Remarkable efficiency of iron(III) versus manganese(III) tetraphenylporphyrins as catalysts for fast and quantitative oxidation of sulfides into sulfones by hydrogen peroxide

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Abstract: The efficiency of various metallo-phtalocyanines (Pht) and -tetraphenylporphyrins (TPP) as catalysts for the H_2O_2 oxidations of dibenzylsulfide, phenylchloroethylsulfide, and thioanisole is investigated in ethanol and acetonitrile, using imidazole as a cocatalyst. Neither $PhtNi^{II}$ nor $TPPCo^{II}$ exhibits any catalytic activity. $PhtMn^{II}$ and $TPPMn^{III}Cl$ accelerate markedly these reactions but do not promote quantitative oxidations, at most 70% of the sulfides being transformed into sulfoxides. In contrast, with $PhtFe^{II}$ sulfoxides are obtained with a 100% yield from sulfides. Finally, the only catalyst able to oxidize sulfides rapidly (<5 min), completely and quantitatively (100% sulfone) is $TPPFe^{III}Cl$ in EtOH. The absence of any by-product, disulfide in particular, suggests that a free sulfenium radical cation is not an active intermediate in these reactions. The marked differences in the behaviour of $TPPMn^{III}Cl$ and $TPPFe^{III}$ Cl are analyzed by comparing the rates of the catalyst decomposition, of the sulfoxide and sulfone formation as a function of the hydrogen peroxide concentration. The results are discussed in terms of a competition between the several oxidative pathways and a possible mechanism for the oxygen transfer to sulfides.

Key words: sulfide, oxidation, H_2O_2, manganese(III) or iron(III) tetraphenylporphyrin.

Résumé : Opérant dans l'éthanol et l'acétonitrile et utilisant l'imidazole comme cocatalyseur, on a étudié l'efficacité de divers métallo-phtalocyanines (Pht) et de -tétraphénylporphyrines (TPP) comme catalyseurs des oxydations par le peroxyde d'hydrogène du sulfure de dibenzyle, du sulfure de chloroéthyle et de phényle et du thioanisole. Ni le $PhtNi^{II}$ ni le $TPPCo^{II}$ ne présente d'activité catalytique. Le $PhtMn^{II}$ et le $TPPMn^{III}Cl$ accélèrent beaucoup ces réactions, mais ils ne conduisent pas à des oxydations quantitatives; au mieux, 70% des sulfures sont transformés en sulfoxydes. Par ailleurs, avec le $PhtFe^{II}$, les sulfures conduisent aux sulfoxydes avec des rendements de 100%. Enfin, le $TPPFe^{III}Cl$ dans l'éthanol est le seul catalyseur à pouvoir oxyder les sulfures rapidement (moins de 5 min), complètement et quantitativement (100% de sulfone). L'absence de sous-produit, en particulier de disulfure, suggère que le cation radicalaire sulfénium libre n'est pas un intermédiaire actif dans ces réactions. On a analysé les différences marquées de comportement du $TPPMn^{III}Cl$ et $TPPFe^{III}Cl$ en procédant à une comparaison des vitesses de décomposition du catalyseur ainsi que les vitesses de formation du sulfoxyde et de la sulfone en fonction de la concentration du peroxyde d'hydrogène. On discute des résultats en fonction d'une compétition entre plusieurs voies d'oxydation et un mécanisme possible pour le transfert d'oxygène aux sulfures.

Mots clés : sulfure, oxydation, peroxyde d'hydrogène, manganèse(III) ou fer(III) tétraphénylporphyrine.

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Introduction

Toxic sulfides and, in particular, mustard $(ClCH_2\text{-}CH_2)_2S$, a warfare agent, are markedly detoxified by transforming them into their corresponding oxidized derivatives, sulfoxides, and sulfones (1). Therefore, strong oxidants, hypochlorite, or *N*-chloramines for

$$[1] \quad R_2S \overset{[O]}{\rightarrow} R_2SO \overset{[O]}{\rightarrow} R_2SO_2$$

example, were currently used[2] as decontaminants (1*b*, 2, 3). In contrast, hydrogen peroxide, a cheap, nonpolluting, and not strongly corrosive oxidant, has not been considered[3] until now for this objective (4). This is not surprising, since it is well known that uncatalyzed hydrogen peroxide oxidations[4] of

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[2] For synthetic, mechanistic, and other purposes, oxidation of sulfides into sulfoxides but not sulfones by a large variety of oxidants is extensively investigated (3).

