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Seeing the Long-Sought Intermediate in the Reaction of Oxoiron(IV) Porphyrin Cation Radicals with Olefins[1]

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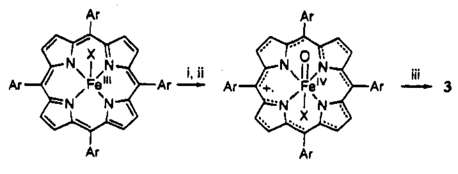
The isolation,[2] characterization,[3] and reactivity of $[(\mathrm{TMP}^{\bullet+})\mathrm{Fe}^{IV}(\mathrm{O})]^+$ ($\mathbf{1}^+$)[4] and related oxoiron(IV) porphyrin cation radical complexes,[3b,5] their involvement in catalytic oxygenation of hydrocarbons,[6−8] and the similarity of their electronic structure to that of compounds I of the relevant enzymes puts them among the most important biomimetic complexes.[3be,9] The intensive mechanistic research on oxygen atom transfer from oxoiron(IV) porphyrin cation radicals to olefins led to the conclusion that intermediates which contain both reactants must exist on the pathway to the final products.[10] Several years ago, Groves and Watanabe reported the direct observation of such an intermediate, which however could not be structurally characterized.[10f] The currently most common structural proposals for the intermediate in metalloporphyrin-catalyzed epoxidation of olefins are metallacycle, charge-transfer, or electron-transfer (ET) complexes.

Scheme 1[a]



2-X (Ar = Mesityl) **1-X**

[a] Reaction conditions: (i) CD_2Cl_2, −78 °C, O_3; (ii) N_2; (iii) + styrene, X = ClO_4^-.

Axial ligands play a major role in the chemistry of hemoproteins and also affect the spectra and reactivity of oxoiron(IV) porphyrin cation radical complexes.[3a,c,7e,11] We have recently demonstrated that the rate of epoxidation of styrene by $\mathbf{1}^+$ complexes (obtained via ozonolysis of the corresponding iron(III) porphyrins, **2-X** in Scheme 1)[12] was modulated by its *trans*-axial ligands: **1-F** > **1-OHCH$_3$** > **1-Cl** > **1-OAc** > **1-OSO$_2$CF$_3$** (**1-Trif**) ≫ **1-OClO$_3$**.[13] Although the combination of **1-OClO$_3$** with styrene afforded no organic products, we later noticed that it induced a distinct color change from brilliant to dark green, similar to that reported by Groves and Watanabe.[10f] We have now decided to concentrate on the reaction of **1-OClO$_3$** with alkenes, with the hope of obtaining new data which will enable a definite formulation of the long-sought intermediate in iron porphyrin catalyzed epoxidation of olefins. The detailed study resulted in the trapping of complex **3**, which allowed its characterization as an ET complex by a combination of NMR and EPR spectroscopies.

Addition of styrene (similar results were obtained with cyclooctene or *cis*-stilbene) to a CD_2Cl_2 solution of **1-OClO$_3$** at −80 °C induced dramatic changes in its ^{1}H NMR spectrum (Figure 1a).[14] The rate of formation of the new complex (**3**) was dependent on the amount of styrene added, but no further reaction occurred for extended periods, as confirmed by NMR and quenching of **3** by *n*-Bu_4NI at −80 °C and GC analysis. The NMR spectrum of **3** (Figure 1b) consists of four upfield-shifted resonances at δ = −55, −18, −14, −9 ppm and one signal at +100 ppm, in the ratio 2:3:3:3:2, which were assigned to the *m*-H, *o*-CH_3, *o*-CH_3, and *p*-CH_3 of the mesityl groups and to the β-pyrrole protons, respectively.[15] This pattern, including the observation of two sets of *o*-CH_3 signals with different line widths, closely resembles that of iron(III) porphyrin cation radical complexes with two different axial ligands.[16] To further establish this conclusion, which is based on $(\mathrm{TPP}^{\bullet+})$ and $(\mathrm{TTP}^{\bullet+})$ derivatives, we prepared $(\mathrm{TMP}^{\bullet+})\mathrm{Fe(Cl)(SbCl_6)}$ (**4**) independently.[17] The NMR spectrum of **4** is shown in Figure 1c, and its comparison with that of **3** confirms the correct assignment and demonstrates the close similarity between the two complexes. Accordingly, we conclude that complex **3**

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[1] Part of these results were presented at the 9th International Symposium on Homogeneous Catalysis, Jerusalem, Israel, August 1994, and at the International Symposium on Molecular Reaction Mechanisms Involving Transition Metals, Experimental and Theoretical Aspects, Florence, Italy, October 1994.

