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Electron Transfer Mechanism in the Oxidation of Aryl 1-Methyl-1-phenylethyl Sulfides Promoted by Nonheme Iron(IV)−Oxo Complexes: The Rate of the Oxygen Rebound Process

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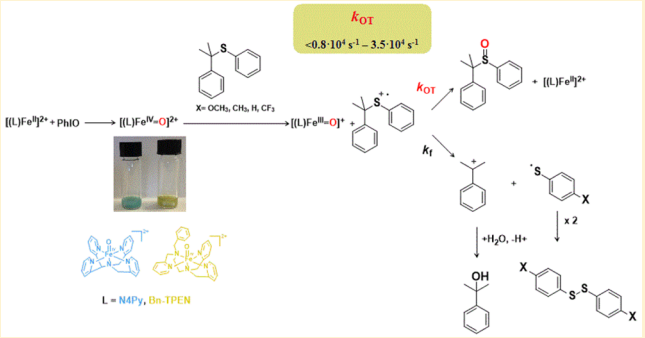
Supporting Information

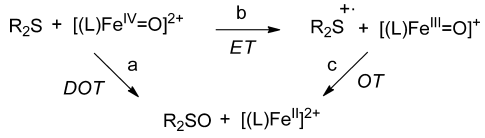
ABSTRACT: The oxidation of aryl 1-methyl-1-phenylethyl sulfides promoted by the nonheme iron(IV)−oxo complexes $[(N4Py)Fe^{IV}{=}O]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$ occurs by an electron transfer−oxygen rebound (ET−OT) mechanism leading to aryl 1-methyl-1-phenylethyl sulfoxides accompanied by products derived from C_α−S fragmentation of sulfide radical cations (2-phenyl-2-propanol and diaryl disulfides). For the first time, the rate constants for the oxygen rebound process (k_{OT}), which are in the range of $<0.8 \times 10^4$ to 3.5×10^4 s^{-1}, were determined from the fragmentation rate constants of the radical cations (k_f) and the S oxidation/fragmentation product ratios.



INTRODUCTION

The oxidation of sulfides to sulfoxides represents one of the most important processes catalyzed by heme and nonheme iron enzymes that has attracted a great deal of interest in view of its relevance in organic synthesis.[1] A great number of heme and nonheme iron complexes, which can mimic the activity of such enzymes, were found to efficiently catalyze the oxidation of sulfides to sulfoxides.[2−15] Product analyses have been accompanied by several mechanistic studies that aimed to ascertain the role of electron transfer processes in the oxidation of sulfides promoted by the active species, high valent iron−oxo complexes. In fact, formation of sulfoxide products can occur either by a direct oxygen transfer or "oxene process" [DOT (Scheme 1, path a)] or by a sequential electron transfer−oxygen transfer process [ET−OT (Scheme 1, paths b and c)].[6−10,16−21]

Scheme 1. DOT versus ET−OT Mechanism for the Oxidation of Sulfides to Sulfoxides Promoted by High Valent Iron(IV)−Oxo Complexes



In this context, we have recently investigated the oxidation of a series of aryl diphenylmethyl sulfides by the nonheme iron(IV)−oxo complex, $[(N4Py)Fe^{IV}{=}O]^{2+}$ [N4Py = *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine] in CH_3CN.[22] Product analysis revealed that formation of aryl diphenylmethyl sulfoxides was accompanied by the formation of fragmentation products (diphenylmethanol, benzophenone, and diaryl disulfides) that unequivocally demonstrated an ET−OT mechanism. Accordingly, these products originate from the fast fragmentation processes of radical cations, involving both C−H and C−S bond cleavage as indicated in Scheme 2.[23−28]

On the basis of the effect of aryl ring substituents on the product distribution, we provided strong evidence that fragmentation of radical cations competes with the oxygen rebound process (Scheme 2). It must be mentioned that while the oxidation of aryl diphenylmethyl sulfides by $[(N4Py)Fe^{IV}{=}O]^{2+}$ proceeds by an ET−OT mechanism, thioanisole oxidation by the same nonheme iron−oxo complex occurs by a DOT process.[9,16]

