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Oxidation of Aryl Diphenylmethyl Sulfides Promoted by a Nonheme Iron(IV)-Oxo Complex: Evidence for an Electron Transfer-Oxygen Transfer Mechanism

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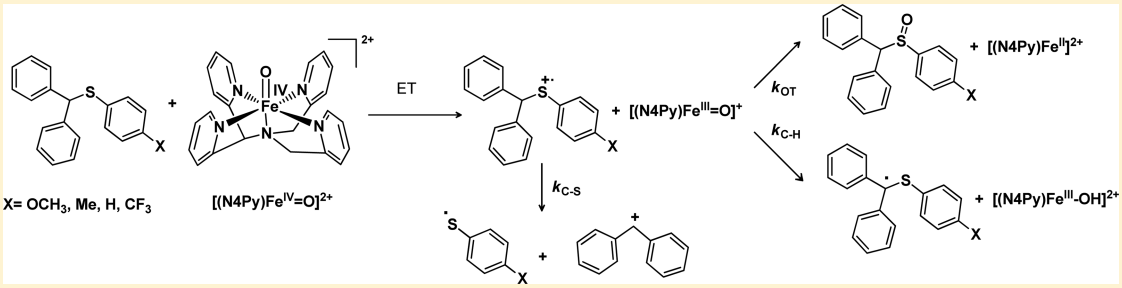
Supporting Information

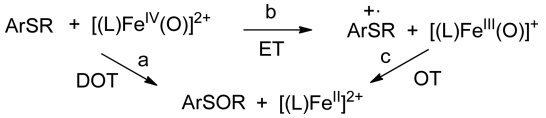


ABSTRACT: The oxidation of a series of aryl diphenylmethyl sulfides (4-X-$C_6H_4SCH(C_6H_5)_2$, where X = OCH_3 (**1**), X = CH_3 (**2**), X = H (**3**), and X = CF_3 (**4**)) promoted by the nonheme iron(IV)-oxo complex $[(N4Py)Fe^{IV}{=}O]^{2+}$ occurs by an electron transfer-oxygen transfer (ET-OT) mechanism as supported by the observation of products (diphenylmethanol, benzophenone, and diaryl disulfides) deriving from α-C−S and α-C−H fragmentation of radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$, formed besides the S-oxidation products (aryl diphenylmethyl sulfoxides). The fragmentation/S-oxidation product ratios regularly increase through a decrease in the electron-donating power of the aryl substituents, that is, by increasing the fragmentation rate constants of the radical cations as indicated by a laser flash photolysis (LFP) study of the photochemical oxidation of **1**−**4** carried out in the presence of *N*-methoxyphenanthridinium hexafluorophosphate ($MeOP^+PF_6^-$).

INTRODUCTION

Among the oxidative processes promoted by the nonheme iron-oxo complex, the oxidation of sulfides has attracted special attention in light of the biological relevance of this process.[1] Moreover, the main products derived from S-oxidation, sulfoxides, are involved in a large number of synthetically useful procedures.[2] The oxidation of sulfides to sulfoxides promoted by heme enzymes such as cytochrome P450 and peroxidases, as well as their biomimetic model compounds, has been the subject of intense mechanistic investigation by several research groups at the end of last century.[3−7] More recently, the mechanism of sulfoxidation of thioanisoles promoted by high-valent iron-oxo species in nonheme iron oxygenases and their synthetic nonheme models has been analyzed in detail.[8] These studies aimed, in particular, to clarify the mechanistic dichotomy that characterizes the oxidation of sulfides by high-valent iron(IV)-oxo complexes between the direct oxygen transfer (or "oxene process") (DOT, Scheme 1, path a) and electron transfer followed by oxygen transfer (ET-OT, Scheme 1, paths b and c) mechanisms.[4−9]

Scheme 1



Product analysis of the oxidation of sulfides that undergo very fast fragmentation processes involving either C−H or C−S bond cleavage from the corresponding radical cations[10−14] in competition with the formation of sulfoxides in oxygen-rebound processes may represent a useful tool to distinguish the DOT and ET-OT pathways. For example, it has previously been reported that the oxidation of aryl alkyl and dialkyl sulfides promoted by chloroperoxidase (CPO) and iron-porphyrin biomimetic model systems in organic solvents led to the exclusive formation of sulfoxides, while in the

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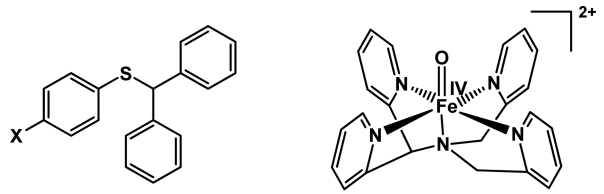
horseradish peroxidase (HRP) and *Coprinus cinereus* peroxidase (CiP) catalyzed oxidations, sulfoxides were accompanied by fragmentation products, thus indicating that the sulfide radical cation formed after the initial ET step undergoes partitioning between the oxygen-rebound (OT in Scheme 1) and fragmentation processes.[4,6] It was also possible to estimate the rate of the oxygen-rebound process from the fragmentation rate constants of the sulfide radical cations and the product distribution in the reaction of aryl benzyl sulfides catalyzed by HRP.[6]

