Hydrogen Peroxide Oxidation of Mustard-Model Sulfides Catalyzed by Iron and Manganese Tetraarylporphyrines. Oxygen Transfer To Sulfides versus H_2O_2 Dismutation and Catalyst Breakdown

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Fe(III)- and Mn(III)-*meso*-tetraarylporphyrin catalysis of H_2O_2 oxidation of dibenzyl and phenyl-2-chloroethyl sulfides, **1**, is investigated in ethanol with the aim of designing catalytic systems for mustard decontamination. The sulfide conversion, the sulfoxide and sulfone yields, the oxygen transfer from H_2O_2 to the sulfide, and the catalyst stability depend markedly on the metal, on the substituents of its ligand, and on the presence or the absence of a cocatalyst, imidazole or ammonium acetate. With Fe, sulfones, the only oxidation products, are readily obtained whatever the ligand (TPP, F_{20}TPP, or TDCPP) and the cocatalyst; the oxygen transfer is fairly good, up to 95% when the catalyst concentration is small ([**1**]/[Cat] = 420); the catalyst breakdown is insignificant only in the absence of any cocatalyst. With Mn, the sulfide conversion is achieved completely when the ligand is TDCPP or TSO_3PP, but not F_{20}TPP or TPP; a mixture of sulfoxide, **2**, and sulfone, **3**, is always obtained with [**2**]/[**3**] = 3.5−0.85 depending on the ligand and the cocatalyst (electron withdrawing substituents favor **3** and NH_4OAc, **2**). The catalyst stability is very good, but the oxygen transfer is poor whatever the ligand and the cocatalyst. These results are discussed in terms of a scheme in which sulfide oxygenation, H_2O_2 dismutation, and oxidative ligand breaking compete. It is shown that the efficiency of the oxygen transfer is related not only to the rate constant of the dismutation route but also to the concentration of the active metal-oxo intermediate, most likely a perferryl or permanganyl species, i.e., to the rate of its formation.

Introduction

The reactivity of mustard, bis-(2-chloroethyl) sulfide, and its sulfide simulants is presently of much interest[1−4] not only because of its high toxicity and its use as a warefare agent,[2] but also because its controlled or uncontrolled world-spread stockpiles should be destroyed in the next few years.[1b,3c] Today, the usual procedure for large scale destruction is incineration. For decontamination of damaged people or material, bleach and/or chlorinated agents working at nonphysiological high pH (10−12) are still currently used, despite much effort in designing milder decontamination agents.[1]

Chemically, most of the difficulties in transforming mustard arise not from its poor reactivity but mainly from its high hydrophobicity.[4] For example, hydrolysis does not provide the expected nontoxic hydrophilic bis-(2-hydroxyethyl) sulfide but toxic polymeric salts arising from the trapping of the readily formed episulfonium ion by the starting sulfide and not by water.[5] Because of this resistance to hydrolysis, oxidation in microheterogeneous aqueous media leading to the hardly or nontoxic corresponding sulfoxide and sulfone[6] has been recently adopted.[3,4] In this strategy, the choice of the oxidant is crucial since efficient decontamination systems must meet a large number of requirements:[3c] fast and complete conversion of the sulfides into sulfoxides or sulfones excluding the formation of more robust disulfides, room temperature, neutral pH, cheap reagents, nonpollutant effluents, etc. In Menger's systems, sodium hypochlorite[3a,b] and, more recently, hydroperoxide anion[3c] are the oxidants working in SDS (sodium dodecyl sulfate) or polyoxyethylene microemulsions. Gonzaga et al.[4] use MMPP (magnesium monoperoxyphthalate) in formamide−water−CPC (cetylpyridinium chloride) microheterogeneous media.

We report now a new approach to sulfide oxidation by the cheap, nonpollutant, and reasonably stable hydrogen peroxide catalyzed by metalloporphyrins. At variance with the usual lab-scale procedures of sulfoxide synthesis,[7] the catalytic route can meet most of the decontamination requirements when the many applications of metalloporphyrin-catalyzed oxidation[8] to epoxidation and

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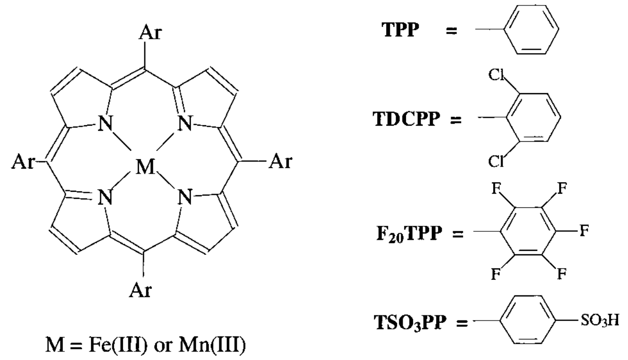
hydroxylation are considered. In contrast to the alkene and alkane reactions, only a few reports on sulfide and sulfoxide oxidations have been published[9,10] since the pioneer work of Oae et al.[11] and Ando et al.[12] These preliminary investigations show that alkene epoxidation can be a source of inspiration for designing catalytic systems convenient for sulfide decontamination. Moreover, they show that, depending on the metal of the catalyst, sulfoxides and/or sulfones are obtained readily, whereas disulfides arising from the coupling of radical cations are not observed, except when the sulfide bears an acidic α-hydrogen atom.[11b] The use of hydrogen peroxide as the oxidant, which was not very efficient because of the competition between the catalase activity (destruction of the oxidant by dismutation) of the catalyst, the ligand oxidation (destruction of the catalyst), and the oxygen transfer (oxygenation activity) to the substrate, is now under control for alkene epoxidation,[13−15] although the mechanism and the nature of the reactive intermediate are still under discussion.[16−19]

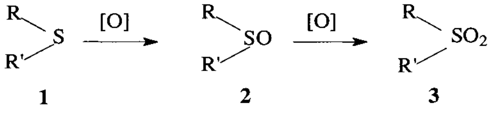
Moreover, for large-scale procedures as required for decontamination, the efficiency of a catalytic system has to be evaluated not only from the efficiency of the substrate oxidation but also from the oxygen transfer of the oxidant to the substrate and from the stability of all the components of the system, which is not necessarily considered in usual lab-scale investigations. In this paper, we show that iron and manganese tetraarylporphyrins provide efficient catalytic systems for sulfide oxidations into sulfones or sulfoxides by hydrogen peroxide, in ethanol, without significant bleaching of the catalyst and marked oxidant dismutation when the metal, the substituents of the porphyrinic ligand, and the cocatalyst are appropiately chosen.

