Supporting Information

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

Wonwoo Nam,*† Sun Kyung Choi,† Mi Hee Lim,†‡ Jan-Uwe Rohde,‡ Inwoo Kim,† Jinheung Kim,§ Cheal Kim,⊥ and Lawrence Que, Jr.*‡

†Department of Chemistry and Division of Molecular Life Sciences, Ewha Womans University, Seoul 120-750, Korea
‡Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, Minnesota 55455, USA
§Department of Chemical Technology, Changwon National University, Kyungnam 641-773, Korea
⊥Department of Fine Chemistry, Seoul National University of Technology, Seoul 139-743, Korea.
Table S1. Percentages of $^{18}$O-incorporation from H$_2^{18}$O into cyclohexene oxide in the epoxidation of cyclohexene by *in situ* generated [(Porp)Fe$^{III}$-OIPh]$^+$ and [(Porp)$^{IV}$Fe=O]$^+$ complexes.\[^{a,b}\]

<table>
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<th>$^{18}$O (%) in cyclohexene oxide$^{[c,d]}$</th>
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<tr>
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<td>[(Porp)Fe$^{III}$-OIPh]$^+$ [(Porp)$^{IV}$Fe=O]$^+$</td>
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<tr>
<td>3a 3b</td>
<td>93 ± 3 92 ± 3 7 ± 2 7 ± 2</td>
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<td>(69)  (63)  (64)  (56)</td>
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</table>

[a] All reactions were run at least in triplicate, and the data reported represent the average of these reactions.  

[b] The reaction procedures for the preparation of the intermediates, 2a, 2b, 3a, and 3b, were the same as those described in Table 1, footnote a.  H$_2^{18}$O (3 µL, 95% $^{18}$O enriched, diluted in 50 µL of CH$_3$CN) was added to a 0.1-cm UV cuvette containing a reaction solution of in situ generated intermediate (2 mM) in a solvent mixture of CH$_3$CN and CH$_2$Cl$_2$ (3:1) at –40 °C.  After 30 s incubation, cyclohexene (0.1 mmol, diluted in a solvent mixture (50 µL) of CH$_3$CN and CH$_2$Cl$_2$ (3:1)) was injected into the reaction solution.  Then, the reaction mixture was directly analyzed by GC/MS (Hewlett-Packard 5890 II Plus gas chromatograph interfaced with Hewlett-Packard Model 5989B mass spectrometer).  $^{16}$O and $^{18}$O compositions in cyclohexene oxide were determined by the relative abundances of mass peaks at m/z = 83 for $^{16}$O and 85 for $^{18}$O.  

[c] $^{18}$O-percentages were calculated based on the mass balance of oxygen derived from H$_2^{18}$O (95% $^{18}$O).  

[d] Numbers in parentheses are the percent yields of cyclohexene oxide based on the intermediates prepared.  Errors are within ±15% of the stated values.
XAS Characterization of

\[(\text{TDFPP})^+\text{Fe}^{\text{IV}}=\text{O}^+] (2b)\) and \[(\text{TDFPP})\text{Fe}^{\text{III}}-\text{OIPh}]^+ (3b)\)

**Reaction Conditions and Sample Preparation:** 2b was generated from [Fe(TDFPP)(CF₃SO₃)] (6 mM in 2 mL CH₃CN) by adding m-CPBA (7.2 mM in 50 µL CH₃CN) at –40 ºC. 3b was generated from [Fe(TDFPP)(CF₃SO₃)] (6 mM in 2 mL CH₃CN) by adding m-CPBA (7.2 mM or 12 mM in 50 µL CH₃CN) at –40 ºC and subsequent addition of PhI (180 mM in 50 µL CH₃CN). Ca. 0.5 ml solution was transferred into a pre-cooled sample cell, covered with Mylar tape, which was then submerged in liquid nitrogen.

**XAS Data Collection and Analysis:** Fe K-edge X-ray absorption spectra (XAS, fluorescence excitation, Ge detector) were recorded on frozen CH₃CN solutions at 10–15 K over the energy range 6.9–8.0 keV. The monochromator was calibrated using the K-edge energy of iron foil at 7112.0 eV (beamline X9B at NSLS, Brookhaven National Laboratory, and beamline 7-3 at SSRL, Stanford Linear Accelerator Center). Data reduction and analysis have been discussed in detail in review articles. Here, the programs EXAFSPAK and SSExafs have been used. General procedures for analysis using the program SSExafs have been described elsewhere.