[3] In contrast, the reactivity of H_2O_2 under basic conditions towards VX, a toxic organophosphorous thioester, has been investigated (4) using the high nucleophilicity of the perhydroxyl anion.

[4] Sulfide half-lives of several hours for reagent concentrations in the 10 mmol range (5).

sulfides are slow (5) whereas decontamination procedures require very fast chemical transformations. Consequently, hydrogen peroxide can be viewed as an efficient oxidant only if its reaction is markedly catalyzed. Biomimetic catalysts and, in particular, metalloporphyrins have been extensively developed for olefin epoxidations and alkane hydroxylations (6). These catalysts should be efficient also for sulfide oxidations, since these latter are oxidized more readily than unsaturated and saturated hydrocarbons (7). However, with the currently investigated catalysts, strong oxidants (iodosobenzene, peracids, etc.) are generally preferred to hydrogen peroxide, in order to avoid the catalyst destruction by hydroxyl radicals readily released by homolytic H_2O_2 decomposition, itself catalyzed by metal complexes (8). Nevertheless, hydrogen peroxide can be used successfully using specially robust porphyrin ligands (9). More recently, metallo-phtalocyanines were shown to be also powerful catalysts for H_2O_2 oxidation of resistant chlorophenols (10). Moreover, depending on the substrate and on the objectives of the authors, iron or manganese or any other transition metal can be the most efficient for oxygen transfer (11).

With regards to sulfides, much less work has been carried out (3*b* and *c*, 12) and, to the best of our knowledge, there is no data that allows for a reasonable choice of a given catalyst (metal and ligand) for promoting their fast and quantitative oxidation into sulfones. In this paper, we report a preliminary investigation of the efficiency of various commercially available biomimetic catalysts for the hydrogen peroxide oxidation of some alkyl sulfides often used to simulate the reaction of mustard (2).

Results and discussion

In the two last columns of Table 1 are shown the yields in sulfoxide and sulfone obtained by oxidation of dibenzyl ($PhCH_2SCH_2Ph$), (2-chloroethyl)phenyl sulfides ($PhSCH_2CH_2Cl$), and thioanisole ($PhSCH_3$), **1**, **2**, and **3**, respectively, by hydrogen peroxide in ethanol and acetonitrile in the presence of catalysts with phtalocyanine, Pht, and meso-tetrakisphenylporphyrin, TPP, as ligands[5] complexing transition metals in various oxidation states, Co(II), Ni(II), Fe(II), Fe(III), Mn(II), Mn(III).

In all the experiments, the initial concentrations of sulfide and catalyst are 8.5×10^{-2} and 2×10^{-3} M, respectively (these values correspond to a substrate/catalyst molar ratio of 42.5). The catalyst concentration is significantly larger than those currently used to compensate for its decomposition, expected because of the well-known fragility of the ligands in the absence of particular substituents. As usual (6–9, 11–13), imidazol (Im) is employed as a cocatalyst in a [Im]:catalyst conc. ratio of 25. Five sulfide equivalents of hydrogen peroxide (35% in water) are added by small portions (10 μL every 5 min) to minimize dismutation of the oxidant and (or) the destruction of the catalyst by reaction of the active metallic species with H_2O_2. Five minutes after the completion of the addition, an aliquot of the reaction mixture is analyzed by GC. The products are identified by GC–MS analysis and (or) by comparison of their retention times to those of authentic samples that were commercially available. When sulfide is not completely consumed, aliquots of the reaction mixture are analyzed at regular time intervals until the sulfide disappearance does not progress significantly.

Table 1. Sulfide oxidation[a] by hydrogen peroxide in the presence of metallo-phtalocyanines (Phth) and -tetraphenylporphyrins (TPP).[b]