Results and Discussion

Dibenzyl sulfide (**1a**) and phenyl-2-chloroethyl sulfide (**1b**) are used as models of mustard (**1c**). On one hand, sulfide oxidation rates are not significantly substituent-dependent,[20]much less than their corresponding hydrolysis rates.[5a]

Scheme 1





(1)

a : R = R' = CH_2Ph ; **b** : R = Ph, R' = CH_2CH_2Cl ; **c** : R = R' = CH_2CH_2Cl.

On the other hand, the lipophilicity of **1b**, a property of interest in view of forthcoming extensions to aqueous microheterogeneous media, is close to that of **1c**, while that of **1a** is markedly greater.[4] With the same objective in mind, ethanol rather than acetonitrile is the solvent, and we have shown previously that these two solvents provide similar efficiencies in sulfide oxidations when tetraphenyl porphyrin (TPP) is the catalyst ligand.[10]

The catalysts are manganese- and iron-*meso*-tetraarylporphyrins (Scheme 1) with various substituents in their phenyl rings. This so-called second generation of porphyrins[21] is investigated since TPP was shown to achieve sulfide oxidation successfully but can be readily bleached in the presence of hydrogen peroxide.[10] Moreover, phenyl-substituted metalloporphyrins are well known to catalyze efficiently H_2O_2 epoxidation of alkenes[13−15] whose reactivity toward oxidation is likely in the same range as that of the investigated sulfides. The third generation of still more robust porphyrins[21] with substituents in the pyrrole β-positions, which are mainly used for the hydroxylation of poorly oxidizable alkanes, is not considered since sulfides are expected to be reactive substrates. Finally, a cocatalyst, imidazole[14,22,23] or ammonium acetate,[23,24] is added in some experiments, in agreement with various catalytic systems previously designed for epoxidation and for some sulfide oxidations.[9c,10,11b]

The effect of the catalytic systems on the sulfide conversion and product distribution (sulfoxide versus sulfone) is measured in experiments carried out at room temperature, according to the usual standard procedure, i.e., by progressive additions of H_2O_2 (35% in water) to

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Table 1. Effect of the Porphyrin Substituents on the Catalyzed Oxidation of 1a and 1b by H_2O_2 in Ethanol[a]

entry	sulfide	catalyst	S %[b]	SO %[c]	SO_2 %[c]	cat %[d]	O transfer %[e]
1	**1a**	(TPP)FeCl[f]	0	0	100	15	50
2	**1a**	(TPP)MnCl[g]	36	64		23	14
3	**1a**	(F_{20}TPP)FeCl	0	0	100	25	40
4	**1a**	(F_{20}TPP)FeCl[h]	0	0	100	94	44
5	**1a**	(F_{20}TPP)FeCl[i,j]	0	0	100	70	95
6	**1a**	(TDCPP)FeCl[i,k]	0	0	100	33	80
7	**1a**	(F_{20}TPP)MnCl	28	64	8	89	17
8	**1a**	(TDCPP)MnCl	0	64	36	93	27
9	**1a**	(TSO_3PP)MnCl	0	46	54	68	31
10	**1b**	(TPP)FeCl[f]	0	37	63	12	33
11	**1b**	(TPP)MnCl[g]	62	38	0	21	8
12	**1b**	(F_{20}TPP)FeCl[g,h]	0	0	100	79	44
13	**1b**	(F_{20}TPP)FeCl[i,l]	0	17	83	19	78
14	**1b**	(F_{20}TPP)MnCl	33	67	0	80	13
15	**1b**	(TDCPP)MnCl	0	65	35	93	27
16	**1b**	(TSO_3PP)MnCl	0	53	47	66	29

[a] Reaction conditions (unless otherwise specified): [Catalyst] = 2×10^{-3} M; [Imidazole] = 5×10^{-2} M; [**1**] = 8.5×10^{-2} M; $[H_2O_2]_{total}$ = 5 × [**1**], 10 μL portion added every 5 min, complete addition in 90 min; room temperature; 94–99% recovered product and/or reagent at the end of the reaction. [b] Recovered sulfide at ±3% at the end of the reaction. [c] Percent of sulfoxide and sulfone in the total recovered compounds at ±3%. [d] Percent of recovered catalyst at ±2%. [e] Percent of oxygen transferred from H_2O_2 to the sulfide calculated from the differences between added and sulfide-incorporated oxygen atoms. [f] $[H_2O_2]_{total}$ = 4 × [**1**] = 3.4×10^{-1} M. [g] $[H_2O_2]_{total}$ = 4.5 × [**1**] = 3.8×10^{-1} M. [h] Without imidazole. [i] Without imidazole and [Cat] = 2×10^{-4} M. [j] $[H_2O_2]_{total}$ = 2.1 × [**1**] = 1.8×10^{-1} M. [k] $[H_2O_2]_{total}$ = 2.5 × [**1**] = 2.1×10^{-1} M. [l] $[H_2O_2]_{total}$ = 2.3 × [**1**] = 2×10^{-1} M.

the ethanolic solution of the reagents ([Catalyst] = 2×10^{-3} M; [Catalyst]/[Cocatalyst]/[Sulfide]:1/25/43, unless otherwise specified). Five minutes after each oxidant addition ($[H_2O_2]$ = about 2×10^{-2} M per addition), the remaining sulfide and the reaction products are analyzed by GC and UV spectrophotometry (Figure S1) for **1a** and **1b**, respectively. The reaction is considered to be finished when no progress in sulfide conversion is observed by further addition of the oxidant.

