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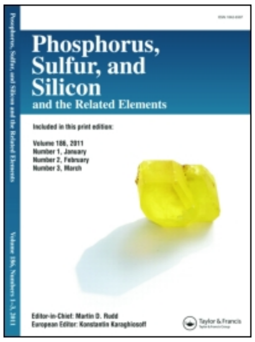

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Role of electron transfer processes in the oxidation of aryl sulfides catalyzed by nonheme iron complexes

Alessia Barbieri, Stefano Di Stefano, Osvaldo Lanzalunga, Andrea Lapi, Marco Mazzonna, and Giorgio Olivo

Dipartimento di Chimica, Sapienza Università di Roma and Istituto CNR di Metodologie Chimiche (IMC-CNR), Sezione Meccanismi di Reazione, c/o Dipartimento di Chimica, Sapienza Università di Roma, Rome, Italy

ABSTRACT
The oxidation of a series of aryl 1-methyl-1-phenylethyl sulfides with H_2O_2 catalyzed by the two tetradentate nonheme-iron complexes $[(PDP)Fe^{II}(SbF_6)_2]$ and $[(BPMCN)Fe^{II}(OTf)_2]$ occurs by an electron transfer-oxygen transfer (ET/OT) mechanism as supported by the observation of products deriving from fragmentation of the corresponding radical cations in association with S-oxidation products (sulfoxides).

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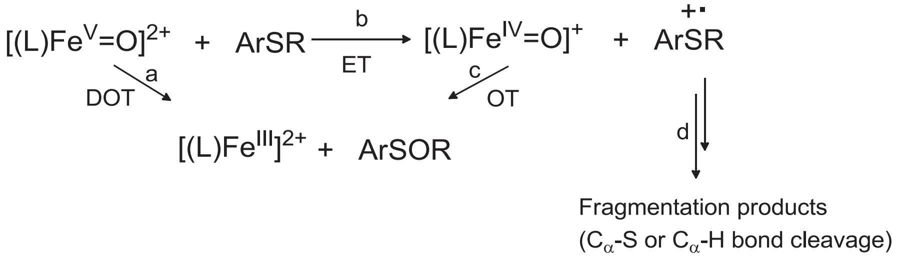
KEYWORDS
Oxidation; sulfide; electron transfer; nonheme iron complexes

GRAPHICAL ABSTRACT



Introduction

The oxidation of sulfides catalyzed by high-valent iron-oxo species in heme and nonheme iron enzymes and their synthetic models, has been the subject of intensive mechanistic investigation in the last decades in light of its biological and synthetic relevance.[1–11] In this context, we have recently investigated the role of electron transfer processes in the *S*-oxidation of aryl sulfides with iodosobenzene, PhIO, catalyzed by the pentadentate iron complexes $[(N4Py)Fe^{II}]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{II}]^{2+}$.[12,13]

The *S*-oxidation of sulfides promoted by the active species, the iron(IV)-oxo complexes $[(N4Py)Fe^{IV}(O)]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}(O)]^{2+}$, can occur either by direct oxygen atom transfer (DOT, Scheme 1, path a) or by sequential electron transfer/oxygen rebound mechanism (ET-OT, Scheme 1, path b-c).[14–20]

Product analysis in the oxidation of aryl diphenylmethyl sulfides and aryl 1-methyl-1-phenylethyl sulfides (Figure 1), represents a useful tool to distinguish the DOT and ET-OT pathways since the corresponding radical cations undergo very fast fragmentation processes, involving either the C_α–H or C_α–S bond cleavage (Scheme 1, path d).[14,21–26] In the oxidations promoted by the iron(IV)-oxo complexes $[(N4Py)Fe^{IV}(O)]^{2+}$ and $[(Bn\text{-}TPEN)Fe^{IV}(O)]^{2+}$ formation of aryl sulfoxides was accompanied by fragmentation products that unequivocally demonstrated the occurrence of an ET-OT mechanism.[12,13]

In the oxidation of aryl 1-methyl-1-phenylethyl sulfides, the exclusive C_α–S bond cleavage of the corresponding radical cations allowed us to estimate the rate constant for the oxygen rebound process (k_{OT}).[13]

In order to gain more information on the role of ET processes in the reactions promoted by nonheme iron complexes, we have extended the mechanistic analysis to the oxidation of aryl 1-methyl-1-phenylethyl sulfides with H_2O_2 catalyzed by two tetradentate nonheme-iron complexes $[(PDP)Fe^{II}(SbF_6)_2]$ and $[(BPMCN)Fe^{II}(OTf)_2]$, where nonheme iron(V)-oxo complexes have been proposed as the active species involved in the oxidative processes.[27–29]