Catalyst	Time (min)[c]	Sulfide	Solvent	%S[d]	%SO[a]	%SO_2[a]
None	2800	$(PhCH_2)_2S$	EtOH	5	95	[f]
PhthNi$^{\mathrm{II}}$[e]	2760			5	95	[f]
TPPCo$^{\mathrm{II}}$	2760			5	95	[f]
PhthMn$^{\mathrm{II}}$	5			30	70	[f]
PhthFe$^{\mathrm{II}}$	5			7	93	[f]
TPPMn$^{\mathrm{III}}$Cl	5			30	70	[f]
TPPFe$^{\mathrm{III}}$Cl	5			0	[f]	99
TPPFe$^{\mathrm{III}}$Cl	5	$PhSCH_2CH_2Cl$		0	[f]	100
TPPFe$^{\mathrm{III}}$Cl	5	$PhSCH_3$		0	[f]	100
TPPMn$^{\mathrm{III}}$Cl	5	$(PhCH_2)_2S$	CH_3CN[g]	25	75	[f]
TPPFe$^{\mathrm{III}}$Cl	5			0	0	99

[a] Sulfoxide, SO, and sulfone, SO_2, are the only products. Product yields are reproducible at ±3%.

[b] Catalyst conc., 2×10^{-3} M; [Im], 5×10^{-2} M; sulfide conc., 8.5×10^{-2} M; $[H_2O_2]_{Tot}$, 0.476 M, added by fraction of 10 μL; room temperature.

[c] Between the last addition of H_2O_2 and the end of the reaction.

[d] Unchanged sulfide.

[e] Catalyst conc., 5×10^{-4} M, because of the poor solubility of the catalyst in EtOH.

[f] This product is not detectable in the corresponding chromatogram.

[g] In this solvent, metallo-phthalocyanines are not soluble at the concentration used in ethanol.

As shown in the three first rows of Table 1, neither Co$^{\mathrm{II}}$TPP nor Ni$^{\mathrm{II}}$Pht catalyzes significantly the oxidation of **1**, since the time required for its almost complete disappearance is similar with and without these catalysts. In contrast, Mn(II) or Fe(II) phtalocyanines exhibit significant catalytic power; 5 min after the complete addition of H_2O_2, most of dibenzylsulfide is transformed into the corresponding sulfoxide. However, Mn(II) is less efficient than Fe(II), since with Mn(II) the reaction stops when 70% of sulfide is oxidized whereas 7% only subsists with Fe(II). The behavior of Mn(II) porphyrin is quite similar to that of the two metallo-phtalocyanines. Compound **1** is significantly oxidized into sulfoxide only. With all these catalysts, no sulfone was obtained. Finally, the only catalyst able to totally oxidize dibenzylsulfide into sulfone is Fe$^{\mathrm{III}}$TPPCl. The reaction is very fast under the reaction conditions, sulfide being completely oxidized in less than 5 min. Moreover, oxidation products, other than sulfoxide and sulfone, are never observed.

In Table 1, are also shown results for (2-chloroethyl)phenyl sulfide **2** and thioanisole **3**. Again, Fe$^{\mathrm{III}}$TPPCl is able to promote the complete and quantitative transformation of these sulfides into the corresponding sulfones directly. At variance with dibenzylsulfide, Mn$^{\mathrm{III}}$TPPCl is not very efficient, **2** being oxidized at most 30% with this catalyst.

In these experiments, ethanol is preferred to acetonitrile in order to minimize sulfide oxidation by $OH^{\cdot}$ radicals, formed by metal-mediated homolysis of H_2O_2, which would lead to unwanted oxidation by-products. It is expected that these radicals react with ethanol more rapidly than with sulfide, since

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[5] On one hand, phtalocyanines, which are important industrial dyes, are very cheap. On the other hand, there is extensive work on metallo-porphyrins as biomimetic catalysts of oxidation (6–9, 11, 12).

ethanol is an $OH^{\cdot}$ trapping agent more efficient than acetonitrile (13). Nevertheless, when the catalyzed oxidations are carried out in acetonitrile (last rows of Table 1), the product distribution is essentially the same as that observed in ethanol. A reasonable conclusion is, therefore, that free $OH^{\cdot}$ radicals do not play a significant role in these sulfide oxidations under the present reaction conditions.

Another remarkable result of this investigation is the absence of any by-product arising from the cleavage of sulfide radical cations as potential intermediates,[6] namely aldehyde

[2]

$$\begin{tikzcd}
 & & & RS\text{-}SR \\
R_2S \arrow[r] & R_2S^{\bullet+} \arrow[r] & R^{+} + RS^{\bullet} \arrow[ur] \arrow[dr] & \\
 & & & RCHO
\end{tikzcd}$$

or alcohol and disulfide (eq. [2]). These two latter products are currently obtained in sulfide oxidation by typical electron transfer (ET) oxidants but not when the H_2O_2 oxidation is catalyzed by metal porphyrins or cytochrome P-450 (14). In particular, our results agree fairly well with the conclusions of Baciocchi et al. (14) in their extensive comparison of sulfide oxidation by ET oxidants and by hydrogen peroxide in the presence of biomometic catalyst. Whereas biomometic oxidations give mainly sulfoxide and small amounts of sulfone, these two compounds are very minor products when the oxidant is a $Co^{III}W$ complex (3*c*).