In all these experiments, the only oxidation products of **1a**–**b** are sulfoxides **2a**–**b** and sulfones **3a**–**b**, which correspond to 94–99% sulfide conversion. Disulfides from **1a** or **1b**, which are readily observable by GC or UV spectroscopy (Figure S1), are never found. This result is in contrast with a previous finding[11b] of Oae et al., who obtained small amounts (0.4–5.8%) of disulfides in the reaction of phenylsulfides, $PhSCH_2X$, with strongly electronwithdrawing X (X = CN, COPh), by (TPP)FeCl catalyzed H_2O_2 oxidation, which is very slow and incomplete (34.5 and 41% sulfide conversion after 2.5 h).

Whatever the catalytic system (Table 1), the addition of the small portions of the oxidant (0.1–0.5 sulfide equiv) promotes a very rapid sulfide oxidation. In most cases, the reaction is finished in less than 2 min. The total amount of H_2O_2 necessary to obtain the maximum sulfide conversion ([**1**] = 8.5×10^{-2} M under the standard conditions) depends on the catalytic system. For example with (F_{20}TPP)FeCl, the sulfide disappears completely after the addition of 2 molar equiv of the oxidant; further H_2O_2 additions converted the initially formed sulfoxide into sulfone (Figure 1, dashed line). In contrast, with the less efficient (TDCPP)MnCl/imidazole system, complete sulfide conversion requires the addition of 4 sulfide equiv of H_2O_2; whereas with a still poorer system, (TDCPP)-MnCl/NH_4OAc, the sulfide conversion is still not yet complete with 6 H_2O_2 equiv (Figure 2).

In parallel to the oxidation products, the destruction of the catalyst by oxidative breaking of its ligand is monitored from the bleaching of its Soret band (Table S2) during and/or at the end of the reactions (Figure S2).

The efficiency of the catalytic systems is evaluated from the following criteria: i) maximum sulfide conversion, ii) product distribution, i.e., mono- versus double-oxidation (eq 1), iii) degree of oxygen transfer from H_2O_2 to the sulfide, i.e., $[H_2O_2]$ necessary to achieve the complete reaction versus the number of oxygen atoms in the oxidation products, and iv) the catalyst stability. All these results, collected in Table 1, are discussed in terms of the usual mechanistic scheme[25] (Scheme 2), showing that the high-valent metal-oxo intermediate (vide infra) can either transfer its oxygen atom to the sulfide and sulfoxide, catalyze the H_2O_2 dismutation, or promote the oxidative breaking of the porphyrin ligand.[15,27]

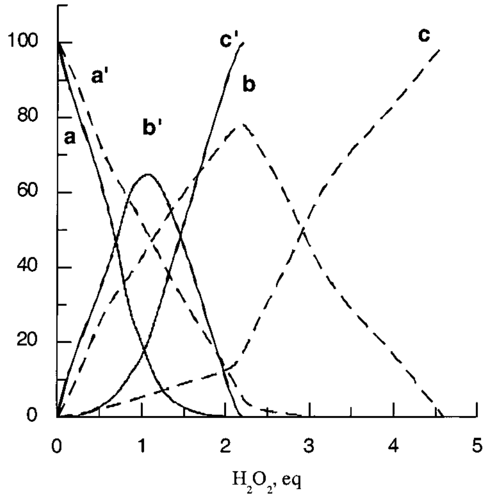

Figure 1. Progress of **1a** oxidation by successive additions of H_2O_2 (H_2O_2, eq: sulfide equivalent of H_2O_2) catalyzed by (F_{20}-TPP)FeCl, and its dependence on the concentration of catalyst. (Full lines, [Cat] = 2×10^{-4} M; dashed lines, [Cat] = 2×10^{-3} M; a and a′, **1a**; b and b′, **2a**; c and c′, **3a**.) Experimental points recorded every 0.3 H_2O_2, eq are omitted for clarity.

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(25) High-valent metal–oxo complexes as active intermediates in Scheme 2 and the term "oxygen transfer" are adopted here pragmatically since the overall process is sulfide oxygenation. However, the following discussion does not imply that the reactive intermediate is necessarily Por–M^V = O or $Por^{+\bullet}$–M^{IV} = O (see Conclusion). Moreover, the detailed mechanism of the sulfide oxidation is not necessarily a direct oxygen transfer, but could also involve an oxygen rebound step,[26] which is not ruled out by our results.

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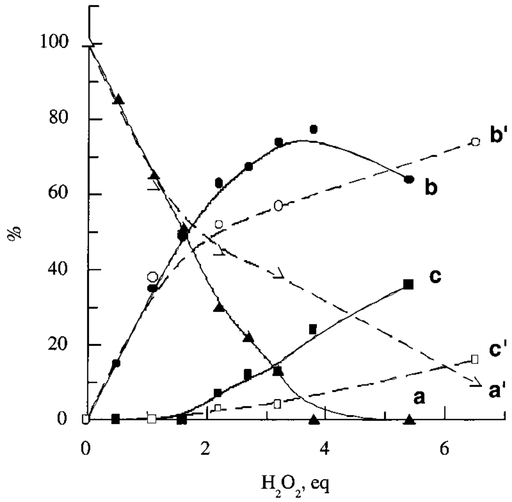
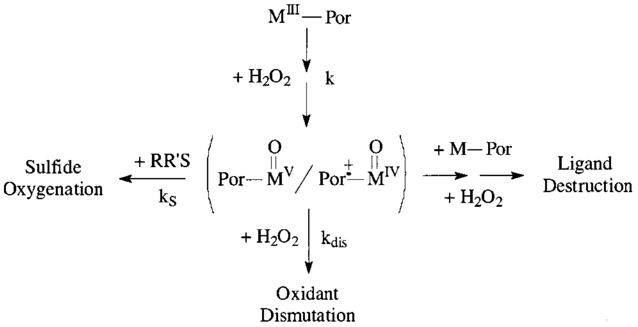


Figure 2. Progress of **1a** oxidation by successive addition of H_2O_2 (H_2O_2, eq: sulfide equivalent of H_2O_2) catalyzed by (TDCPP)MnCl, and its dependence on the nature of the cocatalyst. (Full lines, [Im] = 5 × 10^{-2} M; dashed lines, [NH_4-OAc] = 1.8 × 10^{-1} M; a and a′, **1a**; b and b′, **2a**; c and c′, **3a**.)

