Reversible Formation of Iodosylbenzene–Iron Porphyrin Intermediates in the Reaction of Oxoiron(IV) Porphyrin π-Cation Radicals and Iodobenzene**

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High-valent oxoiron(IV) porphyrin π-cation radicals **2** are generally accepted to be the key reactive intermediates in a variety of oxidation reactions by heme-containing enzymes such as cytochromes P450, peroxidases, and catalases.[1,2] Extensive studies with synthetic iron(III) porphyrin complexes and various terminal oxidants have shown that **2** is generated by heterolytic O−X bond cleavage of $[(\mathrm{Porp})\mathrm{Fe^{III}\text{-}O\text{-}X}]^+$ (**1**) [path A in Eq. (1)].[3] In contrast, there are only two reported instances of the reverse reaction, O−X bond formation between **2** and X [path B in Eq. (1)], as biomimetic examples of haloperoxidases.[4] One is the oxo transfer from an oxomanganese(V) porphyrin complex to bromide ($\mathrm{Br^-}$),[4a] and the other is the generation of a $[(\mathrm{Porp})\mathrm{Fe^{III}\text{-}OCl}]$ complex in the reaction of **2** and $\mathrm{Cl^-}$.[4b]

$$[(\mathrm{Porp})\mathrm{Fe^{III}}]^+ + \mathrm{OX} \rightleftharpoons [(\mathrm{Porp})\mathrm{Fe^{III}\text{-}O\text{-}X}]^+\ (\mathbf{1}) \underset{\mathrm{B}}{\overset{\mathrm{A}}{\rightleftharpoons}} [(\mathrm{Porp})^{+\cdot}\mathrm{Fe^{IV}{=}O}]^+\ (\mathbf{2}) + \mathrm{X} \qquad (1)$$

Iodosylbenzene (PhIO) has been widely used as a terminal oxidant in metal-complex-catalyzed oxidation reactions.[1d] We have shown recently that the reaction of $[\mathrm{Fe(TMP)(CF_3SO_3)}]$[5] with PhIO generates a $[(\mathrm{TMP})^{+\cdot}\mathrm{Fe^{IV}{=}O}]^+$ complex.[6] Although the presence of the iodosylbenzene–iron porphyrin intermediates, [(Porp)Fe-OIPh], has been suggested in PhIO reactions,[7] such intermediates have not been isolated or characterized previously. Herein, we report evidence for the formation of the new $[(\mathrm{Porp})\mathrm{Fe^{III}\text{-}OIPh}]^+$ intermediates **3** in the reaction of $[(\mathrm{Porp})^{+\cdot}\mathrm{Fe^{IV}{=}O}]^+$ complexes and iodobenzene [Eq. (2)]. We also show that the formation of **3** depends on the electronic nature of iron porphyrin complexes and iodobenzene derivatives, and that an equilibrium between **2** and **3** exists. Reactions of oxygen atom transfer from **3** to olefins are briefly discussed as well.

$$[(\mathrm{Porp})^{+\cdot}\mathrm{Fe^{IV}{=}O}]^+\ (\mathbf{2}) + \mathrm{PhI} \rightleftharpoons [(\mathrm{Porp})\mathrm{Fe^{III}{-}O{-}IPh}]^+\ (\mathbf{3}) \qquad (2)$$

Treatment of triflate iron(III) porphyrin complexes, $\mathrm{Fe(TDCPP)(CF_3SO_3)}$ and $\mathrm{Fe(TDFPP)(CF_3SO_3)}$,[5] with 1.2 equiv *m*-chloroperbenzoic acid (*m*-CPBA) in a solvent mixture of $\mathrm{CH_3CN}$ and $\mathrm{CH_2Cl_2}$ at −40°C resulted in the formation of oxoiron(IV) porphyrin π-cation radicals, $[(\mathrm{TDCPP})^{+\cdot}\mathrm{Fe^{IV}{=}O}]^+$ (**2a**) and $[(\mathrm{TDFPP})^{+\cdot}\mathrm{Fe^{IV}{=}O}]^+$ (**2b**), (Figure 1).[8] Upon the addition of 30 equiv PhI to the reaction solutions containing **2a** and **2b**, the color of the reaction solutions immediately changed from green to reddish brown. The formation of new intermediates, **3a** and **3b**, was confirmed by the disappearance of features characteristic of $[(\mathrm{Porp})^{+\cdot}\mathrm{Fe^{IV}{=}O}]^+$ complexes (a weak Soret band and broad Q bands around 500–750 nm) and the appearance of a strong Soret band at ≈420 nm and a Q band at ≈535 nm in the UV/Vis spectra (Figure 1).