In this respect, we deemed it worthwhile to extend the mechanistic analysis of the sulfide oxidation promoted by nonheme iron complexes, at the time limited to thioanisoles,[8] to other model substrates that are expected to undergo fast fragmentation processes with the corresponding radical cations. Diphenylmethyl phenyl sulfide represents an appropriate substrate to test the intermediacy of radical cations in biomimetic oxidation processes.[4] After a comparison of the results of the product analysis in the oxidations promoted by chemical oxidants and photoinduced electron transfer with those observed in the oxidation with H_2O_2 catalyzed by the iron-porphyrin model $TPPFe^{III}Cl$, a direct oxygen transfer was suggested for the latter process.[4,11] We report herein a detailed product and kinetic study on the oxidation of a series of aryl diphenylmethyl sulfides (**1**−**4**) 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 (Figure 1). This study has been integrated by a steady-state and laser flash photolysis (LFP) analysis of the photochemical oxidation of the same substrates carried out in the presence of *N*-methoxyphenanthridinium hexafluorophosphate ($MeOP^+PF_6^-$), which allowed us to determine the fragmentation rate constants of the radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$.[12−14]



1 X=OCH_3
2 X=CH_3
3 X=H
4 X=CF_3

$[(N4Py)Fe^{IV}(O)]^{2+}$

Figure 1. Aryl diphenylmethyl sulfides **1**−**4** and nonheme iron(IV)-oxo complex $[(N4Py)Fe^{IV}(O)]^{2+}$.

RESULTS

Photochemical Oxidation. Through irradiation of a solution of *N*-methoxyphenanthridinium cation ($MeOP^+$) in CH_3CN, N−O bond cleavage occurs with the formation of the phenanthridinium radical cation ($P^{+\bullet}$)[15] which is able to oxidize the aryl diphenylmethyl sulfides by an exergonic ET process (Scheme 2).[16]

In a typical steady-state photolysis experiment, a solution of **1**−**4** (2.5×10^{-2} M) and $MeOP^+PF_6^-$ (5.5×10^{-3} M) in N_2-saturated CH_3CN was irradiated in a photoreactor at 355 nm. The fragmentation products diphenylmethanol, benzophenone, and diaryl disulfide, formed after photolysis, were identified by comparison with authentic specimens and quantitated by GC, GC-MS, and ^1H NMR analysis. No products were detected in the absence of the sensitizer.

The yields, based on the amount of sensitizer, are reported in Table 1. In the last column of this table, the benzophenone/diphenylmethanol molar ratios are also reported.

Table 1. Products and Yields in the Photooxidation of Aryl Diphenylmethyl Sulfides (1−4) Sensitized by $MeOP^+$ in CH_3CN at 25 °C[a]

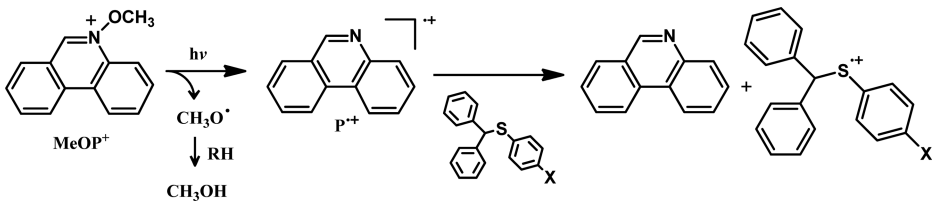
Sulfide	Products (Yield %)[b]			Ratio [CO]/[OH]
	$(C_6H_5)_2CHOH$	$(C_6H_5)_2CO$	ArSSAr	
1 X=OCH_3	13	17	16	1.3
2 X=CH_3	9.0	20	14	2.2
3 X=H	7.1	26	17	3.7
3-*d*[c]	13	15	11	1.2
4 X=CF_3	5.5	31	15	5.5

[a]$MeOP^+PF_6$ (5.5 μmol) and sulfide (25 μmol) in CH_3CN (1 mL) under nitrogen. [b]Yields are based on the amount of sensitizer with an average of at least three determinations. The error is <±5%. [c]Product yields in the oxidation of $(C_6H_5)_2CDSC_6H_5$.

Laser Flash Photolysis Studies. Fragmentation rate constants for radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ were determined by laser flash photolysis experiments. After laser irradiation (λ_{exc} = 355 nm) of N_2-saturated solutions of sulfides **1**−**4** (1.0×10^{-2} M) and $MeOP^+$ (1.6×10^{-4} M) in CH_3CN, broad absorption bands with maxima in the 480−590 nm region of the spectrum (depending on the substrate) were observed after the laser pulse. Time-resolved spectra observed after laser irradiation of the **2**/$MeOP^+$ system are shown in Figure 2. LFP experiments of the **1**/$MeOP^+$, **3**/$MeOP^+$, and **4**/$MeOP^+$ systems are reported in Figures S1−S3 in the Supporting Information.