Scheme 2



Comparison of the Efficiency of Mn- and Fe-Tetraaryl Porphyrines

A first striking result in Table 1 is the analogous behavior of the two sulfides **1a** and **1b**. In most cases (entries 2 and 11, 4 and 12, 8 and 15, 9 and 16), not only the conversion of **1a** and **1b**, but also the catalyst stabilities and the corresponding oxygen transfer rates are very close, whatever the catalytic system. However, with the very efficient iron catalysts (entries 1 and 10, 5 and 13), **1a** is fully oxidized into sulfone whereas some sulfoxide, **2b**, is obtained from **1b**, suggesting that the oxygen transfer from the catalytic intermediate to **2b** is not as fast that to **2a**. The slightly smaller reactivity of **1b**−**2b** bearing substituents more electronwithdrawing that those of **1a**−**2a** (**1a**, $\Sigma\sigma^* = 0.43$; **1b**, $\Sigma\sigma^* = 1.00$) is indicative of the weakly nucleophilic behavior[28] of the sulfides and their sulfoxides toward oxidants. This result is consistent with the small kinetic effects of aryl sulfide substituents (ρ in the range of −1.0) whatever the oxidizing agent:[29]hydrogen peroxide,[28] metal peroxides,[29] N-sulfonyloxaziridines,[20] etc. Therefore, the data of Table 1 can be reasonably extrapolated to mustard itself (**1c**, $\Sigma\sigma^* = 0.8$).

A second important result is the difference in the efficiency of iron− and manganese−porphyrins. When the metal is Fe(III), the sulfides are fully oxidized into sulfones, whereas the oxidation with Mn(III) is never complete, providing at best mixtures of sulfoxide and sulfone. With Mn(III), the ligand substituents influence markedly the sulfide conversion (entries 7−9, 14−16). The more electron withdrawing the phenyl substituents (whose σ values increase on going from F to SO_3H), the larger the conversion and yield in sulfone. The trend in the catalyst stability is different; whereas the catalyst breakdown is small for (F_{20}TPP)MnCl and (TDCPP)-MnCl, the sulfonato catalyst is more significantly lost at the end of the reaction despite its very good sulfide oxygenation. However, in agreement with many other results in the literature, these three Mn−tetraarylporphyrins are markedly robust,[21] more robust than the corresponding unsubstituted TPP. Nevertheless although these Mn catalysts exhibit an excellent stability in these H_2O_2 oxidations, the oxygen transfer from the oxidant to the sulfide is never satisfactory, and it is only slightly improved on going from the unsubstituted to the substituted ligands. This suggests that with the Mn catalysts, a significant part of H_2O_2 is consumed in routes in which the sulfides are not involved and, in particular, by dismutation (Scheme 2) and/or in cocatalyst oxidation (vide infra), since a cocatalyst, imidazole or ammonium acetate, is indispensable for obtaining sulfide oxidation.

With the iron porphyrin (F_{20}TPP)FeCl under the standard conditions (entry 3), i.e., in the presence of imidazole, the sulfide conversion into sulfone is complete, and the oxygen transfer is significantly better than with the analogous Mn catalyst (entry 7), but the catalyst stability is very poor. In agreement with the well known tendency of iron prophyrins to bind imidazole more strongly than manganese porphyrins,[22,30,31] and according to the common practice of using iron porphyrins in protic solvents without any cocatalyst,[32] the suppression of imidazole in the catalytic system (entries 4 and 12) does not damage either the sulfide oxidation or the oxygen transfer, but increases very efficiently the stability of the catalyst, which is almost unchanged at the end of the reaction. Finally, a very efficient catalytic system (entries 5 and 13) is obtained by decreasing the catalyst concentration by a factor of 10; not only sulfides **1a** and **1b** are either totally or almost totally converted into sulfones, but the oxygen transfers are excellent while the catalyst stability remains satisfactory, at least in the case of **1a**. In other words, all the other H_2O_2 consuming routes which are observed with Mn catalysts are suppressed when (F_{20}TPP)FeCl is used in the absence of any cocatalyst and at very small concentration. With Mn catalysts (entries 7−9 and 14−16), the poor efficiency of the oxygen transfer is not improved by decreasing their concentration.

When the iron ligand is TDCPP (entry 6), the catalytic system under the same conditions (no cocatalyst, small [Catalyst]) is also quite efficient with regard to the sulfide oxidation and oxygen transfer, but less with regard to the catalyst stability.