When an ET−OT mechanism is operating, it is possible to estimate the rate of the oxygen rebound step from the fragmentation rate constants of the sulfide radical cations and the product distribution (fragmentation products vs sulfoxides). For instance, this strategy was adopted for the oxidation of aryl

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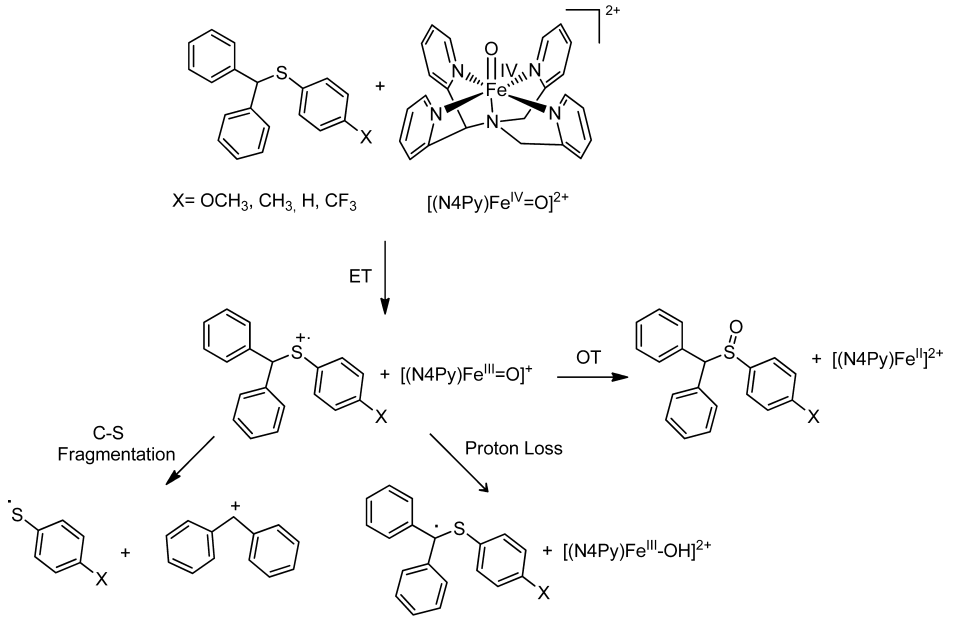
Scheme 2. Oxygen Rebound (OT) versus Fragmentation of Sulfide Radical Cations Generated by Oxidation of Aryl Diphenylmethyl Sulfides with $[(N4Py)Fe^{IV}{=}O]^{2+}$



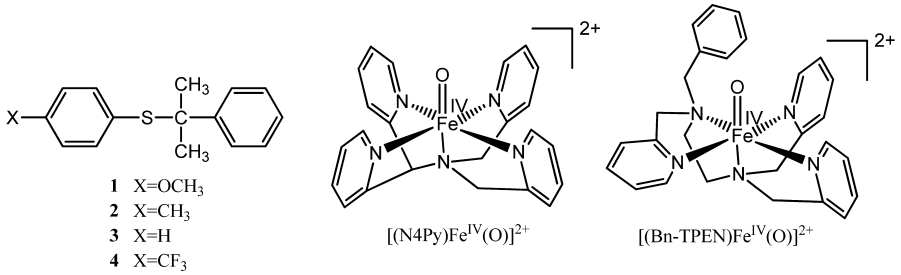


Figure 1. Aryl 1-methyl-1-phenylethyl sulfides **1**−**4** and nonheme iron(IV)−oxo complexes $[(N4Py)Fe^{IV}{=}O]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$.