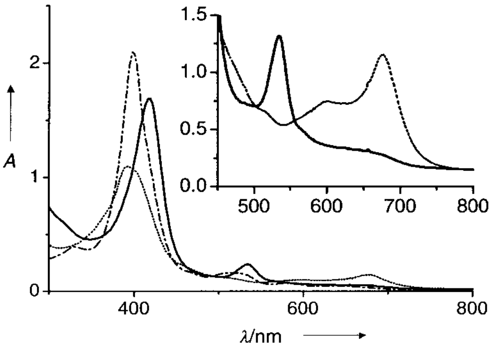

Figure 1. UV/Vis spectra of $[\mathrm{Fe(TDCPP)(CF_3SO_3)}]$ (-·-·-), **2a** (····), and **3a** (——). Reaction conditions: the addition of *m*-CPBA (1×10^{-3} mmol, diluted in 50 μL of $\mathrm{CH_3CN}$) into a 0.1 cm UV cuvette containing a solution of $[\mathrm{Fe(TDCPP)(CF_3SO_3)}]$ (2×10^{-4} mmol) in a solvent mixture (1 mL) of $\mathrm{CH_3CN}$ and $\mathrm{CH_2Cl_2}$ (3:1) at −40°C resulted in the formation of **2a**. Subsequent addition of PhI (30 equiv, diluted in 50 μL of $\mathrm{CH_3CN}$) to the cuvette containing **2a** led to the immediate formation of **3a**. Inset: Q-band region of **2a** (1 mM) and **3a** (1 mM). UV/Vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer equipped with an Optostat^{DN} variable-temperature liquid-nitrogen cryostat (Oxford Instruments).

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author. Table S1 contains results of ^{18}O-labeled water experiments performed with $[(\mathrm{Porp})\mathrm{Fe^{III}{-}OIPh}]^+$ and $[(\mathrm{Porp})^{+\cdot}\mathrm{Fe^{IV}{=}O}]^+$ intermediates (1 page). Details of the Fe K-edge XAS characterization of **2b** and **3b**, experimental data and fits (Figure S1 and S2).

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Insight into the nature of **3b** has been gained from further spectroscopic studies. Upon the addition of 30 equiv PhI to **2b**, the characteristic $S = 3/2$ EPR signals of **2b** were replaced by new features at $g = 5.7$ and 2.0, which indicates the formation of an axially symmetric $S = 5/2$ species (data not shown).[8,9] This observation suggests the reduction of the oxoiron(IV) porphyrin π-cation radical to a high-spin iron(III) state. The disappearance of the high-valent iron-oxo species upon the addition of PhI was confirmed by X-ray absorption spectroscopy (Figure 2). Complex **2b** exhibits an intense 1s→3d pre-edge transition with an area of 38(2) units; this value is much higher than is commonly observed for five-coordinate iron complexes (12–20 units)[10] and can be attributed to the significant distortion imposed by the oxo ligand on the iron coordination environment.[10,11] EXAFS analysis of **2b** shows that its first coordination sphere consists of 1 N/O at 1.67 Å,[11] assigned to the oxo ligand, and 4 N at 2.00 Å, assigned to the porphyrin nitrogen atoms (Figure S1, Supporting Information). Upon conversion into **3b**, its 1s→3d pre-edge transition is halved in intensity to 17(2) units, the 1.67 Å Fe–O distance is no longer observed, and the average Fe–N distance lengthens to 2.07 Å (Figure S2, Supporting Information). Taken together, the spectroscopic data show that PhI reduces the oxoiron(IV) porphyrin π-cation radical to a high-spin Fe^{III} complex; in turn the oxo group must then be transferred to PhI, presumably forming PhIO coordinated to the iron(III) center (see below).