The time evolution of the absorption spectra shows a second-order decay of the transients absorbing at 480−590 nm (see insets of Figure 2 for the LFP experiments with the **2**/

Scheme 2. Generation of Radical Cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ by Photolysis of $MeOP^+$



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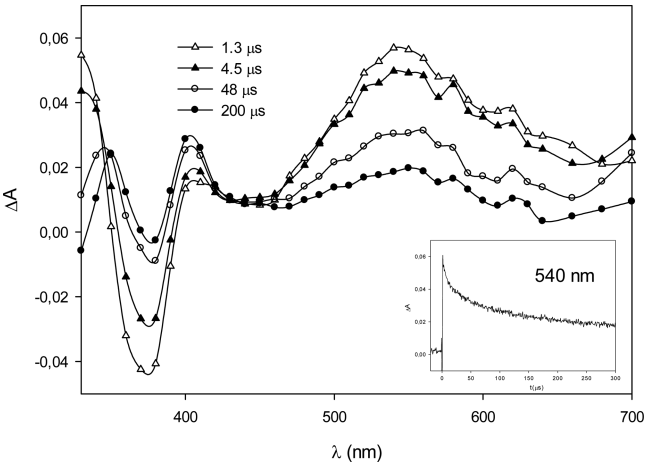

Figure 2. Time-resolved absorption spectra of the $(C_6H_5)_2CHSC_6H_4CH_3$ (**2**) (1.0×10^{-2} M)/$MeOP^+$ (1.6×10^{-4} M) system in N_2-saturated CH_3CN recorded 1.3 (△), 4.5 (▲), 48 (○), and 200 μs (●) after the laser pulse. Inset: decay kinetics recorded at 540 nm. The negative absorption is due to the depletion of the ground state of $MeOP^+$.

$MeOP^+$ system). The decays are always coupled with the growth of an absorption at 340−360 nm.

The k_d/ε values (s^{-1} cm) for $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ were determined at the maximum absorption wavelengths of the radical cations (590, 540, 520, and 480 nm for $\mathbf{1}^{+\bullet}$, $\mathbf{2}^{+\bullet}$, $\mathbf{3}^{+\bullet}$, and $\mathbf{4}^{+\bullet}$, respectively; see insets of Figure 2 and Figures S1−S3 in the Supporting Information). The k_d/ε values are reported in Table 2.

Table 2. Maximum Absorption Wavelengths (λ_{max}) and k_d/ε Values of Aryl Diphenylmethyl Sulfide Radical Cations ($\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$) Generated by Photooxidation of 1−4 Sensitized by $MeOP^+PF_6^-$ (λ_{ecc} = 355 nm)[a] and Peak Oxidation Potentials (E_p) of 1−4

	λ_{max} (nm)	k_d/ε (s^{-1}cm)[b]	E_p[c]
$\mathbf{1}^{+\bullet}$ X=OCH_3	590	2.3×10^5	1.41
$\mathbf{2}^{+\bullet}$ X=CH_3	540	3.1×10^5	1.56
$\mathbf{3}^{+\bullet}$ X=H	520	7.1×10^6	1.65
$\mathbf{4}^{+\bullet}$ X=CF_3	480	1.6×10^7	1.86

[a]From LFP experiments (λ_{exc} = 355 nm) in N_2-saturated CH_3CN. [sulfide] = 1.0×10^{-2} M, [$MeOP^+PF_6^-$] = 1.6×10^{-4} M. [b]Second-order decay rate constants/ε values were recorded at the maximum of absorption of the radical cations. [c]Peak oxidation potentials E_p (V vs SCE in CH_3CN) from cyclic voltammetry (see Supporting Information).

Biomimetic Oxidation by $[(N4Py)Fe^{IV}{=}O]^{2+}$. The iron(IV)-oxo complex $[(N4Py)Fe^{IV}{=}O]^{2+}$ was prepared by oxidation of the corresponding iron(II) complex $[(N4Py)Fe^{II}(OTf)_2]$ (2.5 μmol) with an excess of PhIO (12.5 μmol) in CH_3CN as reported in previous studies.[17] After 10 min from the addition of 50 μmol of sulfides **1**−**4** to the solution of $[(N4Py)Fe^{IV}{=}O]^{2+}$ in CH_3CN at 0 °C, product analysis revealed that sulfoxides 4-X-$C_6H_4SOCH(C_6H_5)_2$ were accompanied by significant amounts of the fragmentation products diphenylmethanol, benzophenone, and diaryl disulfides. No products were observed in the absence of PhIO, while very small amounts of sulfoxides (<1%, based on the amount of oxidant) were formed in the presence of the oxidant and in the absence of the complex $[(N4Py)Fe^{II}(OTf)_2]$. When aryl diphenylmethyl sulfoxides were used as substrates under the same reaction conditions, no products were formed, and the recovery of the sulfoxides was quantitative, thus indicating that fragmentation products diphenylmethanol and benzophenone cannot originate from sulfoxide degradation. Products and yields, based on the amount of oxidant, are reported in Table 3. In the last column of this table, the alkyl fragmentation products (diphenylmethanol + benzophenone)/sulfoxide molar ratios are also reported.

Kinetic studies of the reaction of $[(N4Py)Fe^{IV}(O)]^{2+}$ with aryl diphenylmethyl sulfides were carried out by spectrophotometrically monitoring the decrease in the absorbance at 695 nm (λ_{max} for $[(N4Py)Fe^{IV}(O)]^{2+}$)[17a] in the presence of an excess of **1**−**4** (at least ten times). The rate obeyed pseudo-first-order kinetics, and the pseudo-first-order rate constant (k_{obs}) linearly increased with an increasing concentration of aryl diphenylmethyl sulfides (see Figures S5−S8 in the Supporting Information). The second-order rate constants (k), reported in Table 4, were obtained from the slope of the linear correlation of k_{obs} vs the substrate concentrations.