benzyl sulfides with H_2O_2 catalyzed by horseradish peroxidase.[8] Though aryl diphenylmethyl sulfides represent suitable substrates for testing the intermediacy of radical cations in biomimetic oxidation processes,[6] the occurrence of both C−H and C−S bond cleavages represents a major drawback when the rate of the oxygen rebound process has to be determined. Because the rates of C−H bond cleavage in sulfide radical cations are dependent on the nature of the deprotonating base, it was not possible to directly compare the fragmentation rates of the radical cation in the biomimetic oxidation with those determined by laser flash photolysis (LFP) analysis of the photochemical oxidation of the same substrates performed in the presence of *N*-methoxyphenanthridinium hexafluorophosphate ($MeOP^+PF_6^-$)[22] because of the different bases involved in the C−H bond cleavage processes {$[(N4Py)Fe^{III}{=}O]^+$ and phenanthridine, respectively}. Accordingly, in the biomimetic oxidation promoted by $[(N4Py)Fe^{IV}{=}O]^{2+}$, a larger contribution of the C−S bond cleavage to the overall fragmentation process was observed whereas C−H bond cleavage prevailed in the photochemical process.[22]

For this purpose, to determine the rate of the oxygen rebound process from reduced nonheme iron−oxo complexes to aryl sulfide radical cations (Scheme 1, path c), we have investigated the oxidation of a series of aryl 1-methyl-1-phenylethyl sulfides (**1**−**4**) promoted by two nonheme iron(IV)−oxo complexes: $[(N4Py)Fe^{IV}{=}O]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$ [Bn-TPEN = *N*-benzyl-*N*,*N*′,*N*′-tris(2-pyridylmethyl)-1,2-diaminoethane] (Figure 1). Because no cleavable benzylic C−H bonds are present in the α position with respect to the S atom, fragmentation of radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ exclusively involves the cleavage of the C_α−S bond, as observed in the photochemical oxidations of aryl 1-methyl-1-arylethyl sulfides with $MeOP^+PF_6^-$ and 9,10-dicyanoanthracene/O_2 systems.[26,28]

RESULTS AND DISCUSSION

For product analysis of the biomimetic oxidations, aryl 1-methyl-1-phenylethyl sulfides (**1**−**4**) (50 μmol) were added to a solution of the iron(IV)−oxo complexes prepared by oxidation of $[(N4Py)Fe^{II}]^{2+}$ or $[(Bn\text{-}TPEN)Fe^{II}]^{2+}$ (2.5 μmol) with PhIO[18] (12.5 μmol) in CH_3CN (0.5 mL) and stirred at 0 °C for 90 and 30 min, respectively. The exclusive reaction products, identified by GC, GC−MS, HPLC, and ^{1}H NMR analyses (comparison with authentic specimens), were 2-phenyl-2-propanol, diaryl disulfides, and aryl 1-methyl-1-phenylethyl sulfoxides. In all cases, material recovery was satisfactory (>95%). No products were formed in the absence of PhIO, while small amounts of aryl 1-methyl-1-phenylethyl sulfoxides (<1%, referenced to the amount of oxidant) were observed in the oxidation with PhIO in the absence of nonheme complex $[(N4Py)Fe^{II}]^{2+}$ or $[(Bn\text{-}TPEN)Fe^{II}]^{2+}$.

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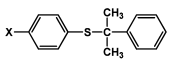
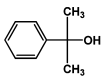
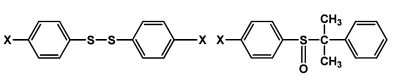
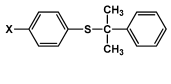
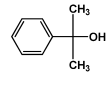
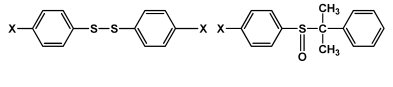
Table 1. Products and Yields of the Oxidation of Aryl 1-Methyl-1-phenylethyl Sulfides (1−4) by $[(N4Py)Fe^{IV}{=}O]^{2+}$ in CH_3CN at 0 °C[a]

Substrate	Products (Yields %)[b]			Ratio [OH]/[SO]
				