These results are in contrast with previous observations of Oae et al. (12) who obtained some disulfide with an analogous catalytic system. However, disulfides were obtained, only when the starting sulfide ($PhSCH_2CN$ or $PhSCH_2COPh$) presents an α-acidic hydrogen favoring the cleavage of the carbon-sulfur bond and the formation of a phenylthiyl radical.

In agreement with Baciocchi results (14), a free sulfur-centered radical cation is not suggested as an active intermediate by our results. Therefore, a mechanism (eq. [3], route *a*) involving a direct oxygen transfer from oxene **4** (6*d*, 8, 15) to sulfide and then to sulfoxide, in a process similar to that for catalyzed epoxidation (9, 11), can be reasonably proposed when the catalyst is $Fe^{III}TPPCl$. Nevertheless, an oxygen transfer from metal-oxo radical **5** formed by homolysis of the perhydroxymetal species (9) (route *b* of eq. [3]):

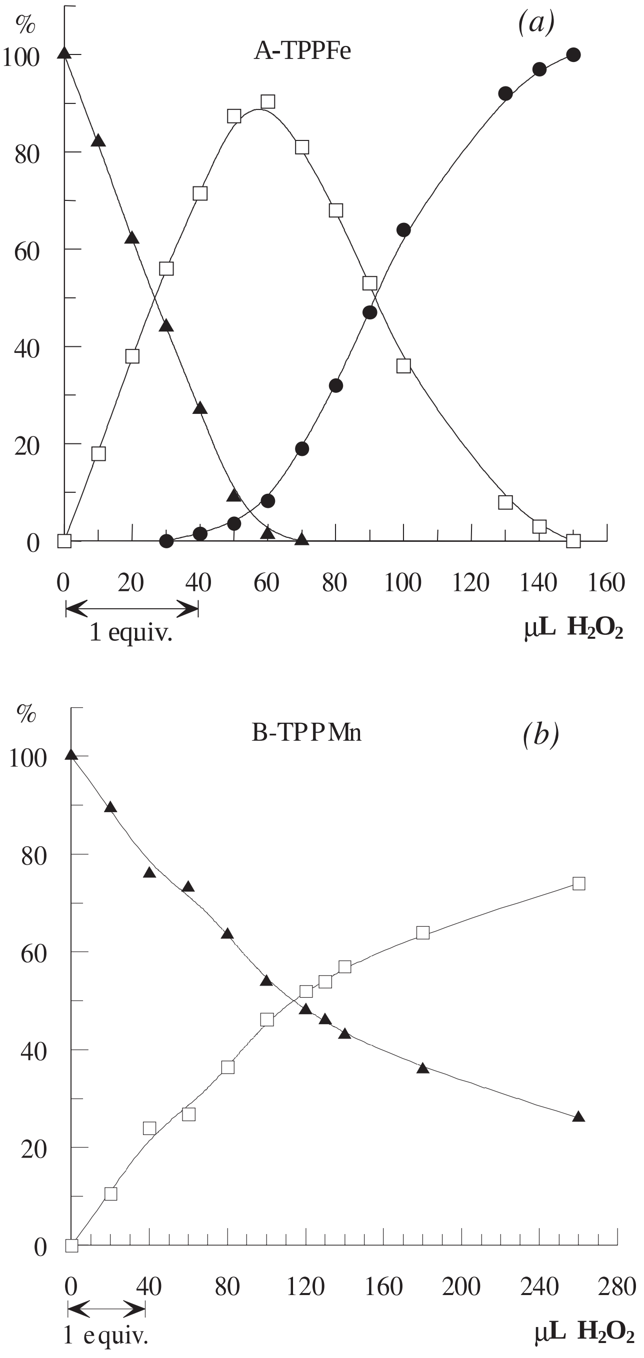
[3]

$$\begin{tikzcd}
\text{Por M} \arrow[r] & \text{PorM-OOH} \arrow[r, "(a)"] \arrow[d, "-OH^{\bullet}\ (b)"'] & \underset{\mathbf{4}}{\text{Por - }\overset{\bullet+}{M}=O} \arrow[r, "+R_2S"] & R_2SO \arrow[d, "+\mathbf{4}"] \\
 & \underset{\mathbf{5}}{PorMO^{\bullet}} \arrow[r, "+R_2S"] & R_2SO & R_2SO_2
\end{tikzcd}$$

cannot be ruled out a priori, in particular when M is Mn(III). However, further results (vide supra) do not support necessarily route *b*.