DISCUSSION

Diphenylmethyl phenyl sulfide **3** represents a useful mechanistic probe to distinguish the intermediacy of sulfide radical cations in biomimetic and enzymatic oxidation processes.[4] Products derived from the C−S bond cleavage were formed as major products in the photochemical oxidation of **3** with tetranitromethane.[11] The absence of fragmentation products, coupled with the exclusive formation of diphenylmethyl phenyl sulfoxide and diphenylmethyl phenyl sulfone in the oxidation of **3** with H_2O_2 catalyzed by the iron-porphyrin $TPPFe^{III}Cl$ in CH_3CN, fully supported the occurrence of a direct oxygen transfer (DOT) mechanism for the oxidation promoted by the heme biomimetic model in organic solvents.[4,18]

In order to investigate in detail the fragmentation processes of aryl diphenylmethyl sulfide radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ and determine their fragmentation rate constants, we have analyzed the photochemical oxidation of sulfides **1**−**4** in the presence of *N*-methoxyphenanthridinium hexafluorophosphate. This approach proved to be well-suited and was applied with success for the generation of sulfide radical cations and the analysis of their fragmentation processes.[12−14] The formation of diphenylmethanol and diaryl disulfides in the steady-state photolysis experiments can be rationalized on the basis of the α-C−S bond cleavage in the intermediate radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$, producing the diphenylmethyl cation and the arylsulfenyl radical depicted in Scheme 3 (path a). The cation leads to diphenylmethanol by reaction with traces of water present in CH_3CN,[19] and arylsulfenyl radicals dimerize to diaryl disulfides.

Benzophenone could be formed by further oxidation of diphenylmethanol under these reaction conditions; however, the possibility that benzophenone might derive through the α-C−H deprotonation of the radical cation (Scheme 3, path b) by the base phenanthridine,[20] a process that competes efficiently with C−S bond cleavage in aryl sulfide radical cations, cannot

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Table 3. Products and Yields in the Oxidation of Aryl Diphenylmethyl Sulfides (1−4) by $[(N4Py)Fe^{IV}{=}O]^{2+}$ in CH_3CN at 0°C[a]

Sulfide	Products (Yield %)[b]				Ratio [OH+CO]/[SO]
	$(C_6H_5)_2CHOH$	$(C_6H_5)_2CO$	$ArSOCH(C_6H_5)_2$	ArSSAr	
1 X=OCH_3	14	2	73	6	0.22
2 X=CH_3	12	6	48	8	0.38
3 X=H	15	7	30	9	0.73
3-*d*[c]	16	-	43	5	0.37
4 X=CF_3	18	15	7	14	4.7

[a]Iodosylbenzene (12.5 μmol), $[(N4Py)Fe^{II}(OTf)_2]$ (2.5 μmol), and 4-X-$C_6H_4SCH(C_6H_5)_2$ (50 μmol) in CH_3CN (500 μL). [b]Yields (mol %) are based on the amount of oxidant PhIO with an average of at least three determinations. The error is <±5%. [c]Product yields in the oxidation of $(C_6H_5)_2CDSC_6H_5$.

Table 4. Second-Order Rate Constants (k) for the Oxidation of Aryl Diphenylmethyl Sulfides (1−4) and Thioanisole by $[(N4Py)Fe^{IV}{=}O]^{2+}$ in CH_3CN at 8°C[a]

sulfide	k (M^{-1} s^{-1})
1	0.17
2	0.12
3	8.6×10^{-2}
4	3.9×10^{-2}
thioanisole	0.20

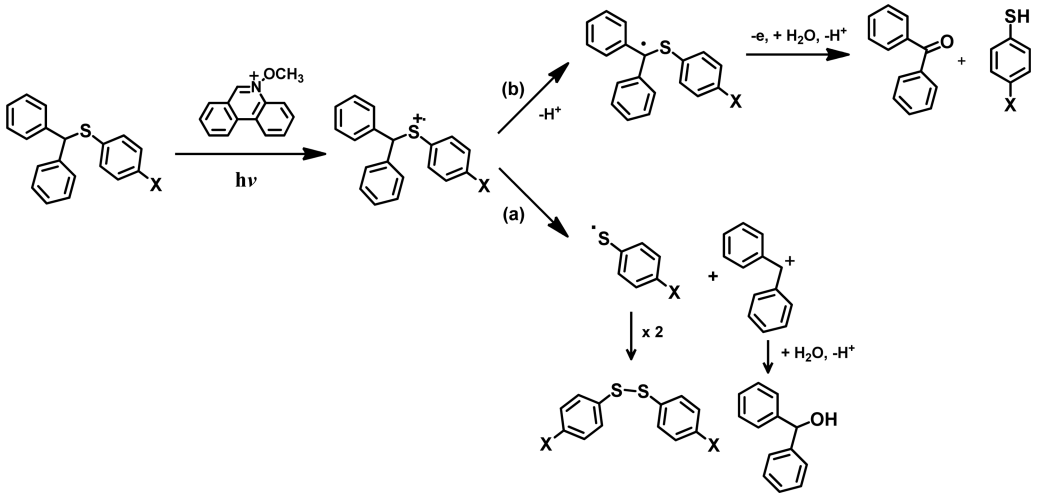
[a]$[(N4Py)Fe^{IV}{=}O]^{2+}$ (1.2×10^{-3} M) and substrate ($8-30 \times 10^{-3}$ M) in CH_3CN (1 mL).