1 X=OCH_3	31±2	14±1	64±5	0.48
2 X=CH_3	39±2	15±1	44±4	0.89
3 X=H	40±4	16±2	25±2	1.6
4 X=CF_3	48±5	22±2	8.4±0.5	5.7

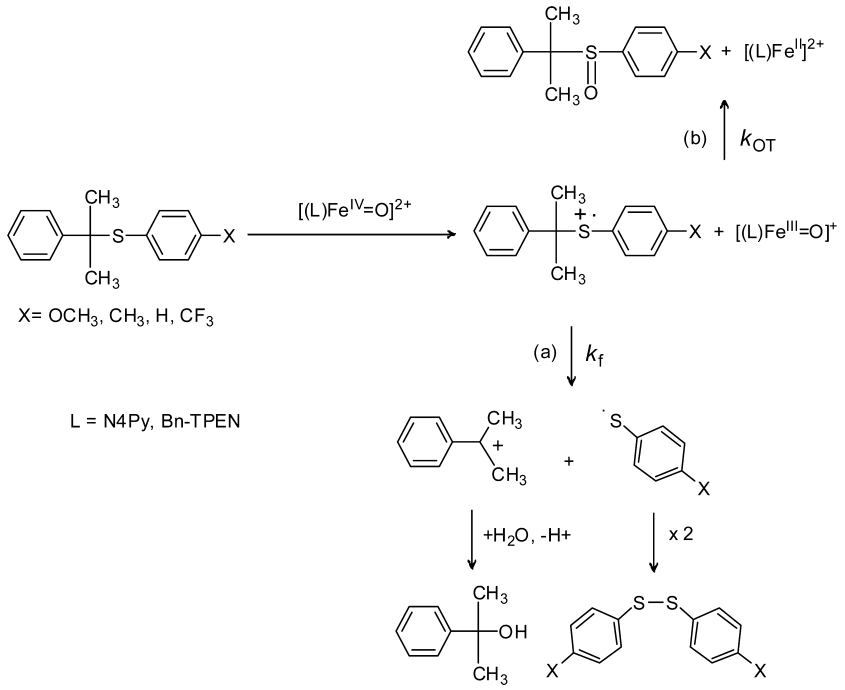
[a]Iodosylbenzene (12.5 μmol), $[(N4Py)Fe^{II}(OTf)_2]$ (2.5 μmol), and aryl 1-methyl-1-phenylethyl sulfides (50 μmol) in CH_3CN (500 μL). [b]Yields (in mole percent) refer to the amount of oxidant PhIO.

Table 2. Products and Yields of the Oxidation of Aryl 1-Methyl-1-phenylethyl Sulfides (1−4) by $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$ in CH_3CN at 0 °C[a]

Substrate	Products (Yields %)[b]			Ratio [OH]/[SO]
				
1 X=OCH_3	56±4	27±2	44±4	1.3
2 X=CH_3	62±5	25±2	33±2	1.9
3 X=H	64±6	28±4	18±2	3.6
4 X=CF_3	70±5	27±3	10±1	7.0

[a]Iodosylbenzene (12.5 μmol), $[(Bn\text{-}TPEN)Fe^{II}(OTf)_2]$ (2.5 μmol), and aryl 1-methyl-1-phenylethyl sulfides (50 μmol) in CH_3CN (500 μL). [b]Yields (in mole percent) refer to the amount of oxidant PhIO.

Scheme 3. Fragmentation versus Oxygen Rebound Processes in the Oxidation of Aryl 1-Methyl-1-phenylethyl Sulfides (1−4) by $[(N4Py)Fe^{IV}{=}O]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$ in CH_3CN



Products and yields, referenced to the amount of oxidant, are reported in Tables 1 and 2 for the oxidations promoted by $[(N4Py)Fe^{IV}{=}O]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$, respectively.