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Table 2. Effect of the Cocatalyst on 1a Oxidation by H_2O_2 Catalyzed by Fe and Mn Porphyrins[a]

catalyst	cocatalyst[c]	cat %[b]	O transfer %[b]	time[d] (min)	S %[b]	SO %[b]	SO_2 %[b]
(TPP)FeCl	Im	15	50[e]	5	36	64	0
	NH_4OAc	10	13[f]	5	55	45	0
(TPP)FeCl	Im	23	14[g]	5	0	0	100
	NH_4OAc	24	10[g]	5	44	49	7
(F_{20}TPP)FeCl	No	94	44[g]	5	0	0	100
	Im	25	40[f]	5	0	0	100
	NH_4OAc	0	33[h]	5	12	88	0
(F_{20}TPP)MnCl	No	82	19[f]	1440	7	89	4
	Im	89	17[f]	5	28	65	9
	NH_4OAc	93	24[i]	5	0	78	22
(TDCPP)MnCl	No	*i*	1[f]	1440	83	7	0
	Im	93	27[f]	5	0	64	36
	NH_4OAc	93	16[f]	5	10	74	16
(TSO_3PP)MnCl	No	*j*	20[f]	90	0	99	1
	Im	68	31[f]	5	0	<50	>50
	NH_4OAc	45	19[f]	5	8	87	5

[a] Reaction conditions: room temperature; solvent, EtOH; $[\mathrm{Cat}] = 2 \times 10^{-3}$ M; $[\mathrm{Cocat}] = 5 \times 10^{-2}$ M; $[\mathbf{1a}] = 8.5 \times 10^{-2}$ M. [b] See footnotes b–e in Table 1. [c] Im = imidazole; NH_4OAc = ammonium acetate. [d] Maximum time necessary for the end of the sulfide oxidation progress. [e ,f,g,h] and [i]are for 4, 5, 4.5, 2.6, and 6.5 sulfide equiv, respectively, of H_2O_2 (35% in water) added to the reaction mixture 10 μL by 10 μL every 5 min, or longer for very slow oxidations. [j] Not determined.

Although the turnover of these catalysts cannot be calculated because of the poor stability of some of them, their efficiency can be qualitatively estimated in terms of number of transfered oxygen atoms per mole of catalyst. With the stable (TDCPP)MnCl–imidazole system, this number is 58 (entry 8 of Table 1); it reaches 850 with the more efficient (F_{20}TPP)FeCl at small concentration (entry 5).

In conclusion, the efficiency of the metalloporphyrin catalyzed H_2O_2 oxidations of the mustard-model sulfides depends on the metal of the catalyst and, to a smaller extent, on the porphyrin substituents. Complete sulfide conversion into sulfone (Fe) or a mixture of sulfoxide and sulfone (Mn) is achieved with most of the investigated catalysts, the only exception is observed for (F_{20}TPP)-MnCl. The excellent stability of Mn–porphyrins can also be reached with Fe–porphyrins when working under particular conditions. The oxygen transfer is quite good with iron, but not with manganese catalysts. This is a surprising result since previous data have shown that Mn–porphyrins generally exhibit a catalase activity (H_2O_2 dismutation) similar to or smaller than that of their Fe analogues.[14,33] In the results of Table 1, the main difference between the catalytic Mn and Fe systems is the presence or the absence of imidazole as a cocatalyst which can be H_2O_2 oxidized. Therefore, not only H_2O_2 dismutation (Scheme 2) but also the cocatalyst oxidation can be a route for H_2O_2 consumption at the origin of the poor oxygen transfer with Mn catalysts. Consequently, we investigate the role of the cocatalyst in these sulfide oxidations.

The Effect of the Cocatalyst on the Catalyst Stability

Recently, in view of minimizing the loss of oxidant arising from cocatalyst oxidation, imidazole has been replaced successfully by unoxidable ammonium acetate, which can play the same roles as imidazole in the formation of the high-valent metal–oxo intermediate.[23,24] For example, (TDCPP)MnCl catalyzes H_2O_2 epoxidation of a variety of alkenes in the presence of NH_4OAc, with yields as good as those obtained in the presence of Im but with markedly smaller amounts of oxidant.[24] This interesting improvement is, unfortunately, not observed for sulfide oxidation, as shown in Table 2 and S1 for **1a** and **1b**, respectively. Although the degree of sulfide conversion is not markedly altered, the oxygen transfer does not increase by using NH_4OAc instead of Im, neither with Mn– nor Fe–porphyrins. Clearly, the poor efficiency of the oxygen transfer to sulfides does not result from a competition between sulfide and imidazole oxidations.

In parallel to this result, the effect of the cocatalyst on the catalyst stability is investigated (Figure 3). The excellent stability of Mn–porphyrins (Figure 3A) is not significantly altered by changing the cocatalyst. Moreover, the acceleration it provides (compare reaction times for the Mn catalysts with or without cocatalyst) does not depend on its nature, Im or NH_4OAc. In contrast, the presence of a cocatalyst accelerates dramatically the Fe catalyst breakdown (Figure 3B), without changing the sulfide conversion or the oxygen transfer.

These cocatalyst effects, acceleration of sulfide oxidation for Mn–porphyrins and increase in the ligand destruction for Fe–porphyrins, can be rationalized considering the well-established roles of a cocatalyst.[8] First, it acts as an acid–base couple in the formation of the high-valent metal–oxo intermediates[16,17] (eq 2).

$$\mathrm{Por\ M^{III}} + \mathrm{H_2O_2} + \mathrm{B} \rightleftharpoons \mathrm{Por\ M^{III}} - \mathrm{OOH} + \mathrm{BH^+} \rightarrow \mathrm{Por\ M^{V}} = \mathrm{O} + \mathrm{B} + \mathrm{H_2O} \quad (2)$$

In protic solvents which can act as a proton donor, such as methanol or ethanol, this role is not important, as shown by the unnecessary presence of a cocatalyst with the iron catalytic systems.[32] Nevertheless, with Mn the proton donation by the solvent does not promote the formation of the high-valent intermediate in concentrations large enough for oxidizing the sulfides. The second role of a cocatalyst is the stabilization of the intermediate by electron donation to the electron deficient metallic center.[8,18] This effect is more important for Fe- than for Mn catalysts since imidazole binds the iron centers more strongly than the manganese ones, in particular in water.[22,30,31,34] In this context, the finding that the route for ligand breakdown (Scheme 2) is highly favored by

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(33) (a) Belal, R.; Momenteau, M.; Meunier, B. *J. Chem. Soc., Chem. Comm.* **1989**, 412. (b) Belal, R.; Momenteau, M.; Meunier, B. *New J. Chem.* **1989**, *13*, 853.