be excluded.[4,6,11,21] Oxidation of the α-sulfenyl carbon radical, followed by reaction with water, leads to benzophenone and arylthiols. The occurrence of competition between α-C−H and α-C−S bond fragmentation in radical cations $\mathbf{1}^{+\bullet}-\mathbf{4}^{+\bullet}$ is in accordance with the significant decrease of the benzophenone/diphenylmethanol product ratio in the oxidation of the deuterated sulfide $C_6H_5SCD(C_6H_5)_2$ (**3**-*d*) (see Table 1).

The presence of electron-withdrawing aryl substituents should favor both the fragmentation pathways through an increase of the α-C−H bond acidity and the C−S bond cleavage rate constants in radical cations $\mathbf{1}^{+\bullet}-\mathbf{4}^{+\bullet}$.[12,13,21d] The increase of the benzophenone/diphenylmethanol relative proportion observed from $\mathbf{1}^{+\bullet}$ (4-OCH_3) to $\mathbf{4}^{+\bullet}$ (4-CF_3) clearly indicates that the substituent effect on the acidity of the α-C−H bond prevails over the effect on the α-C−S bond fragmentation.

The formation of radical cations $\mathbf{1}^{+\bullet}-\mathbf{4}^{+\bullet}$ produced after the electron transfer from sulfides **1**−**4** to the phenanthridine radical cation ($P^{+\bullet}$) was supported by the observation in the LFP experiments of their characteristic absorption bands centered at 480−590 nm.[6,12−14] The time evolution of the

Scheme 3. Formation of Fragmentation Products from Competitive α-C−H vs α-C−S Bond Cleavage in Radical Cations $\mathbf{1}^{+\bullet}-\mathbf{4}^{+\bullet}$



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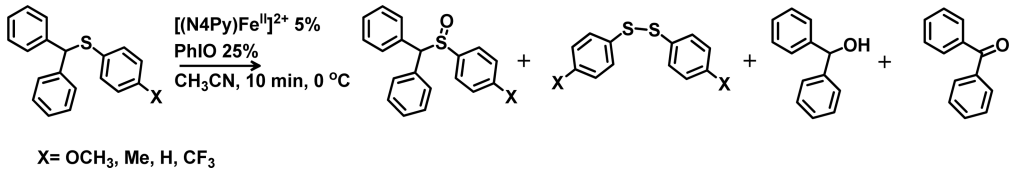
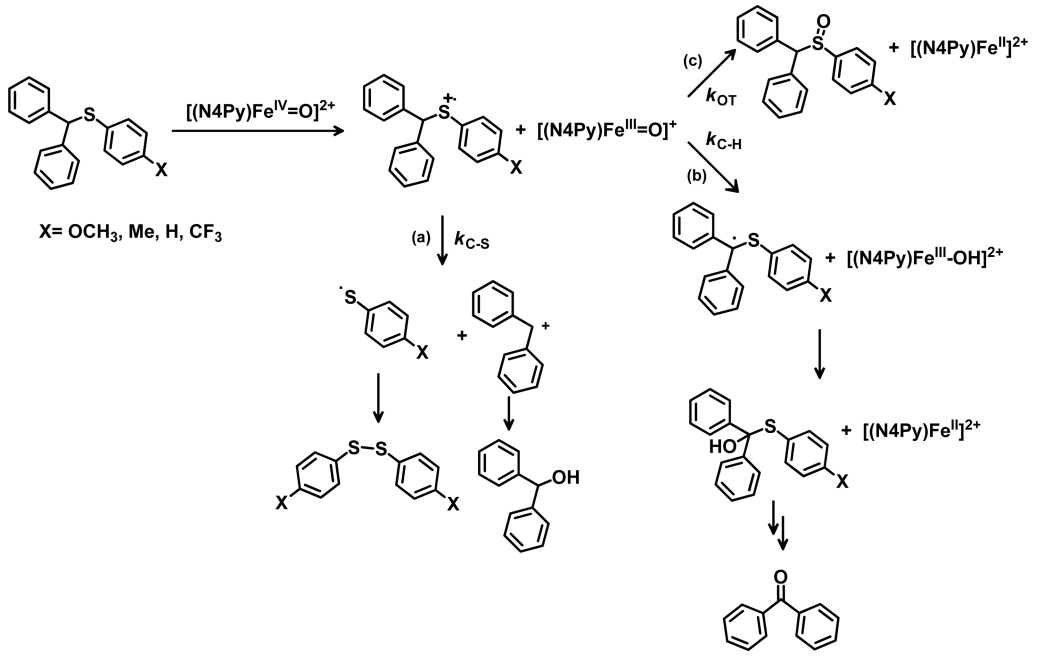
Scheme 4. Products Formed in the Oxidation of Sulfides 1−4 by $[(N4Py)Fe^{IV}{=}O]^{2+}$ in CH_3CN at 0 °C



Scheme 5. α-C−S and α-C−H Bond Fragmentation vs Oxygen-Rebound Processes in the Oxidation of Sulfides 1−4 by $[(N4Py)Fe^{IV}{=}O]^{2+}$ in CH_3CN



absorption spectra shows a second-order decay of the radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ (see insets of Figure 2 and Figures S1−S3 in the Supporting Information) which can be attributed to the main decay process occurring in the deprotonation of $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ by phenanthridine produced after the electron transfer from **1**−**4** to $P^{+\bullet}$ (see Scheme 2).