From the data reported in Tables 1 and 2, it can be readily noted that higher yields of oxidation products are observed for the oxidations promoted by $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$ than for

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those promoted by $[(N4Py)Fe^{IV}{=}O]^{2+}$, in accordance with the stronger oxidizing ability of the former iron(IV)−oxo complex as also found in the oxidation of *para*-substituted thioanisoles.[18] Moreover, regular increases in the total yields of oxidation products are observed with both iron−oxo complexes with an increase in the electron releasing power of the aryl substituents, in accordance with the electrophilic nature of the oxidizing species $[(N4Py)Fe^{IV}{=}O]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$.[18] As previously observed in the oxidation of aryl diphenylmethyl sulfide by $[(N4Py)Fe^{IV}{=}O]^{2+}$,[22] the S oxygenation products (sulfoxides) are accompanied by significant amounts of fragmentation products (2-phenyl-2-propanol and diaryl disulfides). Thus, also the oxidation of **1**−**4** promoted by $[(N4Py)Fe^{IV}{=}O]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$ involves an ET process with formation of radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$. C_α−S bond cleavage of $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ leads to the 2-phenyl-2-propyl cation and an arylsulfenyl radical as described in path a of Scheme 3. The cation leads to 2-phenyl-2-propanol by reaction with traces of water present in CH_3CN,[29] while arylsulfenyl radicals dimerize to diaryl disulfides.[26−28,32]

Fragmentation of radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ occurs in competition with the oxygen rebound process from the reduced iron(III)−oxo complexes to the radical cations leading to sulfoxides [OT (Scheme 3, path b)].[22] In accordance with the presence of the two competitive decay pathways for $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ (oxygen rebound and C_α−S fragmentation), a regular increase in the 2-phenyl-2-propanol/aryl 2-phenyl-2-propyl sulfoxide product ratios (Tables 1 and 2) is observed with an increase in the electron withdrawing (EW) effect of the aryl substituents as shown in Figure 2.

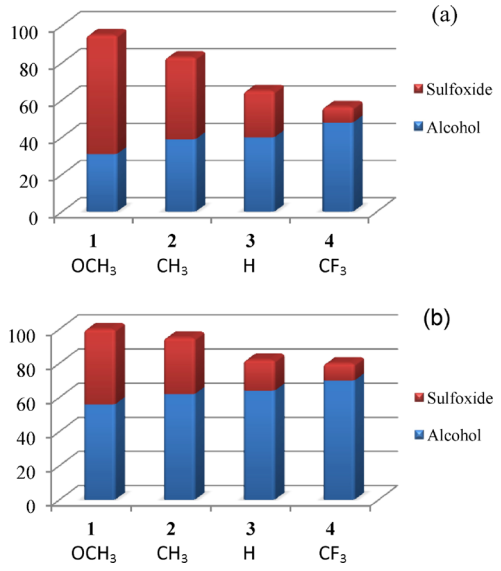

Figure 2. Yields (percent referenced to the amount of oxidant) of aryl 1-methyl-1-phenylethyl sulfoxides and 2-phenyl-2-propanol in the oxidation of aryl 1-methyl-1-phenylethyl sulfides **1**−**4** by (a) $[(N4Py)Fe^{IV}{=}O]^{2+}$ and (b) $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$ in CH_3CN at 0 °C.

Such an increase in the relative amount of the C_α−S fragmentation products observed with an increase in the EW power of the X substituents results from the enhancement of the fragmentation rate constants of the radical cations on going from $\mathbf{1}^{+\bullet}$ to $\mathbf{4}^{+\bullet}$, as already reported for the oxidation of aryl diphenylmethyl sulfides by $[(N4Py)Fe^{IV}{=}O]^{2+}$.[22] The rates of C_α−S bond cleavage of a series of aryl 1-methyl-1-arylethyl sulfide radical cations, including $\mathbf{1}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$, have been previously determined by laser flash photolysis (LFP) in the photochemical oxidation of the sulfides performed in the presence of $MeOP^+PF_6^-$ in CH_3CN at 25 °C.[26,33] In the same way, we have now determined the rate constants for fragmentation of $\mathbf{2}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ (k_f) at 0 °C by fitting the exponential decays at the maximum absorption wavelengths (see Experimental Section, Table 3, and Figures S5−S7).

Table 3 shows that fragmentation rates increase regularly from $\mathbf{1}^{+\bullet}$ to $\mathbf{4}^{+\bullet}$ in the same way as the 2-phenyl-2-propanol/aryl 1-methyl-1-phenylethyl sulfoxide molar ratios increase going from **1** to **4** as reported in Tables 1 and 2.