Results and discussion

Oxidations of aryl 1-methyl-1-phenylethyl sulfides (**1**, X=, OCH_3; **2**, X= CH_3; **3**, X= H; **4**, X= Cl) by H_2O_2 catalyzed by $[(PDP)Fe^{II}(SbF_6)_2]$ and $[(BPMCN)Fe^{II}(OTf)_2]$ were carried out by addition of the oxidant (60µmol) to a solution of the substrate (60µmol) and the iron complex (1.5µmol) in CH_3CN (600µL) stirred at 0°C for 6 min. Reaction

CONTACT Osvaldo Lanzalunga osvaldo.lanzalunga@uniroma1.it Dipartimento di Chimica, Sapienza Università di Roma and Istituto CNR di Metodologie Chimiche (IMC-CNR), Sezione Meccanismi di Reazione, c/o Dipartimento di Chimica, Sapienza Università di Roma, P.le A. Moro 5, I-00185 Rome, Italy.

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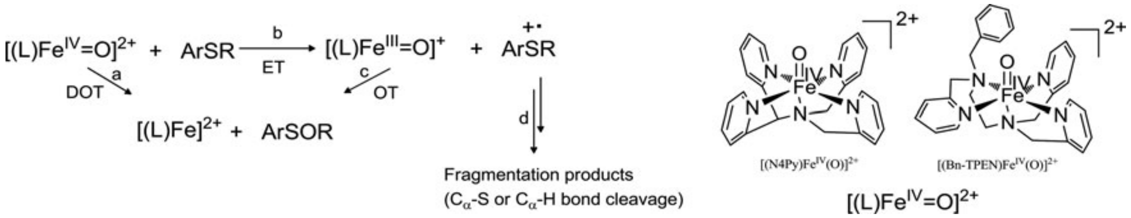


Scheme 1. Mechanism of oxidation of aryl sulfides promoted by the iron(IV)-oxo complexes$[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ and $[(\mathrm{Bn\text{-}TPEN})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{O})]^{2+}$.

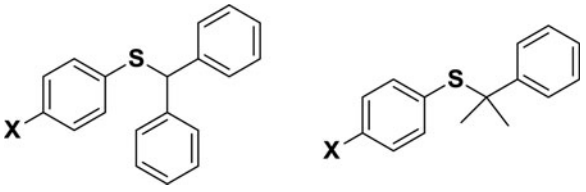


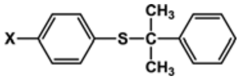
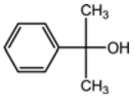
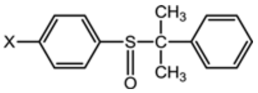
Figure 1. Aryl diphenylmethyl sulfides and aryl 1-methyl-1-phenylethyl sulfides.

products were identified by ^{1}H NMR analyses (comparison with authentic specimens). 2-Phenyl-2-propanol and diaryl disulfides were the main products accompanied by minor amounts of aryl 1-methyl-1-phenylethyl sulfoxides. Aryl 1-methyl-1-phenylethyl sulfones were also observed in trace amounts ($<$1%). No products were formed in the absence of H_2O_2, while small amounts of aryl sulfoxides ($<$1%, referred to the amount of oxidant) were observed in the oxidation with H_2O_2 in the absence of the nonheme complexes $[(\mathrm{PDP})\mathrm{Fe}^{\mathrm{II}}(\mathrm{SbF}_6)_2]$ and $[(\mathrm{BPMCN})\mathrm{Fe}^{\mathrm{II}}(\mathrm{OTf})_2]$.

Yields of the fragmentation product 2-phenyl-2-propanol and of the *S*-oxidation products aryl 1-methyl-1-phenylethyl sulfoxides, referred to the amount of oxidant, are reported in Table 1 and in Table 2 for the oxidations catalyzed by $[(\mathrm{PDP})\mathrm{Fe}^{\mathrm{II}}(\mathrm{SbF}_6)_2]$ and $[(\mathrm{BPMCN})\mathrm{Fe}^{\mathrm{II}}(\mathrm{OTf})_2]$, respectively.