The markedly different behavior of the Mn(III) and Fe(III) porphyrins is rather surprising, since these two catalysts behave quite similarly in olefin epoxidation (11). In the view of better understanding the origin of this difference, we investigated in more detail the progress of the oxidation of **1** as hydrogen peroxide is added. The results are shown in Figs. 1*a* and *b*. With $Fe^{III}TPPCl$, the very first additions of H_2O_2 quantitatively transform sulfide into sulfoxide. The further additions are still very efficient, since after the addition of 1 equiv. of H_2O_2, 75% of H_2O_2 is used in sulfide–sulfoxide oxidation, the remaining 25% of sulfide being unchanged. With 1.5 equiv. of H_2O_2, sulfide is totally consumed, the sulfoxide yield reaches

Fig. 1. The progress of the hydrogen peroxide oxidation of dibenzylsulfide with the oxidant addition in the presence of M(III) porphyrins; (*a*) M = Fe; (*b*) M = Mn; △, sulfide; □, sulfoxide; ●, sulfone. (Room temperature. Initial concentrations in ethanol: 0.085 M sulfide; 0.05 M imidazole; 0.002 M $TPPM^{III}$ Cl. 40 µL H_2O_2 (35% in water) corresponds to 1 sulfide conc. equiv.).



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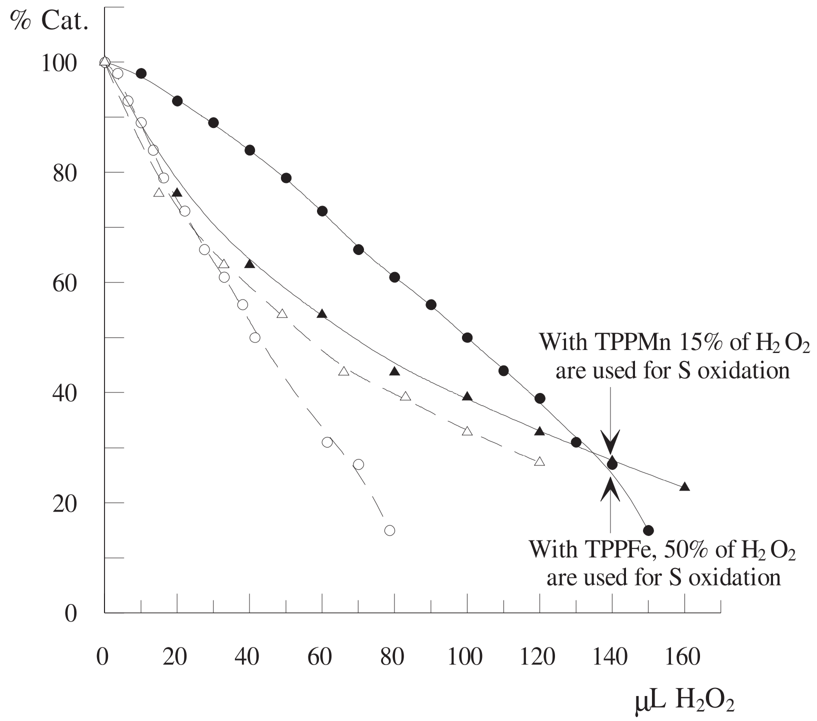
[6] However, the formation of this sulfur radical cation by electron transfer from oxene (eq. [3]) and its very fast recombination with **4** cannot be totally excluded.