Because the radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ produced in the oxidations of **1**−**4** by $[(N4Py)Fe^{IV}{=}O]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$ undergo partitioning between the oxygen rebound and the C_α−S bond fragmentation shown in Scheme 3, it is possible to estimate the rate of the oxygen rebound step (k_{OT}) from the overall fragmentation rate (k_f) of the radical cations and the ratio of the yields of the sulfoxides and the fragmentation product 2-phenyl-2-propanol according to eq 1 (see Tables 1 and 2).[34] The values of k_{OT} are listed in columns 4 and 5 of Table 3 for $[(N4Py)Fe^{IV}{=}O]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$, respectively.

$$k_{OT} = k_f[ArSOC(CH_3)_2C_6H_5]/[C_6H_5C(CH_3)_2OH] \quad (1)$$

Interestingly, the k_{OT} values with all the sulfides and both nonheme iron(IV)−oxo complexes are on the same order of magnitude (see Table 3), thus supporting a common ET−OT oxidation mechanism involving a competition between the oxygen rebound (OT) and C_α−S fragmentation of radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$. The lower k_{OT} values found with $[(Bn\text{-}TPEN)Fe^{III}{=}O]^{+}$ can be reasonably explained on the basis of a stronger steric hindrance of Bn-TPEN with respect to that of the N4Py iron ligand. Finally, it has to be noted that the k_{OT} values are slightly higher than those determined in the oxidation of aryl benzyl sulfides with H_2O_2 catalyzed by horseradish peroxidase,[8] where the OT process involves the reaction of aryl sulfide radical cations with a heme iron(IV)−oxo complex.

CONCLUSIONS

The ET−OT mechanism previously proposed for the oxidation of aryl diphenylmethyl sulfides by $[(N4Py)Fe^{IV}{=}O]^{2+}$ is a rather general process that also operates with both *tert*-alkyl aryl sulfides, such as aryl 1-methyl-1-phenylethyl sulfides, and other nonheme iron(IV)−oxo complexes like $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$. The rate constant for the oxygen rebound step has been determined for the first time to range between $<0.8 \times 10^4$ and 3.5×10^4 s^{-1}, with values very close to those measured for the heme enzyme horseradish peroxidase. The dependence of the rate constants of the oxygen rebound process on the ligand and sulfide structures will be investigated in the future via the analysis of the oxidation of a more extended series of *tert*-alkyl aryl sulfides promoted by different nonheme iron(IV)−oxo complexes.

EXPERIMENTAL SECTION

Instruments and General Methods. Oxidation products were identified by comparison of their GC and/or GC−MS retention times with those of authentic compounds. GC analyses were conducted on a gas chromatograph equipped with a capillary methylsilicone column (30 m × 0.25 mm × 25 μm). GC−MS analyses were performed with a

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Table 3. Maximum Absorption Wavelengths and C_α−S Fragmentation Rate Constants (k_f) of Aryl 1-Methyl-1-phenylethyl Sulfide Radical Cations ($1^{+\bullet}$−$4^{+\bullet}$) Generated by Photooxidation of 1−4 Sensitized by $MeOP^+PF_6^-$ (λ_{exc} = 355 nm) and Oxygen Rebound Rate Constants (k_{OT}) for the Oxidation of 1−4 by $[(N4Py)Fe^{IV}{=}O]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$ in CH_3CN at 0 °C

	λ_{MAX}	$k_f(10^4\ s^{-1})^a$	$k_{OT}(10^4\ s^{-1})^b$	
			$[(N4Py)Fe^{IV}{=}O]^{2+}$	$[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$
1 X=OCH_3	570	< 1	< 2.1	< 0.8
2 X=CH_3	550	3.0	3.5	1.6
3 X=H	530	3.4	2.0	1.0
4 X=CF_3	510	6.7	1.2	0.9