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[4] Abbreviations used: TMP, TPP, and TTP, the dianions of tetramesityl-, tetraphenyl-, and tetratoluylporphyrin, respectively; $(\mathrm{TMP}^{\bullet+})$, $(\mathrm{TPP}^{\bullet+})$, and $(\mathrm{TTP}^{\bullet+})$, the one-electron-oxidized porphyrin dianions; $\mathbf{1}^+$, the cationic oxoiron(IV) complex of $(\mathrm{TMP}^{\bullet+})$ without specifying its trans ligand.

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[12] The major advantage of ozone as oxidant was that it did not introduce any potential ligand for $\mathbf{1}^+$. Oxidation of the various **2-X** complexes by *m*-CPBA in the absence of methanol resulted in mixtures of $\mathbf{1}^+$ with various axial ligands (NMR), while in the presence of methanol, **1-OHCH$_3$** was invariably formed (see also ref 3c).

[13] Gross, Z.; Nimri, S. *Inorg. Chem.* **1994**, *33*, 1731.

[14] Most NMR experiments were performed with styrene-d_8, but experiments with regular styrene and saturation of its signals gave identical results.

[15] The three methyl groups (integration) at −9, −18, and −14 ppm were assigned to the *p*-CH_3 and the *o*-CH_3 groups of the TMP ligand, respectively, on the basis of their relative distance from the metal, whose paramagnetism determines both the isotropic shift and the line widths (La Mar, G. N.; Walker, F. A. In *The Porphyrins, Vol. 4*; Dolphin, D., Ed.; Academic Press: New York, 1979; Chapter 2). The resonances at −55 and +100 ppm were assigned to the *m*-aryl and β-pyrrole protons, respectively, by ^{2}H NMR of β-pyrrole-deuterated **3**.

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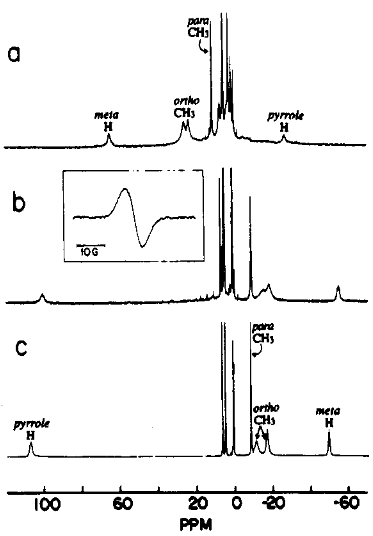


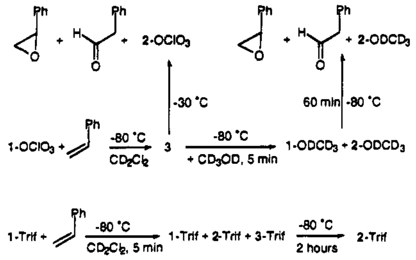
Figure 1. ^{1}H NMR (200 MHz, CD_2Cl_2, −80 °C) spectra of complexes: (a) **1**-$OClO_3$; (b) **3** (**1**-$OClO_3$ + styrene-d_8); (c) **4**. Inset: EPR spectrum of **3** (**1**-$OClO_3$ + styrene) at −80 °C.

contains an iron(III) porphyrin cation radical with two different axial ligands, ClO_4^- and O^{2-}, produced by one-electron reduction of the $Fe^{IV}{=}O$ bond in **1**-ClO_4.

The identification of the olefinic moiety of the complex was based on EPR examination of the reaction mixtures. Addition of olefins to a preformed solution of **1**-$OClO_3$ at −80 °C, EPR-silent at this temperature, resulted in the appearance of strong signals at $g \approx 2$ (g = 2.0041, 2.0041, and 2.0018 for the complexes with styrene (**3**, Figure 1b, inset), styrene-d_8 (**3a**), and *cis*-stilbene (**3b**), respectively), which disappeared upon heating (formation of **2**-$OClO_3$) and recooling. At −80 °C, the peak-to-peak line widths (ΔH_{pp}) of the signals of all complexes were very similar (≈6.3 G), but in frozen solutions (T = 130 K), the signal of **3** was broader than that of **3a** (ΔH_{pp} = 7.5 and 5.5 G, respectively). Since all known iron porphyrin derivatives, including complex **4**, which we checked as well, are EPR-silent in solution at −80 °C, the signals of **3**, **3a**, and **3b** at $g \approx 2$ must be due to the corresponding olefin cation radicals. Although we have not obtained hyperfine coupling for **3** (the EPR spectra ($CFCl_3$, T = 140 K) of the cation radicals of styrene (resolved multiplet) and *cis*-stilbene (broad singlet) are known),[18] we attribute this to the proximity of the organic radical to the iron porphyrin. The fact that the signal of **3** is somewhat broader than that of **3a** is consistent with expectation, considering the much smaller hyperfine coupling constant of deuterium.[19] In conclusion, on the basis of the EPR and NMR investigations, we suggest that **3** is an ET complex, $[(TMP^{\bullet+})Fe^{III}(O)(OClO_3)]^-[styrene]^{\bullet+}$, formed by one-electron transfer from styrene to **1**-$OClO_3$, resulting in an oxygen−iron bond order of 1.5 in **3**. The presence of the oxy ligand in **3** is required in order to accommodate the reactivity data (*vide supra*) and is supported by independent evidence for a similar species, $(TMP^{\bullet+})Fe^{III}(OH)(ClO_4)$.[20]