Fig. 2. Catalyst decomposition during dibenzylsulfide oxidation with H_2O_2 addition: ●, TPPFe^{III}Cl; ▲, TPPMn^{III}Cl. The open marks (○ and △) are obtained by correcting the added H_2O_2 from the amount consumed by sulfide oxidation. Reaction conditions are identical to those in Fig. 1.



a maximum at about 95% whereas some sulfone is present. The last additions of H_2O_2 are used for sulfoxide oxidation into sulfone. Finally, after the incorporation of 4 equiv. of H_2O_2, the yield in sulfone is quantitative. There are several conclusions from this experiment. Firstly, oxidation of sulfide into sulfoxide and of sulfoxide into sulfone are consecutive reactions, sulfoxide being an intermediate. This implies that sulfoxide oxidation is slower than that of sulfide, so that sulfone appears only when sulfide is almost completely transformed into sulfoxide. Secondly, at every stage of the reaction progress, the transformation of sulfide and sulfoxide is quantitative, without formation of any other oxidation products. Thirdly, hydrogen peroxide is not quantitatively used for sulfide oxidation, since 4 equiv., as compared to sulfide, are necessary for the complete transformation in sulfone, which requires 2 equiv. only. Clearly, other H_2O_2-consuming processes are involved.

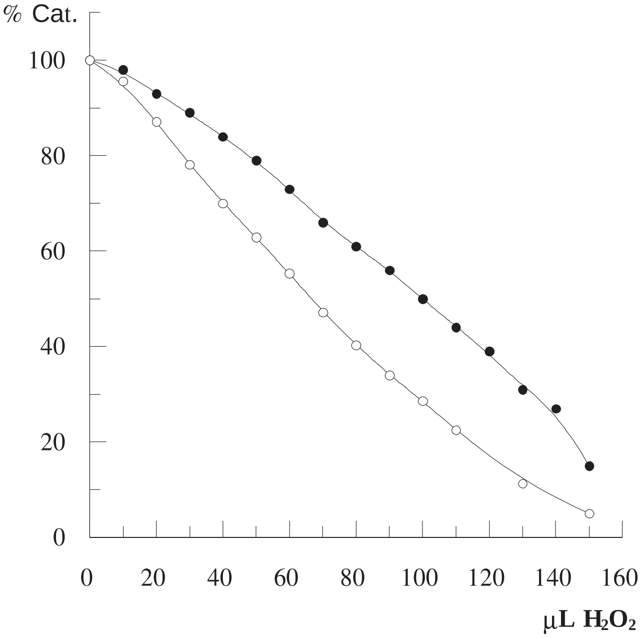
The results with Mn^{III}TPPCl are completely different (Fig. 1*b*). Sulfide is still exclusively transformed into sulfoxide but the efficiency of the oxidant is very small, since after the addition of 1 equiv. of H_2O_2, only 20% of the sulfide is oxidized. After a more and more rapid efficiency decrease, the reaction stops when about 30% of sulfide still subsists.

Therefore, the difference between the two metal porphyrins is that most of hydrogen peroxide is consumed by processes in which sulfide is not involved when Mn^{III}TPPCl is the catalyst whereas with Fe^{III}TPPCl, the H_2O_2 consumption by sulfide is an important route. This difference explains also why no sulfone is obtained with Mn^{III}TPPCl, since sulfoxide oxidation can start only when there is no more sulfide.

To gain some insights on the competing processes that consume hydrogen peroxide, the destruction of the catalysts was monitored spectroscopically at their Soret band (λ_{max} = 466 nm and 415 nm in ethanol for Mn(III) and Fe^{III}TPPCl, respectively), during oxidation of **1** under concentrations identical to those used in the previous experiments. In Fig. 2 is shown the decrease in the concentration of the two catalysts as the reaction progresses. Mn^{III}TPPCl is destroyed rapidly with the first H_2O_2 additions, and then its disappearance is progressively slowed down. Fe^{III}TPPCl is also consumed, although in the first H_2O_2 additions its concentration decreases less rapidly. With 140 μL of H_2O_2 (i.e., 3.5 sulfide equiv.), about 25% of the two catalysts are still preserved, i.e., the catalyst concentration is still 8×10^{-5} M with an initial concentration of 2×10^{-3} M. This remaining amount is enough to promote further substrate oxidation, since sulfide, added at this stage of the reaction, is transformed into sulfoxide. Nevertheless, there is a very large difference between the two catalysts insofar as after the addition of 140 μL H_2O_2, 57% of the added H_2O_2 has been consumed by sulfide, in the presence of Fe^{III}TPPCl, whereas with Mn^{III}TPPPCl, 17% of H_2O_2 has been used for this reaction. Figure 3 shows the disappearance of Fe^{III}TPPCl consecutive to successive additions of H_2O_2 in experiments similar to those of Figs. 1 and 2 but in the absence of sulfide. The comparison of Figs. 2 and 3 exhibits that the catalyst is markedly less consumed when sulfide is present. In other words, it seems that the presence of sulfide exerts some "protection" of the catalyst. However, this conclusion is artificial, since H_2O_2 is used partly in sulfide oxidation. When the amount of added H_2O_2 is corrected for the sulfide uptake, the rates of the ligand destruction by H_2O_2 are not markedly different with Mn(III) and Fe(III).