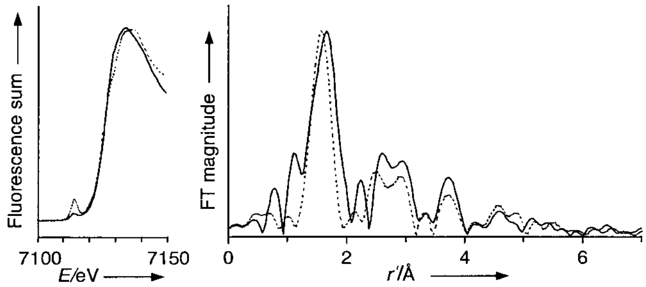

Figure 2. X-ray absorption near-edge structures (Fe K-edge XANES, fluorescence excitation, left panel) and Fourier transforms of the Fe K-edge EXAFS data (right panel) of **2b** (---) and **3b** (——) in frozen CH_3CN solution at T = 10–15 K.

The formation of the intermediates **3** in the reactions of **2** and PhI depends significantly on the electronic nature of the iron porphyrin complexes and iodobenzene derivatives. For example, **3** was not observed in the reaction of PhI and $[(TMP)^{+\bullet}Fe^{IV}{=}O]^+$, which contains an electron-rich porphyrin ligand, under identical reaction conditions. Similarly, **3a** and **3b** do not form in the reactions of **2a** and **2b** with the electron-poor F_5C_6I. Interestingly, in the intermediate case of 1,2-difluoro-4-iodobenzene ($F_2C_6H_3I$), both **2** and the new intermediate **3** were present in the reaction solutions, and the amount of **3** observed was proportional to the amount of $F_2C_6H_3I$ added to the reaction solutions (Figure 3). These results demonstrate clearly that there is an equilibrium between **2** and **3** [Eq. (2)], which favors the new intermediate **3** when the porphyrin ligand of $[(Porp)^{+\bullet}Fe^{IV}{=}O]^+$ complexes is electron-deficient and/or the iodobenzene derivative is electron-rich.

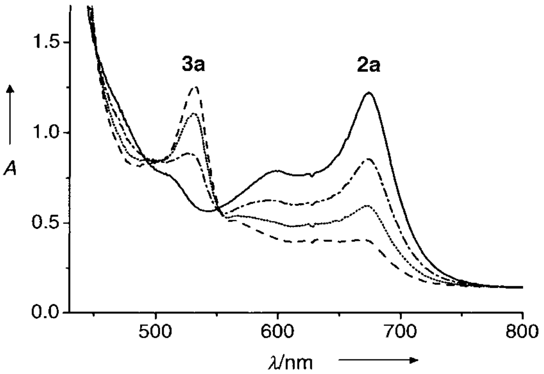

Figure 3. UV/Vis spectra showing the formation of **3a** as a function of the amount of 1,2-difluoro-4-iodobenzene ($F_2C_6H_3I$) added to the solution of **2a**. Reaction conditions: **2a** (1 mM) was prepared as described in Figure 1. $F_2C_6H_3I$ (diluted in 50 μL of CH_3CN) was added to the solution of **2a** (**2a**, ——; **2a** + 5 equiv $F_2C_6H_3I$, -·-·-; **2a** + 20 equiv $F_2C_6H_3I$, ·····; **2a** + 60 equiv $F_2C_6H_3I$, ---).

The reactivity of **3** towards olefins was then examined. Addition of olefins to **3a** and **3b** converted these intermediates immediately back into the starting iron(III) porphyrins, and analysis of the resulting solutions revealed epoxides as major products with retention of stereochemistry (Table 1). Interestingly, the epoxidation of cyclohexene by **3a** and **3b**, when performed in the presence of $H_2{}^{18}O$,[12] resulted in ≈92% ^{18}O incorporation from $H_2{}^{18}O$ into the cyclohexene oxide product, while **2a** and **2b** under the same conditions afforded 7% ^{18}O incorporation (Scheme 1; also see Table S1, Supporting Information). These results demonstrate that the intermediates **3a** and **3b** readily exchange their oxygen atoms with labeled water. Because it has been suggested previously that the exchange of the iodosylbenzene oxygen with labeled water is greatly facilitated by the coordination of iodosylbenzene to a Lewis acidic metal center [Eq. (3)],[13] the observation of such a high ^{18}O incorporation in the reactions of **3a**