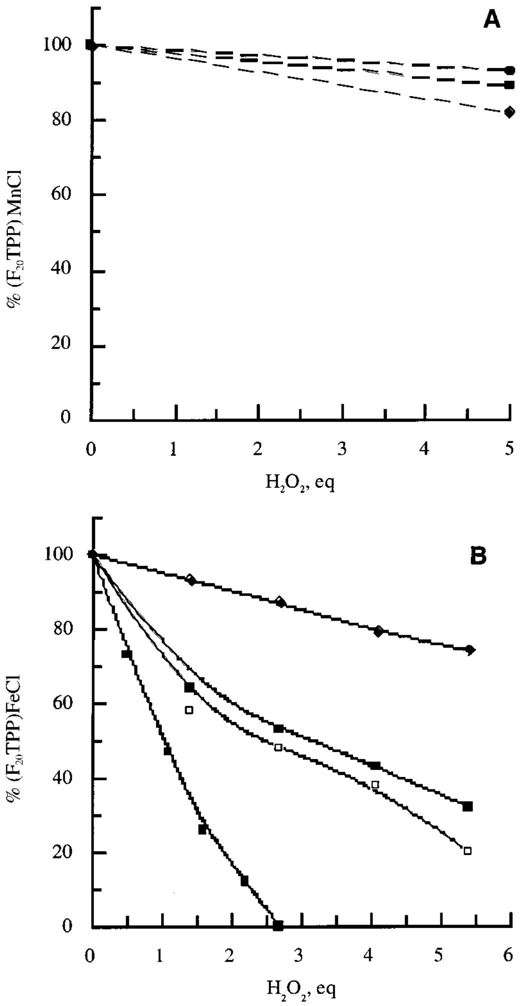

Figure 3. Effect of the cocatalyst on the stability of the catalyst during **1a** oxidation, [Cat] = 2 × 10^{-3} M; [**1a**] = 8.5 × 10^{-3} M, $[H_2O_2]_{total}$ = 0.5 M. A, $(F_{20}TPP)MnCl$; B, $(F_{20}TPP)FeCl$. ◆ without cocatalyst; ■ [imidazole] = 5 × 10^{-2} M; □ [imidazole] = 0.43 M; ● [ammonium acetate] = 0.13 M.

cocatalysts when M is Fe but not Mn is surprising. This difference arises probably from their different electronic distributions.[8,34,35] With Mn, the porphyrin ligand is not strongly altered by the metal oxidation ($Mn^{III} \rightarrow Mn^{V}$), whereas with Fe ($Fe^{III} \rightarrow Fe^{IV}$), the ligand is oxidized (Por → $Por^{+\bullet}$) so that its further oxidative breaking is likely to be easy. The reason the strong binding of the metal to an electron donating cocatalyst favors this oxidative process is obscure, unless it contributes efficiently to the stabilization of the radical cation in the porphyrin ligand.

In conclusion, the poor efficiency of the oxygen transfer with Mn catalysts in the presence of Im cannot be attributed to the cocatalyst oxidation, since this oxygen transfer is not markedly improved using NH_4OAc instead of Im. Therefore, the H_2O_2 consumption by the cocatalyst is not a significant route in the overall mechanism (Scheme 2) and is not to be considered.

Effect of the Catalyst Concentration on the Oxygen Transfer

A remarkable improvement of the oxygen transfer is observed with $(F_{20}TPP)FeCl$ when its concentration is decreased by a factor of 10 (Table 1; entries 4 and 5 with [Sulfide]/[Catalyst] = 42 and 420, respectively). This is shown in Figure 1, where the oxygen transfer to the sulfide at [Cat] = 2 × 10^{-4} M is compared to that at [Cat] = 2 × 10^{-3} M. At the smallest [Cat], only 2.2 sulfide equiv of H_2O_2 are necessary to obtain the complete sulfide conversion into sulfone. In other terms, the parallel H_2O_2 consuming reactions are strongly minimized. In particular, H_2O_2 dismutation is almost totally inhibited. The same effect is observed with (TPP)FeCl in the presence of imidazole (Figure 4). After the addition of 1.1 sulfide equiv of H_2O_2, the sulfide conversion is 70% only when [Cat] = 2 × 10^{-3} M. It increases smoothly up to 98% with [Cat] = 4 × 10^{-4} M. Further [Cat] decrease diminishes very rapidly the sulfide conversion because of a significant breakdown of the catalyst (entry 5, Table 1 and ref 10). Therefore, the efficiency of sulfide oxidation results from a subtle balance between the catalyst stability and the oxidant dismutation. A decrease in the concentration of the iron catalyst decreases the ligand resistance but decreases the dismutation, providing a very efficient oxygen transfer. In contrast, with Mn catalysts and, in particular, with (TDCPP)MnCl, the improvement of the sulfide conversion and oxygen transfer is much smaller (Table 3).

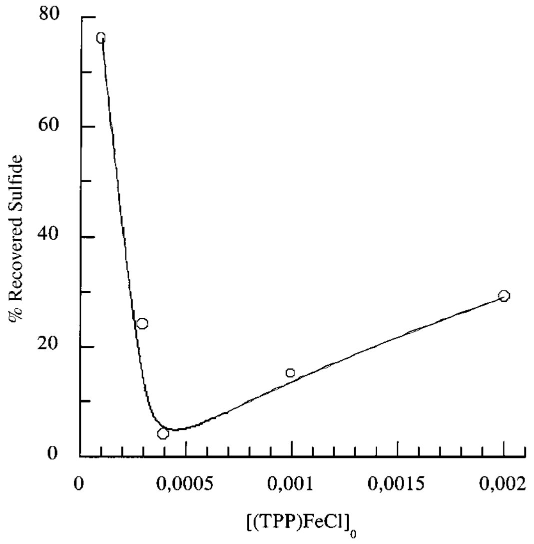

Figure 4. Effect of the concentration of the catalyst ((TPP)-FeCl) on **1a** oxidation by H_2O_2 ([**1a**] = 8.5 × 10^{-2} M; [Im] = 5 × 10^{-2} M; [H_2O_2] = 9.3 × 10^{-2} M added progressively).