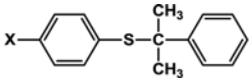
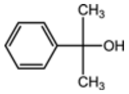
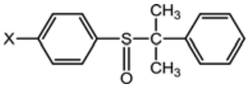
The formation of fragmentation products in the oxidation of aryl 1-methyl-1-phenylethyl sulfides **1–4** is a clear indication of the occurrence of an ET process from the sulfides to $[(\mathrm{PDP})\mathrm{Fe}^{\mathrm{V}}{=}\mathrm{O}]^{2+}$ and $[(\mathrm{BPMCN})\mathrm{Fe}^{\mathrm{V}}{=}\mathrm{O}]^{2+}$ (Scheme 2, path a). As previously reported for the oxidations of the same substrates promoted by $[(\mathrm{N4Py})\mathrm{Fe}^{\mathrm{IV}}{=}\mathrm{O}]^{2+}$ and $[(\mathrm{Bn\text{-}TPEN})\mathrm{Fe}^{\mathrm{IV}}{=}\mathrm{O}]^{2+}$,[13] 2-phenyl- 2-propanol and diaryl disulfides are formed after C–S bond cleavage of radical cations producing the 2-phenyl-2-propyl cation and the arylsulfenyl radical (Scheme 2, path b). The cation leads to 2-phenyl-2-propanol by reaction with traces of water present in CH_3CN, while arylsulfenyl radicals dimerize to diaryl disulfides.[21–26] Fragmentation of radical cations $\mathbf{1}^{+\bullet}$-$\mathbf{4}^{+\bullet}$ occurs in competition with the oxygen rebound process from the reduced iron(IV)-oxo complexes to the radical cations leading to sulfoxides (OT, Scheme 2, path c). In accordance with the presence of the two competitive decay pathways for $\mathbf{1}^{+\bullet}$-$\mathbf{4}^{+\bullet}$ (C–S fragmentation and oxygen rebound), a regular increase of the 2-phenyl-2-propanol / aryl sulfoxide product ratios (Tables 1–2) are observed by increasing the electron withdrawing effect of the aryl substituents.

Table 1. Products and yields in the oxidation of aryl 1-methyl-1-phenylethyl sulfides (**1–4**) with H_2O_2 catalyzed by $[(\mathrm{PDP})\mathrm{Fe}^{\mathrm{II}}(\mathrm{SbF}_6)_2]$ in CH_3CN at 0°C.[a]

Substrate	Products (Yields %)[b]		
			Ratio[OH]/[SO]
1 X=OCH$_3$	5.7	2.7	2.1
2 X=CH$_3$	19	1.8	11
3 X=H	25	1.7	15
4 X=Cl	27	1.0	26

[a] H_2O_2 (60 μmol), $[(\mathrm{PDP})\mathrm{Fe}^{\mathrm{II}}(\mathrm{SbF}_6)_2]$ (1.5 μmol) and aryl 1-methyl-1-phenylethyl sulfides (60 μmol) in CH_3CN (600 μL) at 0°C in 6 min.
[b] Yields (mol %) refer to the amount of oxidant.

Table 2. Products and yields in the oxidation of aryl 1-methyl-1-phenylethyl sulfides (**1–4**) with H_2O_2 catalyzed by $[(\mathrm{BPMCN})\mathrm{Fe}^{\mathrm{II}}(\mathrm{OTf})_2]$ in CH_3CN at 0°C.[b]

Substrate	Products (Yields %)[b]		
			Ratio[OH]/[SO]
1 X=OCH$_3$	19	2.6	7.3
2 X=CH$_3$	38	2.4	16
3 X=H	49	1.4	35
4 X=Cl	44	0.7	68

[a] H_2O_2 (60 μmol), $[(\mathrm{PDP})\mathrm{Fe}^{\mathrm{II}}(\mathrm{SbF}_6)_2]$ (1.5 μmol) and aryl 1-methyl-1-phenylethyl sulfides (60 μmol) in CH_3CN (600 μL) at 0°C in 6 min.
[b] Yields (mol %) refer to the amount of oxidant.