Accordingly, the decays are always coupled with the growth of an absorption at 340−360 nm. This can be assigned to the C-centered radicals 4-X-$C_6H_4SC^{\bullet}(C_6H_5)_2$ produced after proton loss of the radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ and is supported by the absorption spectrum of the radical $(C_6H_5)_2C^{\bullet}SC_6H_5$ recorded 4 μs after laser flash photolysis of a solution of $(C_6H_5)_2CHSC_6H_5$ (3.1×10^{-2} M) and dicumyl peroxide (1 M) in N_2-saturated CH_3CN (see Figure S4 in the Supporting Information).[22]

Examination of the data for the biomimetic oxidation of sulfides **1**−**4** by $[(N4Py)Fe^{IV}{=}O]^{2+}$ (Table 3) indicates that sulfoxides are accompanied by significant amounts of fragmentation products (diphenylmethanol, benzophenone, and diaryl disulfides) (Scheme 4). The yields of diaryl disulfides are less than half of those of diphenylmethanol and benzophenone, which is probably due to a further oxidation of the disulfides under the reaction conditions. The total yields of the oxidation products increased from 40% for **4** (the least reactive) to 89% for **1** (the most reactive) due to an increase in the electron-donating power of the aryl substituents. In accordance with these results and the electrophilic nature of the oxidizing species $[(N4Py)Fe^{IV}{=}O]^{2+}$,[8a] a negative ρ-value (−1.1) was determined in the Hammett correlation when the $\log(k_X/k_H)$ values for the oxidation of **1**−**4** by $[(N4Py)Fe^{IV}{=}O]^{2+}$ were plotted against the substituent constants σ^+ (see Table 4 and Figure S9 in the Supporting Information).

The formation of fragmentation products is a clear indication of the occurrence of an electron transfer process from sulfides **1**−**4** to $[(N4Py)Fe^{IV}{=}O]^{2+}$.[24] Diphenylmethanol and diaryl disulfides are formed after the α-C−S bond cleavage of radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$ as described in path a of Scheme 3 for the steady-state photolysis of the **1**−**4**/$MeOP^+$ systems and in path a of Scheme 5 for the oxidation of **1**−**4** by $[(N4Py)Fe^{IV}{=}O]^{2+}$. Formation of benzophenone might be attributed either to the α-C−H fragmentation of radical cations $\mathbf{1}^{+\bullet}$−$\mathbf{4}^{+\bullet}$, likely promoted by the reduced iron(III)-oxo complex $[(N4Py)Fe^{III}{=}O]^{+}$ (Scheme 5, path b),[25] or to the oxidation of diphenylmethanol. The former process is in accordance with the observation that benzhydrol yields are almost constant, while benzophenone yields are strongly dependent on the arylthio substituent, which is not compatible with a further oxidation of diphenylmethanol. In addition, an almost constant diphenylmethanol/benzophenone product ratio is observed by increasing the reaction time from 1 to 10 min (see Figure S11 in the Supporting Information). Evidence in favor of the former process is also provided by the results of the oxidation of the deuterated sulfide **3**-*d* (see Table 3). The presence of an α-C−D bond led to the disappearance of benzophenone among the reaction products and to an increase in yields of diphenylmethanol and diphenylmethyl phenyl sulfoxide. This result can be attributed to a reduced rate of deprotonation from $\mathbf{3}\text{-}d^{+\bullet}$ by $[(N4Py)Fe^{III}{=}O]^{+}$ and a complete suppression of path b in

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Scheme 5. The increase of the benzophenone/diphenylmethanol relative proportion observed from $1^{+\bullet}$ (4-OCH_3) to $4^{+\bullet}$ (4-CF_3) parallels the results observed in the oxidation of **1**−**4** photosensitized by $MeOP^+$.

The occurrence of an electron transfer process from sulfides **1**−**4** to $[(N4Py)Fe^{IV}{=}O]^{2+}$, evidenced by the formation of fragmentation products, indicates that sulfoxides are likely formed after the oxygen-rebound (OT) process from the reduced iron(III)-oxo complex to the radical cations $1^{+\bullet}$−$4^{+\bullet}$. Thus, the α-C−S and α-C−H bond fragmentations of radical cations $1^{+\bullet}$−$4^{+\bullet}$ occur in competition with the oxygen rebound as shown in Scheme 5 (paths a, b, and c).[27] It has to be noted that a similar partition between oxygen-rebound and fragmentation processes in radical cations of alkyl aryl sulfides was reported for the oxidation catalyzed by horseradish peroxidase (HRP)[6] and *C. cinereus* peroxidase (CiP).[4]

The competition between the S-oxidation and fragmentation pathways for radical cations $1^{+\bullet}$−$4^{+\bullet}$ is fully consistent with the marked dependence on the nature of the aryl substituents of the product distribution and, in particular, the sulfoxide/fragmentation product ratios reported in the last column of Table 3 and in the histogram of Figure 3.