Table 3. Effect of the Catalyst Concentration on 1a Oxidation by H_2O_2[a]

catalyst	[Cat], M	O transfer %[b]	S %	SO %	SO_2 %
(TPP)MnCl	2 × 10^{-3}	14 (5)	30	70	0
(TPP)MnCl	1 × 10^{-3}	10 (5)	50	50	0
(TPP)FeCl	2 × 10^{-3}	71 (1)	29	71	0
(TPP)FeCl	5 × 10^{-4}	96 (1)	4	96	0
$(F_{20}TPP)FeCl$[c]	2 × 10^{-3}	44 (5)	0	0	100
$(F_{20}TPP)FeCl$[c]	2 × 10^{-4}	95 (2.1)	0	0	100
(TDCPP)MnCl	2 × 10^{-3}	31 (3.2)	13	74	13
(TDCPP)MnCl	2 × 10^{-4}	38 (3.2)	0	80	20

[a] Reaction conditions: room temperature; solvent, EtOH; [Cat] = 2 × 10^{-3} M; [Im] = 5 × 10^{-2} M; [**1a**] = 8.5 × 10^{-2} M; H_2O_2 (35% in water) progressively added. [b] In parentheses: added sulfide equivalent of total H_2O_2. [c] Without imidazole.

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The effect of the catalyst concentration on H_2O_2 dismutation and its competition with oxygen transfer to the sulfide can be rationalized in terms of Scheme 2, in which the ligand destruction route is negligible since it does not contribute to the H_2O_2 outcome because of the insignificant concentration of the catalyst as compared to the other reagents. Moreover, in this Scheme, the cocatalyst oxidation, another H_2O_2 consuming route, is not considered since, in our study, this route does not exist (vide supra). According to this simplified scheme, the oxidant consumption is expressed by eq 3. The analogous expression for the sulfide, S, conversion is given by eq 4.

$$-\frac{\mathrm{d}[\mathrm{H_2O_2}]}{\mathrm{d}t} = k[\mathrm{M}][\mathrm{H_2O_2}] + k_{\mathrm{dis}}[\mathrm{M^v} = \mathrm{O}][\mathrm{H_2O_2}] \qquad (3)$$

$$-\frac{\mathrm{d}[\mathrm{S}]}{\mathrm{d}t} = k_{\mathrm{S}}[\mathrm{M^v} = \mathrm{O}][\mathrm{S}] \qquad (4)$$

When eqs 3 and 4 are combined, the relative rates of sulfide and oxidant conversions, i.e., the degree of oxygen transfer to the sulfide, is obtained, eq 5.

$$\frac{\mathrm{d}[\mathrm{H_2O_2}]}{\mathrm{d}[S]} = \frac{k[\mathrm{M}][\mathrm{H_2O_2}]}{k_{\mathrm{S}}[\mathrm{M^v} = \mathrm{O}][\mathrm{S}]} + \frac{k_{\mathrm{dis}}[\mathrm{H_2O_2}]}{k_{\mathrm{S}}[\mathrm{S}]} \qquad (5)$$

Application of the steady-state assumption to the intermediate $M^V = O$, the formation of which is rate-limiting,[36] gives eq 6.

$$[\mathrm{M^V} = \mathrm{O}] = \frac{k[\mathrm{M}]\,[\mathrm{H_2O_2}]}{k_{\mathrm{dis}}[\mathrm{H_2O_2}] + k_{\mathrm{S}}[\mathrm{S}]} \qquad (6)$$

Combination of eqs 5 and 6 leads[37] to eq 7, in which the [M] dependence of the oxygen transfer appears.

$$\frac{\mathrm{d}[\mathrm{H_2O_2}]}{\mathrm{d}[\mathrm{S}]} = \frac{k[\mathrm{M}] + k_{\mathrm{dis}}[\mathrm{M^V} = \mathrm{O}]}{k[\mathrm{M}] - k_{\mathrm{dis}}[\mathrm{M^V} = \mathrm{O}]} \qquad (7)$$

According to eq 7, the efficiency of the oxygen transfer to the sulfide depends on the relative values of the two terms, $k[M]$ and $k_{dis}[M^V = O]$. The good oxygen transfer ($d[H_2O_2]/d[S]$ close to unity; entries 5, 6,and 13 in Table 1) with Fe catalysts at small concentrations exhibits a $k_{dis}[M^V = O]$ that is almost negligible as compared to k[M]; $k_{dis}[M^V = O] \ll k[M]$. In contrast, at larger [FePor] or with Mn–porphyrins, $k_{dis}[M^V = O] < k[M]$. This can occur because of significant k_{dis} values and/or significant concentrations of the reactive intermediate. In the case of Fe but not Mn, $[M^V = O]$ is probably large since $Fe^V = O$ is generated much faster than $Mn^V = O$, whereas the rates of disappearance of both species are in similar ranges.[30] (In water at pH close to neutrality, k for Mn catalysts is several powers of 10 smaller than that for Fe catalysts.[30])

In conclusion, the results of Table 1 on the oxygen transfer do not imply necessarily that the rate constant for H_2O_2 dismutation is larger with Mn than with Fe–tetraarylporphyrins.[33] Also, the better efficiency of Fe- versus Mn-catalysts in the sulfide oxidation, despite the poor stability of the Fe–porphyrins, results likely from the faster formation of the corresponding reactive intermediates.

Conclusion

This investigation of H_2O_2 oxidation of sulfides in a protic solvent shows that catalysis by Fe(III)– and Mn(III)–tetraarylporphyrins can provide an interesting route to the transformation of mustard and related sulfides into sulfoxides and sulfones. The method meets most of the requirements for a useful decontamination procedure: neutral pH, room temperature, nonpollutant effluents, readily available reagents, and, mainly, fast and quantitative conversion of the sulfide into sulfone and nontoxic sulfoxide. Mn–porphyrins are preferred if the desired oxidation product is the sulfoxide, but Fe–porphyrins are preferred if sulfone can be tolerated, since the catalytic efficiency of the latter is significantly better.