[a]From LFP experiments in N_2-saturated CH_3CN, where [sulfide] = 1.0×10^{-2} M and $[MeOP^+PF_6^-] = 1.6 \times 10^{-4}$ M. [b]Calculated from eq 1.

mass detector (EI at 70 eV) coupled with a gas chromatograph equipped with a melted silica capillary column (30 m × 0.2 mm × 25 μm) covered with a methylsilicone film (5% phenylsilicone, OV5). HPLC analyses were performed on a chromatograph equipped with a C18 column (core−shell 5 μm, 25 mm × 4.6 mm). NMR spectra were recorded on a 300 MHz spectrometer and were internally referenced to the residual proton solvent signal. Laser flash photolysis experiments were performed with a laser kinetic spectrometer providing 8 ns pulses using the third harmonic (355 nm) of a Q-switched Nd:YAG laser. The laser energy was adjusted to ≤10 mJ/pulse through the use of the appropriate filter. A 3.5 mL Suprasil quartz cell (10 mm × 10 mm) was used for all experiments.

Materials. All commercial chemicals employed were of the highest purity available and used without further purification. CH_3CN (spectrophotometric grade) was distilled over CaH_2 under argon prior to use. *N*-Methoxyphenanthridinium hexafluorophosphate was prepared according to a literature procedure.[35] Iodosylbenzene was prepared by a literature method and stored at 0 °C under an inert atmosphere.[36] $(N4Py)Fe(OTf)_2$ and $(Bn\text{-}TPEN)Fe(OTf)_2$ were prepared by metalation of the ligand N4Py[37] and Bn-TPEN,[38] respectively, with $Fe(OTf)_2$ according to a literature method.[39] $[(N4Py)Fe^{IV}{=}O]$ and $[(Bn\text{-}TPEN)Fe^{IV}{=}O]$ were prepared by reacting $Fe(N4Py)(OTf)_2$ and $Fe(Bn\text{-}TPEN)(OTf)_2$, respectively, with excess solid PhIO.[39] Aryl 1-methyl-1-phenylethyl sulfides **1**−**3** were prepared by acid-catalyzed reaction of 4-X-thiophenols with 2-phenyl-2-propanol according to a literature method[40] and characterized according to the data reported in the literature.[26,41] 4-Trifluoromethylphenyl 1-methyl-1-phenylethyl sulfide **4** was prepared by a procedure reported in the literature[42] with some modification. A solution of 500 mg (2.8 mmol) of 4-trifluoromethylthiophenol in 0.8 mL of dry diethyl ether was added to phenylmagnesium bromide prepared from 420 mg (2.7 mmol) of bromobenzene and 68 mg (2.8 mmol) of magnesium in 5 mL of dry diethyl ether. The mixture was refluxed for 15 min, and then 456 mg (2.3 mmol) of 2-phenyl-2-propyl bromide was added. The resulting mixture was refluxed for 3.5 h. A standard aqueous workup followed by purification by silica gel column chromatography with hexane as the eluent gave 450 mg (67%) of **4**: white solid; mp 35−36 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (s, 6H), 7.19−7.36 (m, 5H), 7.41−7.49 (m, 4H) (Figure S1); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.4, 52.3, 119.2−130.9 (q, J = 270 Hz), 125.5−125.6 (q, J = 3.7 Hz), 127.1, 127.4, 128.7, 130.4−131.3 (q, J = 1.1 Hz), 136.1, 138.6−138.7 (q, J = 1.4 Hz), 146.5 (Figure S2); EI-MS (70 eV) m/z (relative intensity) 77 (7), 91 (35), 103 (9), 115 (5), 119 (100), 178 (9), 296 (M^+, 1). Anal. Calcd for $C_{16}H_{15}F_3S$: C, 64.85; H, 5.10; S, 10.82. Found: C, 65.04; H, 5.07; S, 10.95.