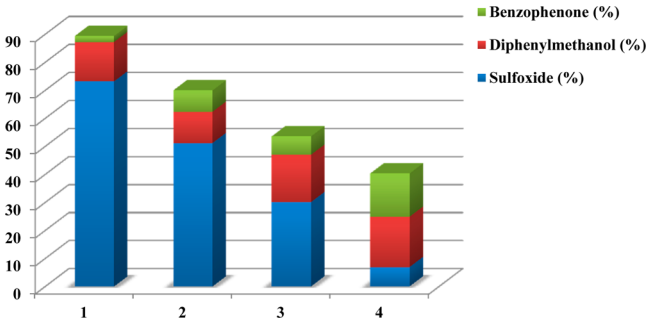

Figure 3. Yields (% based on the amount of oxidant) of fragmentation products (benzophenone and diphenylmethanol) and sulfoxides in the oxidation of sulfides **1**−**4** by $[(N4Py)Fe^{IV}{=}O]^{2+}$ in CH_3CN at 0 °C.

The relative amount of fragmentation products regularly increases through a decrease in the electron-donating effect of the aryl substituents, that is, by increasing the fragmentation rate constants of the radical cations as indicated by the results of the LFP experiments (Table 2).[28] In the oxidation of 4-OCH_3−$C_6H_4SCH(C_6H_5)_2$ by $[(N4Py)Fe^{IV}{=}O]^{2+}$, the sulfoxide is by far the major product because the corresponding radical cation $1^{+\bullet}$ is characterized by the lower fragmentation rate constant in the series. Conversely, the oxidation of 4-CF_3−$C_6H_4SCH(C_6H_5)_2$ by the same iron(IV)-oxo complex leads to larger amounts of diphenylmethanol and benzophenone. In this case, the fragmentation process of $4^{+\bullet}$ competes more efficiently with the oxygen rebound.

The proposed ET-OT mechanism for the oxidation of aryl diphenylmethyl sulfides by $[(N4Py)Fe^{IV}(O)]^{2+}$ appears to be in contrast with the DOT mechanism recently reported by Nam and Fukuzumi for the sulfoxidation of thioanisoles promoted by the same nonheme iron(IV)-oxo complex.[29] A reasonable explanation for the different mechanism occurring in the oxidation of thioanisoles and aryl diphenylmethyl sulfides might be based on the presence of the more bulky diphenylmethyl sulfur substituent in **1**−**4**. This substituent hampers the direct oxygen atom transfer from $[(N4Py)Fe^{IV}(O)]^{2+}$ to the sulfur atom[30] as supported by the rate constant determined for the reaction of $[(N4Py)Fe^{IV}(O)]^{2+}$ with thioanisole in CH_3CN at 8 °C (0.2 M^{-1} s^{-1}) being higher than that of the reaction with diphenylmethyl phenyl sulfide (0.086 M^{-1} s^{-1}). The endergonic[31] and relatively slow electron transfer process should not be significantly affected by steric hindrance as would be expected for the DOT pathway, which requires a closer approach to the iron-oxo moiety. Thus, the electron transfer process from **1**−**4** to $[(N4Py)Fe^{IV}(O)]^{2+}$ has the chance to favorably compete with the DOT pathway. Previous studies have highlighted the importance of steric requirements and the accessibility of substrates to the iron-oxo centers to the reactivity of heme and nonheme iron complexes.[4,5,8f,34]

CONCLUSIONS

The observation of products deriving from α-C−S and α-C−H fragmentation of radical cations $1^{+\bullet}$−$4^{+\bullet}$ (diphenylmethanol, benzophenone, and diaryl disulfides), which are formed together with sulfoxides in the oxidation of aryl diphenylmethyl sulfides promoted by the nonheme iron(IV)-oxo complex $[(N4Py)Fe^{IV}{=}O]^{2+}$, demonstrates, with no doubt, that an electron transfer-oxygen transfer (ET-OT) mechanism occurs. The ET-OT process is also supported by the increase of the fragmentation/S-oxidation product ratios through a decrease in the electron-donating power of the aryl substituents, that is, by increasing the fragmentation rate constants of the radical cations $1^{+\bullet}$−$4^{+\bullet}$, as indicated by the results of LFP experiments of the photochemical oxidation of **1**−**4** by $MeOP^+$. A substrate structural dependence of the oxidation mechanism of aromatic sulfides by $[(N4Py)Fe^{IV}{=}O]^{2+}$ can be evinced through the direct oxygen transfer process proposed for the oxidation of thioanisoles by the same iron(IV)-oxo complex. Further information on this topic will be provided by future mechanistic analyses of the oxidations of an extended series of sulfides promoted by nonheme high-valent iron-oxo complexes now in progress in our laboratory.