**Fourier Transforms and Fitting Results:** The \(r'\) space spectrum of 2b exhibits prominent features centered at \(r' = 1.6, 2.5, \) and 2.9 Å (Figure S1), where \(r'\) corresponds to the actual metal-scatterer distance \(r\) after a phase shift correction of approximately 0.4 Å \((r \approx r' + 0.4 \text{ Å})\). The \(r'\) space spectrum of 3b exhibits prominent features centered at \(r' = 1.7, 2.6 \) and 2.9 Å (Figure S2). Furthermore, the Fourier Transforms of 2b and 3b have peaks near 3.3, 3.7, and 4.6 Å in common, which can be assigned to carbon scatterers of the porphinato ligand.

The best fit to the Extended X-ray Absorption Fine Structure (EXAFS) data of 2b consists of four shells: 1 N/O at 1.67 Å, 4 N at 2.00 Å, 8 C at 3.02 Å, and 4 C at 3.35 Å, accounting for a multiply bound oxo group, the nitrogen donor atoms, and \(\alpha\) and \(meso\) carbon atoms of the porphinato ligand (Figure S1). The first-shell fitting is performed on the basis of nitrogen scatterers, because backscattering atoms which differ in \(Z\) by 1 are typically not distinguished by EXAFS. The characterization of 2b is in good agreement with results for corresponding
complexes bearing the TMP ligand: \[(\text{TMP})^+\text{Fe}^{IV}\text{=O}(X)] / [(\text{TMP})\text{Fe}^{IV}\text{=O}(X)]^– (\text{TMP} = 5,10,15,20\text{-tetramesitylporphinato dianion, } X = \text{Cl, Br})\].

The first coordination sphere of \(3b\) can be fit well with a single shell of 5 N at 2.06 Å (Figure S2). Though the five-coordinate model affords the most reasonable combination of Debye-Waller factors and goodness-of-fit values (GOF), the question, whether the iron center is five or six-coordinate in this complex, cannot be determined due to the limited accuracy for coordination numbers as determined by EXAFS analysis.\(^2,5\) The small Debye-Waller factors of the N and C shells in \(2b\) and \(3b\) indicate a small spread of Fe–N and Fe···C distances in the rigid porphinato ligand. Distances between the metal center and the atoms of the porphinato ligand, as determined from the best fit, are comparable to those of \([(\text{TDFPP})\text{Fe–OCH}_3]\) established by single crystal structure determination: 4 N at 2.05–2.10 Å, 8 C at 3.04–3.14 Å, and 4 C at 3.48–3.53 Å.\(^7\)


Figure S1. Fourier transform of the Fe K-edge EXAFS data ($r'$ space) and Fourier-filtered EXAFS spectrum ($k^3 \chi'(k)$, inset) of [(TDFPP)$^{4+}$Fe$^{IV}$=O]$^+$ (2b), Fourier-transformed range $k = 2$–15 Å$^{-1}$ (Back-transformation range $r' = 0.85$–3.20 Å), experimental data (●●●) and best fit (—). Fitting: 1 N/O at 1.67 Å ($\Delta \sigma^2$, $-0.0009 \text{Å}^2$), 4 N at 2.00 Å (0.0007), 8 C at 3.02 Å (0.0044), and 4 C at 3.35 Å ($-0.0001$).
Figure S2. Fourier transform of the Fe K-edge EXAFS data ($r'$ space) and Fourier-filtered EXAFS spectrum ($k^2 \chi(k)$, inset) of [(TDFPP)Fe$^{III}$–OIPh]$^+$ (3b), Fourier-transformed range $k = 2$–15 Å$^{-1}$ (Back-transformation range $r' = 0.55$–3.50 Å), experimental data (•••) and best fit (—). Fitting: 5 N at 2.06 Å ($\Delta \sigma^2$, 0.0014 Å$^2$), 8 C at 3.06 Å (0.0014), 4 C at 3.41 Å (0.0004).