Several NMR experiments were performed in order to confirm that **3** is on the main reaction pathway from reactants to products (Scheme 2).

Scheme 2



Complex **3** was stable in solution at temperatures up to −30 °C, at which it was slowly converted to **2**-$OClO_3$. GC analysis (quenching at −30 °C) showed that styrene oxide (17%) and phenylacetaldehyde (5%) were formed.[21] In a similar experiment, 100 equiv of styrene was added to a solution of **1**-Trif, the least reactive $\mathbf{1}^+$ complex to react with styrene at −80 °C and produce styrene oxide. Examination of the spectrum after about 5 min revealed a mixture of **1**-Trif (the reactant), **2**-Trif (the product), and a complex very similar to **3** (**3**-Trif). In about 2 h both **1**-Trif and **3**-Trif were fully converted into **2**-Trif, still at −80° C. By choosing a ratio of 30:1 between styrene and the more reactive **1**-Cl complex, we could observe **1**-Cl and **2**-Cl simultaneously, but in this case only a clean conversion to **2**-Cl was observed, without any intermediate. Our conclusion is that the axial ligand in **1**-X determines if an intermediate is formed in observable quantities and if it will react further to the final iron(III) product at low temperatures. An even more conclusive experiment was performed on **3** itself, by changing its axial ligand via addition of CD_3OD to a preformed solution of **3** at −80 °C. About 5 min after the addition of CD_3OD, the spectrum of **3** was fully replaced by that of a mixture of **1**-$ODCD_3$ and **2**-$ODCD_3$. This must mean that **3** was destabilized by the ligand exchange of ClO_4^- by CD_3OD and that it was converted into a mixture of the reactant (**1**-$ODCD_3$) and the product (**2**-$ODCD_3$).[22] In the course of an hour the spectrum changed gradually to that of **2**-$ODCD_3$ alone, while GC analysis revealed the formation of styrene oxide (24%) and phenylacetaldehyde (20%). All these observations clearly demonstrate that complex **3** is a true intermediate in the reaction of **1**-$OClO_3$ with styrene and suggest strongly that similar complexes lie on the reaction pathway of the other **1**-X complexes as well.

In conclusion, we have trapped an intermediate in the reaction of oxoiron(IV) porphyrin cation radical complexes with olefins, identified it as an ET complex,[23] and provided evidence that it lies along the reaction pathway to the final products.

Acknowledgment. We are grateful to Prof. J. T. Groves (Princeton University) for very helpful discussions and correspondence. This research was supported by the Henri Gutwirth Fund for the Promotion of Research.

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(17) Complex **4** was obtained by oxidation of (TMP)FeCl by [dibenzo-1,4-dioxin cation radical]$^{\bullet+}$[$SbCl_6^-$] as described in ref 16. Its NMR spectrum is completely different from that with two identical axial ligands, $(TMP^{\bullet+})Fe(ClO_4)_2$, which was reported by Groves et al.: Groves, J. T.; Quinn, R.; McMurry, T. J.; Lang, G.; Boso, B. *J. Chem. Soc., Chem. Commun.* **1984**, 1445.

(18) Bonazzola, L.; Michaut, J.-P.; Roncin, J.; Misava, H.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1990**, 347.

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(21) One referee has pointed out that the epoxide/aldehyde ratio in the present study is substantially lower than in other reports[10d] and has suggested that an axial ligand effect might be involved in the higher ratios. Other variables must be important, too, since we have found in preliminary studies of this subject that the rate at which solutions of **3** were warmed up affected the product ratio significantly.

(22) The reversibility of the formation of the intermediate and the effect of MeOH on its decomposition were previously observed in kinetic studies as well.[10d,f]

(23) One referee has suggested that the ET process is accompanied by bond formation, formulating complex **3** as $(TMP^{\bullet+})Fe^{III}(OClO_3)(OCH_2\text{-}CH^{\bullet}C_6H_5)$. Although this possibility cannot be ruled out by our results, it is disfavored by secondary isotope effect studies.[7b]