EXPERIMENTAL SECTION

Steady-State Photolysis. Photooxidation reactions were carried out in a photoreactor equipped with two phosphor-coated Hg lamps (360 nm, 14 W each). A 1 mL solution containing the aryl diphenylmethyl sulfide (25 μmol) and $MeOP^+$ (5.5 μmol) in N_2-saturated CH_3CN was irradiated in a rubber cap sealed jacketed tube for 5 min at 25 °C. After the addition of an internal standard, the mixtures were analyzed by GC and ^1H NMR. All fragmentation products were identified by comparison with authentic specimens of diphenylmethanol, benzophenone, and diaryl disulfides. The material balance was satisfactory (>90%) in all cases. Blank experiments, carried out by irradiating the solutions in the absence of $MeOP^+$, did not show any product formation.

Laser Flash Photolysis Experiments. Laser flash photolysis experiments were carried out with an Applied Photophysics LK-60 laser kinetic spectrometer providing 8 ns pulses using the third harmonic (355 nm) of a Quantel Brilliant-B 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. N_2-saturated CH_3CN solutions of $MeOP^+PF_6^-$ (1.6×10^{-4} M) and aryl diphenylmethyl sulfides (1.0×10^{-2} M) were used. All experiments were carried out at 25 ± 0.5 °C under magnetic stirring. Data were collected at individual wavelengths with an Agilent Infinium oscilloscope and analyzed with the kinetic package implemented in the instrument. The transient spectra were obtained by a point-to-point technique, monitoring the change of absorbance (ΔA) after the laser flash at intervals of 10 nm over the spectral range of 330−700 nm. The error estimated on the rate constants was ±10%. Rate constants for the decay of the radical

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cations $1^{+\bullet}$–$4^{+\bullet}$ were obtained by monitoring the change of absorbance at the maximum absorption wavelengths (480–590 nm).

Product Analysis of the Oxidation of 1–4 by $[(N4Py)Fe^{IV}{=}O]^{2+}$. Iodosylbenzene (12.5 μmol) was added to a stirred solution of $[(N4Py)Fe^{II}(OTf)_2]$ (2.5 μmol) in acetonitrile (500 μL). The mixture was vigorously stirred at room temperature for 15 min to generate in situ the product $[(N4Py)Fe^{IV}{=}O]$. Afterward, 50 μmol of aryl diphenylmethyl sulfides **1**–**4** was added to the solution, and the mixture was vigorously stirred at 0 °C for an additional 10 min. Next, 25 μmol of an aqueous solution of $Na_2S_2O_5$ and the internal standard was added. The mixture was extracted with Et_2O, and the organic layer was dried over Na_2SO_4 and analyzed by HPLC and ^1H NMR. All products formed were identified by comparison with authentic specimens of diphenylmethanol, benzophenone, diaryl disulfides, and aryl diphenylmethyl sulfoxides. Blank experiments carried out in the absence of the oxidant did not show any product formation. Small amounts of aryl diphenylmethyl sulfoxides (<1%, based on the amount of oxidant) were instead observed in the oxidation with PhIO in the absence of the complex $[(N4Py)Fe^{II}(OTf)_2]$.

Kinetic Studies of the Oxidation of 1–4 by $[(N4Py)Fe^{IV}{=}O]^{2+}$. Kinetic measurements were performed on a diode array UV–vis spectrophotometer using a quartz cuvette (10 mm path length) at 8 °C. A solution of $[(N4Py)Fe^{IV}{=}O]^{2+}$ (1.2 mM in CH_3CN) was prepared by oxidation of the corresponding iron(II) complex $[(N4Py)Fe^{II}(OTf)_2]$ with an excess of solid PhIO (2.5 equiv).[17] After 30 min, the solution was filtered, and aryl diphenylmethyl sulfides (**1**–**4**) (8–30 mM) were added. The rates of oxidation of **1**–**4** were monitored following the decay of the $[(N4Py)Fe^{IV}{=}O]^{2+}$ absorption band at 695 nm.[17a] The second-order rate constants (k) were obtained from the slope of the linear correlation of the pseudo-first-order rate constant (k_{obs}) vs the substrate concentrations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00099.

Starting materials; time-resolved absorption spectra after LFP of the $MeOP^+$/**1**, $MeOP^+$/**3**, and $MeOP^+$/**4** systems in CH_3CN; absorption spectrum of $(C_6H_5)_2C^{\bullet}SC_6H_5$; plots of k_{obs} vs substrate concentration in the reaction of $[(N4Py)Fe^{IV}(O)]^{2+}$ with aryl diphenylmethyl sulfides; Hammett plot for oxidation of aryl diphenylmethyl sulfides **1**–**4** by $[(N4Py)Fe^{IV}{=}O]^{2+}$; cyclic voltammetry; and product yields of the oxidation of **3** with $[(N4Py)\text{-}Fe^{IV}(O)]^{2+}$ as a function of reaction time (PDF)

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Notes

The authors declare no competing financial interest.

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(29) A one-step oxygen atom transfer mechanism was also proposed for the sulfoxidation of thioanisoles in the presence of perchloric acid (70% $HClO_4$).[8c] A mechanistic switch occurs from direct oxygen transfer to either metal ion-coupled electron transfer or proton-coupled electron transfer in the presence of $Sc(OTf)_3$ or triflic acid (HOTf), respectively.[8b,d]
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