In addition to their relative efficiency in sulfide oxidation, large differences in the behavior of Mn– and Fe–porphyrins are also observed. Whereas Mn–porphyrins are highly stable, the oxygen transfer is poor whatever the cocatalyst, the presence of which is indispensable. In contrast, with Fe–porphyrins the oxygen transfer can be very good despite their moderate stability, even in the absence of any cocatalyst. These differences are partly understood by the relative rates of formation of the active catalyst intermediate in terms of Scheme 2 and the derived eq 7, in which this intermediate is assumed to be the high-valent metal–oxo, perferryl or permanganyl, species. Nevertheless, it must be noted that our use of Scheme 2 implies only the existence, but not the structure, of any intermediate. In the case of iron, the most recent data are[15,16,18,19] unambiguously consistent with the $Por^{+\bullet}{-}Fe^{IV} = O$ radical cation, formally identical to $Por{-}Fe^V = O$, and not with other alternatives such as the peroxo, $PorFe^{III}{-}OOH$, or the ferryl, $Por{-}Fe^{IV} = O$, species, since the active intermediate arises from the heterolytic cleavage of the O–O bond of the peroxo complex. An analogous structure for the manganese intermediate is presently less straightforward.[35] However, our results do not suggest significant differences in the structure of the intermediates arising from Mn– and Fe–porphyrins. In particular, both are able to transfer their oxygen atom not only to the nucleophilic sulfide but also to the less nucleophilic or even electrophilic sulfoxide since sulfones are obtained with the two catalysts.

More work is in progress to obtain data relevant to the mechanism of these metalloporphyrin-catalyzed H_2O_2 oxidations of sulfides and also to extend the scope of these catalytic systems from ethanol to aqueous micellar media.

Experimental Section

Physical Measurements. UV–vis spectra were recorded on a Perkin–Elmer lambda II spectrophotometer. Gas Chromatography analyses were carried out on a Delsi Nermag 200 gas chromatograph equipped with a F.I.D. detector and a CP–Sil 5 column. The products were identified by comparison of

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(36) This has been shown for alkene epoxidation[13,16,19] and can be reasonably extended to sulfide oxidation.

(37) A referee has underlined that other equations in which the [M] dependence is hidden can be obtained by combining eqs 5 and 6. Moreover, the H_2O_2 consumption (eq 3) could be second order or higher in $M^V = O$. However, even if eq 7 is too simple for a fully quantitave analysis of kinetic data, it points to the role of the concentration of the reactive intermediate in the oxygen transfer, whatever the $[M^V = O]$ order.

their retention times with authentic samples or by GC−MS (I.T.D. Finigan 800).

Materials. Ethanol (H.P.L.C. grade, Prolabo) was used as received. Hydrogen peroxide (H_2O_2 35% in water, Acros) was stored at 5 °C and titrated every two weeks. Sulfides, sulfoxides, and sulfones were purchased from Aldrich or Acros and used as received, with the exception of dibenzyl sulfoxide, which was recrystallized in methanol. The absence of any oxidation product in the commercial sulfides was checked before use by GC. All the catalysts were commercial (Aldrich) and used without further purification.

Oxidation Procedure. To 5 mL of a reaction mixture (0.085 M sulfide, 0.05 M cocatalyst, ammonium acetate or imidazole, and 0.002 M catalyst) in ethanol was added directly the commercial solution of hydrogen peroxide by small amounts with a microsyringe. The oxidant is added 10 per 10 μL with a delay of 5 min between each addition to prevent hydrogen peroxide dismutation. For dibenzyl sulfide, GC analysis were performed on aliquots withdrawn directly from the reaction mixture; yields were measured by GC with the internal standard method, in which the signals corresponding to authentic samples of sulfide, disulfide, sulfoxide, and sulfone are well separated. The yields for $PhSCH_2CH_2Cl$ oxidation, which cannot be obtained by GC because sulfone and sulfoxide exhibit very close retention times, were measured by UV−vis spectroscopy combining the absorbances at 253 and 240 nm (Figure S1). The amounts of sulfoxide and sulfone in the reaction mixture are obtained from the absorbances of the reaction mixture at 253 nm (ϵ_S, 5900; ϵ_{SO}, 1800 L mol^{-1} cm^{-1}) and 240 nm (ϵ_{SO}, 2740; ϵ_{SO2}, 40 L mol^{-1} cm^{-1}). The sulfide disappearance at the beginning of the reaction (negligible sulfone) is evaluated by the absorbance change at 253 nm using eq 8, where A_0 and A_t are the initial absorbance and that for the considered aliquot, respectively.

$$[S]_t/[S]_o = (\epsilon_S A_t - \epsilon_{SO} A_0)/A_0(\epsilon_S - \epsilon_{SO}) \tag{8}$$

The sulfoxide/sulfone ratio is evaluated at 240 nm (no sulfide absorbance) at the end of the sulfide conversion with $[SO]_t/([SO]_t + [SO_2]_t) = [SO]_t/([S]_0)$, assuming that the conversion of sulfoxide into sulfone is quantitative. All the reactions were carried out at room temperature, without any buffer, and under aerobic conditions.

Measurements of the Catalyst Breakdown. The disappearance of the porphyrins was monitored by UV−vis spectrophotometry by the decrease of their Soret band (Table S2); 8 μL of the reaction mixture were taken with a microsyringe and diluted directly in the cell containing 2 mL of ethanol. The percentage of the remaining catalyst was then calculated.

Acknowledgment. We are grateful to Dr P. Battioni for her generous gift of most of these catalysts and for fruitful discussion.

Supporting Information Available: Oxidation data for **1b** and the cocatalyst effect (Table S1); spectroscopic data of **1b**, its oxidation products (Figure S1), and the metalloporphyrins in EtOH (Table S2 and Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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