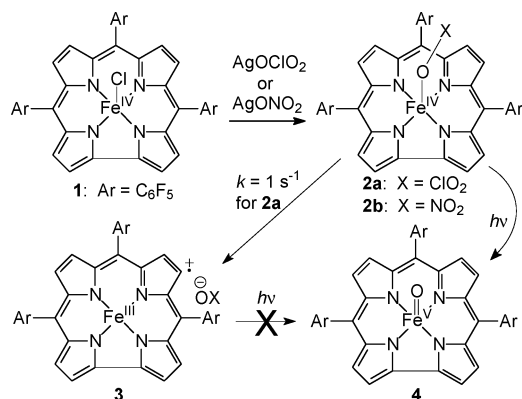


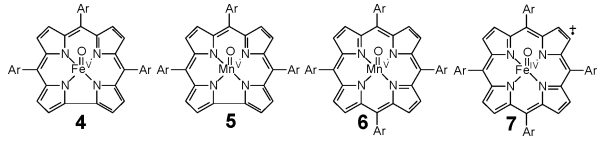
Figure 1. (A) Time-resolved spectrum for transient **4** (22 °C, CH₃CN) at 0.5, 2, 4, 8, 12, and 20 ms after formation. (B) Time-resolved decay spectrum from reaction of neutral iron(III)–corrole with mCPBA (22 °C, CH₃CN) over 20 ms. (C) Observed rate constants for reactions of **4**.

LFP of **2a** in CH₃CN 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(NO₃) in CH₃CN; 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 355 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.

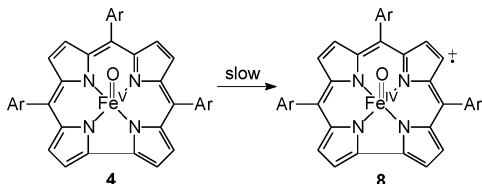
Species **4** reacted rapidly when produced in CH₃CN solutions. In the absence of an organic reductant, the pseudo-first-order decay rate constant was $k = 200$ s^{−1}. In the presence of organic reductants, the pseudo-first-order decay rate constants increased linearly with substrate concentration (Figure 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 $k_{\text{ox}} = (7.4 \pm 0.3) \times 10^3$ M^{−1} s^{−1} (cyclohexene), $k_{\text{ox}} = (5.9 \pm 0.2) \times 10^3$ M^{−1} s^{−1} (*cis*-cyclooctene), $k_{\text{ox}} = (5.7 \pm 0.3) \times 10^2$ M^{−1} s^{−1} (ethylbenzene), and $k_{\text{ox}} = (1.6 \pm 0.2) \times 10^2$ M^{−1} s^{−1} (ethylbenzene-*d*₁₀).

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

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 ₂ CH ₃	570	n.d.	130000	4

^a In units of M⁻¹ s⁻¹. Ar = (C₆F₅). 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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