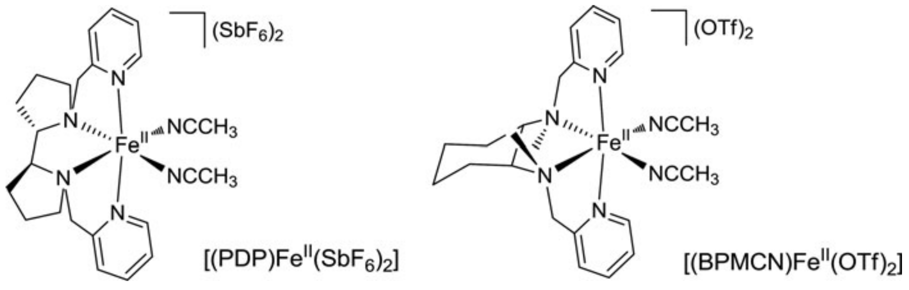
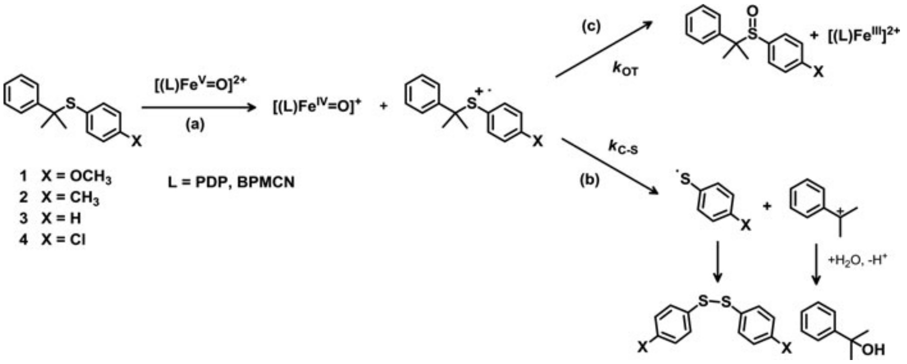
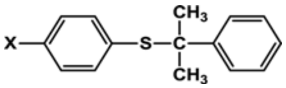


Figure 2. Tetradentate nonheme-iron complexes [(PDP)Fe^{II}(SbF$_6$)$_2$] and [(BPMCN)Fe^{II}(OTf)$_2$].



Scheme 2. Competition between C–S fragmentation and oxygen rebound in the oxidation of aryl 1-methyl-1-phenylethyl sulfides **1–4** promoted by the iron(V)-oxo complexes[(PDP)Fe^{V}=O]$^{2+}$ and [(BPMCN)Fe^{V}=O]$^{2+}$.

Table 3. C–S Fragmentation rate constants (k_f) of aryl 1-methyl-1-phenylethyl sulfide radical cations (**1**$^{+\bullet}$-**4**$^{+\bullet}$) and oxygen rebound rate constants (k_{OT}) for the oxidation of **1–4** by [(PDP)Fe^{V}=O]$^{2+}$ and [(BPMCN)Fe^{V}=O]$^{2+}$.

	k_f(10^4 s^{-1})[a]	k_{OT}(10^3 s^{-1})	
		[(PDP)Fe^{V}=O]$^{2+}$	[(BPMCN)Fe^{V}=O]$^{2+}$
1 X=OCH$_3$	<1	<4.7	<1.4
2 X=CH$_3$	3.0	2.8	1.9
3 X=H	3.4	2.3	0.97
4 X=Cl	3.7	1.4	0.59

[a] From LFP experiments, see ref. 21.

It is interesting to note that [(BPMCN)Fe^{V}=O]$^{2+}$ resulted a better oxidant with respect [(PDP)Fe^{V}=O]$^{2+}$ leading to significantly higher yields of the fragmentation product, 2-phenyl-2-propanol. The higher 2-phenyl-2-propanol / aryl sulfoxide product ratios observed in the oxidations promoted by [(BPMCN)Fe^{V}=O]$^{2+}$ (see Tables 1–2) might be rationalized on the basis of a minor efficiency of the oxygen rebound process from the reduced iron(IV) oxo complex [(BPMCN)Fe^{IV}=O]$^{+}$ with respect to [(PDP)Fe^{IV}=O]$^{+}$. The rate constants of the oxygen rebound step (k_{OT}) can be calculated from the fragmentation rate (k_f) of the radical cations, previously determined by laser flash photolysis experiments of the photochemical oxidations of **1–4** by *N*-methoxyphenanthridinium ion,[13] and the ratio of the yields of the sulfoxides and the fragmentation product 2-phenyl-2-propanol by applying the following equation:

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

From the k_{OT} values reported in Table 3, it can be noted that the oxygen rebound process promoted by [(PDP)Fe^{IV}=O]$^{+}$ with all the substrates investigated is significantly faster than that promoted by [(BPMCN)Fe^{IV}=O]$^{+}$.

Conclusions

The oxidations of aryl 1-methyl-1-phenylethyl sulfides with H_2O_2 catalyzed by the tetradentate nonheme iron complexes [(PDP)Fe^{II}(SbF$_6$)$_2$] and [(BPMCN)Fe^{II}(OTf)$_2$] involve an electron transfer-oxygen rebound mechanism as previously proposed for the oxidations of the same substrates promoted by nonheme iron(IV)-oxo complexes [(N4Py)Fe^{IV}=O]$^{2+}$ and [(Bn-TPEN)Fe^{IV}=O]$^{2+}$. The role of the ET process in the *S*-oxidations of a more extended series of aryl sulfides catalyzed by other nonheme iron complexes will be investigated in future studies.

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