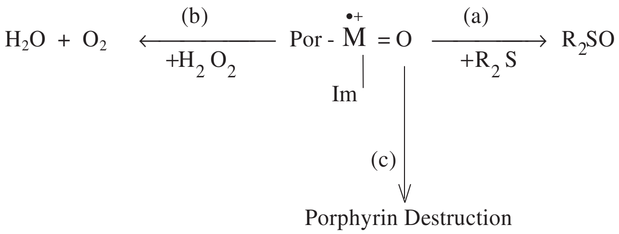
Therefore, the oxidative destruction of the two catalysts is promoted by hydrogen peroxide via similar processes,

Fig. 3. Comparison of $TPPFe^{III}Cl$ decomposition by hydrogen peroxide in the presence (●) and in the absence (○) of dibenzylsulfide. Reaction conditions are identical to those in Fig. 1.



independently on the catalyzed sulfide oxidation route. Since the efficiencies of the two catalysts are very different, there must be a much more efficient route for the H_2O_2 consumption in the presence of $Mn^{III}TPPCl$ than with $Fe^{III}TPPCl$. This route is most likely the dismutation of hydrogen peroxide, which is well known to be metal-catalyzed and which would be favoured, particularly by the Mn(III) catalyst. Our results suggest, therefore, that among the various possible fates of the oxene species, which is assumed to be the active form of the catalyst for sulfide oxidation as for alkene epoxydation (9, 11), route *c* (eq. [4]) is of comparable importance when M is Mn(III) or Fe(III).

[4]



In contrast, route *a* is highly favoured as compared to route *b* with iron but not with manganese catalyst. There are two possible interpretations for the observed metal dependence of the competition between these two routes. The H_2O_2 dismutation could be catalyzed by manganese complex more efficiently than by iron complex. This is unlikely in the view of previous data on alkene epoxidation (6*a*), which show that H_2O_2 consumption is similarly fast with the two catalysts in the presence of imidazole, i.e., the rate of route *b* does not markedly depend on the nature of the metal. Since our results suggest that route *a* is favored with iron but not with manganese, a reasonable conclusion is that the oxygen transfer from the high-valent oxo complex to sulfides is probably faster with Fe(III) than with Mn(III) catalyst.

In conclusion, this preliminary work points out that among the investigated biomimetic catalysts, the most efficient catalyst for quantitative and fast oxidation of sulfide into sulfone by hydrogen peroxide is $Fe^{III}TPPCl$. The efficiency of the analogous Mn(III) complex is markedly smaller. Regarding the selective biomimetic oxidations of sulfide into sulfoxide, Fe(II) phtalocyanine can be used successfully. Therefore, with readily oxidizable sulfides, a significant role of both the metal and its ligand on the oxygen-transfer ability of these catalysts is evidenced. More work, in particular using more robust ligands (16) and aqueous media, is in progress with the objective of designing performant catalytic systems for toxic sulfide oxidation.

Experimental section

Physical measurements

The UV-vis spectra were recorded on a Perkin–Elmer lambda II spectrophotometer. Gas chromatography analysis was carried out on a Delsi–Nermag 200 gas chromatograph equipped with a fid detector and a CP-Sil 5 column. The products were identified by comparison of their retention times with authentic samples or by GC–MS (I.T.D. Finigan 800).

Materials

Acetonitrile and ethanol (HPLC grade, Prolabo) were used as received. Hydrogen peroxide (H_2O_2 35% in water, Acros) was stored at 5°C and titrated every month. Sulfides, sulfoxides, and sulfones were purchased from Aldrich or Acros and used as received. 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 imidazole, and 0.002 M catalyst, in ethanol or in CH_3CN) was added directly the commercial solution of hydrogen peroxide by small amounts with a microsyringe. The oxidant is added 10 μL per 10 μL with a delay of 5 min between each addition, to prevent hydrogen peroxide dismutation. The GC analysis was performed on aliquots withdrawn directly from the reaction mixture. Yields were measured by GC with the internal standard method. All the reactions were carried out at room temperature, without any buffer and under aerobic conditions.