Laser Flash Photolysis (LFP) Studies. N_2-saturated CH_3CN solutions of $MeOP^+PF_6^-$ (1.6×10^{-4} M) and aryl 1-methyl-1-phenylethyl sulfides (1.0×10^{-2} M) were employed under magnetic stirring. The transient spectra of the $MeOP^+$/**2** and $MeOP^+$/**4** systems (for the transient spectra of $MeOP^+$/**1** and $MeOP^+$/**3** systems, see ref 26) were obtained at 25 ± 0.5 °C by a point-to-point technique, monitoring the change in absorbance (ΔA) after the laser flash at intervals of 10 nm over the spectral range of 390−650 nm (see Figures S3 and S4). The first-order rate constants for the fragmentation of radical cations $2^{+\bullet}$−$4^{+\bullet}$ (k_f) were obtained by fitting the absorbance decay data at the maximum absorption wavelengths (510−570 nm) to the exponential equation (see Figures S5−S7). Rate constants k_f refer to 0 ± 0.5 °C. Five to seven kinetic runs were performed with each solution and the rate constants averaged. The error estimated on the rate constants was ±10%.

Product Analysis of the Oxidation of 1−4 by $[(N4Py)Fe^{IV}{=}O]^{2+}$. $[(N4Py)Fe^{IV}{=}O]$ was generated in situ at room temperature by adding iodosylbenzene (12.5 μmol) to a stirred solution of $[(N4Py)Fe^{II}(OTf)_2]$ (2.5 μmol) in acetonitrile (500 μL).[39] The mixture was vigorously stirred at room temperature for 15 min; then the solution was cooled at 0 °C, and 50 μmol of aryl 1-methyl-1-phenylethyl sulfides (**1**−**4**) were added. After the mixture had been vigorously stirred for 90 min, 25 μmol of a $Na_2S_2O_5$ aqueous solution and the internal standard were added. The mixture was extracted with Et_2O, and the organic layer was dried over Na_2SO_4 and analyzed by HPLC, GC, and ^{1}H NMR. All products formed (2-phenyl-2-propanol, aryl disulfides, and aryl 1-methyl-1-phenylethyl sulfoxides) were identified by comparison with authentic specimens. No products were observed in blank experiments performed in the absence of the oxidant. Only small amounts of aryl 1-methyl-1-phenylethyl sulfoxides (<1% referenced to the amount of oxidant PhIO) were observed in the oxidation with PhIO in the absence of the $[(N4Py)Fe^{II}(OTf)_2]$ complex.

Product Analysis of the Oxidation of 1−4 by $[(Bn\text{-}TPEN)Fe^{IV}{=}O]^{2+}$. $[(Bn\text{-}TPEN)Fe^{IV}{=}O]$ was generated in situ at 0 °C by adding iodosylbenzene (12.5 μmol) to a stirred solution of $[(Bn\text{-}TPEN)Fe^{II}(OTf)_2]$ (2.5 μmol) in acetonitrile (500 μL).[39] The mixture was vigorously stirred for 5 min at 0 °C, and then 50 μmol of aryl 1-methyl-1-phenylethyl sulfides (**1**−**4**) was added. After the mixture had been vigorously stirred for 30 min, 25 μmol of a $Na_2S_2O_5$ aqueous solution and the internal standard were added. The mixture was extracted with Et_2O, and the organic layer was dried over Na_2SO_4 and analyzed by HPLC, GC, and ^{1}H NMR. Reaction products were identified as reported above for the oxidation promoted by $[(N4Py)Fe^{IV}{=}O]$. No products were observed in blank experiments performed in the absence of the oxidant. Only small amounts of aryl 1-methyl-1-phenylethyl sulfoxides (<1% referenced to the amount of oxidant PhIO) were observed in the oxidation with PhIO in the absence of the $[(Bn\text{-}TPEN)Fe^{II}(OTf)_2]$ complex.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02434.

^{1}H NMR and ^{13}C NMR spectra of 4-trifluoromethylphenyl 1-methyl-1-phenylethyl sulfide (**4**) and time-resolved absorption spectra and decay kinetics after LFP of the $MeOP^+$/**2**−**4** systems in CH_3CN (PDF)

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Notes

The authors declare no competing financial interest.

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