Table 1: Epoxidation of olefins by in situ generated **3a** and **3b**.[a]

Substrate	Products	Yields [%][b] **3a**	 **3b**
cyclohexene	cyclohexene oxide	72	65
	cyclohexenol	<2	<2
	cyclohexenone	<1	<1
cis-stilbene	*cis*-stilbene oxide	63	56
	trans-stilbene oxide	<1	<1
	benzaldehyde	<2	<2

[a] All reactions were monitored by UV/Vis spectral changes of reaction solutions. Reaction conditions: **2a** and **2b** were prepared by reacting triflate iron(III) porphyrin complexes (1×10^{-3} mmol) with 1.2 equiv *m*-CPBA (1.2×10^{-3} mmol, diluted in 50 μL of CH_3CN) in a solvent mixture (0.5 mL) of CH_3CN and CH_2Cl_2 (3:1) at −40 °C. **3a** and **3b** were prepared by adding 30 equiv PhI (3×10^{-2} mmol, diluted in 50 μL of CH_3CN) to the reaction solutions containing **2a** and **2b**. Oxygenation reactions were performed by the addition of olefins (0.1 mmol, diluted in 50 μL of CH_2Cl_2) to the reaction solutions of **3a** and **3b** at −40 °C. PPh_3 (1×10^{-2} mmol, diluted in 50 μL of CH_3CN) was added to the reaction mixture prior to product analyses. [b] Based on the amounts of **3a** and **3b** prepared. Errors are within ± 15% of the stated values.

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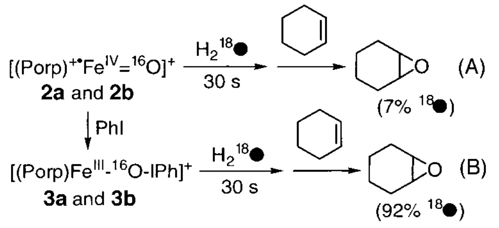

Scheme 1. Results of ^{18}O-labeled water experiments.

and **3b** strongly supports the coordination of PhIO to the iron center in **3**.[7,14,15]

$$LM^{n+}-{}^{16}O-I-Ph + H_2^{18}\bullet \rightleftharpoons LM^{n+}-{}^{18}\bullet-I-Ph + H_2^{16}O \qquad (3)$$

In summary, we have demonstrated that new $[(Porp)Fe^{III}-OIPh]^+$ intermediates are generated in the reaction of $[(Porp)^{+\bullet}Fe^{IV}=O]^+$ and PhI and that the electronic nature of iron porphyrin complexes and iodobenzene derivatives markedly influences the equilibrium between these two forms. The observation that olefins are epoxidized upon their addition to solutions of **3** raises the possibility that **3** itself may be the epoxidizing agent. This is an intriguing prospect, but we cannot at present exclude the possibility that the small amount of **2** present in the equilibrium between **2** and **3** is responsible for the observed reactivity.[16] Future studies will be directed towards addressing the question of whether such a "second oxidant" is involved in the olefin epoxidations.[17,18]

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[5] Abbreviations of porphyrin ligands: TMP = *meso*-tetramesitylporphinato dianion; TDCPP = *meso*-tetrakis(2,6-dichlorophenyl)porphinato dianion; TDFPP = *meso*-tetrakis(2,6-difluorophenyl)porphinato dianion.

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[16] We have shown very recently that when the anionic ligand of iron(III) porphyrin catalysts is the triflate anion ($CF_3SO_3^-$), oxoiron(IV) porphyrin π-cation radicals are the reactive epoxidizing intermediate in the catalytic epoxidation of olefins by PhIO: W. Nam, S. W. Jin, M. H. Lim, J. Y. Ryu, C. Kim, *Inorg. Chem.* **2002**, *41*, 3647–3652.

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