Measurements of the catalyst destruction

The disappearance of the porphyrins were monitored by UV-vis spectrophotometry by the decrease of their Soret band (415 nm for $TPPFe^{III}Cl$, 466 nm for $TPPMn^{III}Cl$ in ethanol). Eight microliters of the reaction mixture was taken with a microsyringe and diluted directly in the cell containing 2 mL of ethanol. The percentage of remaining catalyst was then calculated.

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References

1. (*a*) E.E. Reid. *In* Chemistry of bivalent sulfur. Chemical Publishing Co., New York. 1960. Chap. 5; (*b*) Y.C. Yang, J.A. Baker, and J.R. Ward. Chem. Rev. **92**, 1729 (1992).
2. (*a*) J.H. Ramsden, R.S. Drago, and R. Riley. J. Am. Chem. Soc. **111**, 3958 (1989); (*b*) Y.C. Yang, L.L. Szafraniec, and W.T. Beaudry. J. Org. Chem. **55**, 3664 (1990).
3. (*a*) M. Madesclaire. Tetrahedron, **42**, 5459 (1986); (*b*) F. Pautet, R. Barret, L. Favre, and M. Daudon. Pharmazie, **43**, 437 (1988); (*c*) V. Conte, F. Di Furia, and G. Modena. *In* Organic peroxides. *Edited by* W. Ando. Wiley, New York. 1992. p. 559; (*d*) E. Baciocchi, O. Lanzalunga, and B. Pirozzi. Tetrahedron, **53**, 12287 (1997).
4. Y.C. Yang, L.L. Szafraniec, W.T. Beaudry, and C.A. Bunton. J. Org. Chem. **58**, 6964 (1993).
5. M.A.P. Dankleff, R. Curci, J.O. Edwards, and H.Y. Pyun. J. Am. Chem. Soc. **90**, 3209 (1968), and refs. cited therein.
6. (*a*) P. Battioni, J.P. Renaud, J. Bartoli, M. Reina-Artiles, M. Fort, and D. Mansuy. J. Am. Chem. Soc. **110**, 8462 (1988); (*b*) T.C. Bruice. Acc. Chem. Res. **24**, 243 (1991); (*c*) B. Meunier. Chem. Rev. **92**, 1411 (1992); (*d*) T.G. Traylor, C. Kim, J.L. Richards, F. Xu, and C.L. Perrin. J. Am. Chem. Soc. **117**, 3468 (1995).
7. J.T. Groves and P. Viski. J. Org. Chem. **55**, 3628 (1990).
8. T.G. Traylor and F. Xu. J. Am. Chem. Soc. **112**, 178 (1990).
9. T.G. Traylor, S. Tsuchiya, Y.S. Byun, and C. Kim. J. Am. Chem. Soc. **115**, 2775 (1993).
10. A. Sorokin and B. Meunier. Chem. Eur. J. **2**, 1308 (1996).
11. D. Ostovic and T.C. Bruice. Acc. Chem. Res. **25**, 314 (1992).
12. (*a*) S. Oae, Y. Watanabe, and K. Fujimori. Tetrahedron Lett. **23**, 1189 (1982); (*b*) Y. Watanabe, T. Iyanagi, and S. Oae. Tetrahedron Lett. **23**, 533 (1982).
13. J.O. Edwards and R. Curci. *In* Catalytic Oxidation with hydrogen peroxide as oxidant. *Edited by* G. Strukul. Kluwer, Dordrecht. 1992. p. 112.
14. (*a*) E. Baciocchi, M. Crescenzi, E. Fasella, and M. Mattioli. J. Org. Chem. **57**, 4684 (1992); (*b*) E. Baciocchi, O. Lanzalunga, and F. Marconi. Tetrahedron Lett. **35**, 9771 (1994).
15. T.G. Traylor and J.P. Ciccone. J. Am. Chem. Soc. **111**, 8413 (1989).
16. D. Dolphin, T.G. Traylor, and L.Y. Xie. Acc. Chem. Res. **30**, 251 (1997).