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OXIDATION OF SULFIDE WITH ArIO CATALYZED WITH TPPM(III)Cl

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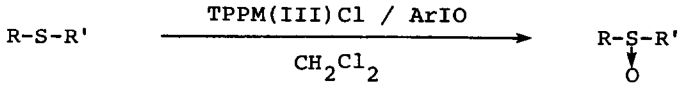
Various sulfides were easily converted to the corresponding sulfoxides in high yields in TPPM(III)Cl-catalyzed oxidation with ArIO, to which the influence of structures of sulfides and iodosylaromatics, and kinds of metals centered on the catalysts were investigated.

Oxometalloporphyrins as models of active intermediates in the catalytic oxygenation cycles of peroxidase and cytochrome P-450, have recently been prepared.1) The catalytic oxidation using metalloporphyrin and various oxygen sources such as iodosylbenzene has been reported for several substrates.1,2) However, detail investigation has not been studied for the reactivity of oxometalloporphyrin toward substrates, especially sulfur compounds. Since products are usually inactive and limited, sulfur compounds, e.g. sulfides, as substrates have been expected to lead the clear oxidation system allowing to search the reactivity and nature of intermediary oxometalloporphyrins in the biological oxygenations.

In our interest of the models of biological oxidations, we examined the oxidation of sulfides with systems of metalloporphyrins and iodosylaromatics, and found that the metalloporphyrins were capable of catalyzing oxygen transfer to form the corresponding sulfoxides highly selectively.3)

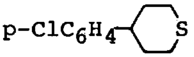
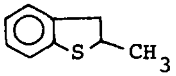
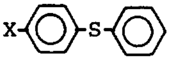
In a typical run, a mixture of diphenyl sulfide(7a, 5 mmole), iodosylbenzene(1 mmole) and TPPFe(III)Cl(0.045 mmole)# was stirred in CH_2Cl_2 at -18°C under argon atmosphere. Several aliquots were continuously withdrawn at intervals from the reaction mixture as the oxidation proceeded, immediately excess iodosylbenzene being degraded by shaking with $Na_2S_2O_3$ solution. The yield of diphenyl sulfoxide(7a') as a sole product was determined by GLC using a calibration curve, or by isolation with column chromatography.



$$\text{R-S-R'} \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{TPPM(III)Cl / ArIO}} \text{R-}\underset{\substack{\downarrow\\ \text{O}}}{\text{S}}\text{-R'}$$

Chloro-5,10,15,20-tetraphenylporphyrinatoiron(III) is abbreviated as TPPFe(III)Cl.

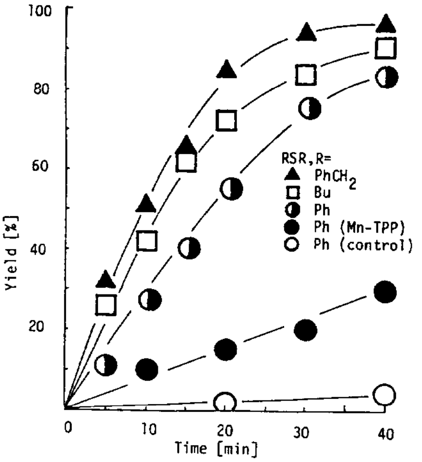
Table I Oxidation of Sulfides with TPPM(III)Cl - PhIO 1)

Substrate		TPPM(III)Cl M =	Time	Temp	Isolated Yield 2,3) of Sulfoxide
$PhCH_2SCH_2Ph$	1	Fe	35 min.	-18°C	94 % (13 %)
BuSBu	2	Fe	42	-18	89 (58)
EtSEt	3	Fe	25	-18	90 (90) 4)
$^tBuSBu^t$	4	Mn	10	20	90 (< 5)
	5	Fe 5)	60	-18	85 (11)
	6	Fe	60	-18	70 (-)
 7 X= H	7a	Fe	50	-18	87 (5)
X= H	7a	Fe	3	20 - 23	81 7) (4) 7)
X= OMe	7b	Mn	60 6)	20 - 23	76 (21)
X= Me	7c	Mn	60 6)	20 - 23	80 (25)
X= NO_2	7d	Mn	60 6)	20 - 23	77 (16)

1) Molar ratio: sulfide(5 mmole), TPPM(III)Cl(0.045 mmole) and PhIO(1 mmole) in CH_2Cl_2 (solvent, 7 ml) under argon. 2) The yields were based on PhIO. 3) Yields parenthesized were those obtained in control experiments without TPPM(III)Cl. 4) Reaction time was 28 min. 5) Twice amount of TPPFe(III)Cl(0.092 mmole) was used. 6) Reaction time was too long, since the oxidation usually completed within 15 min. 7) GLC yield.

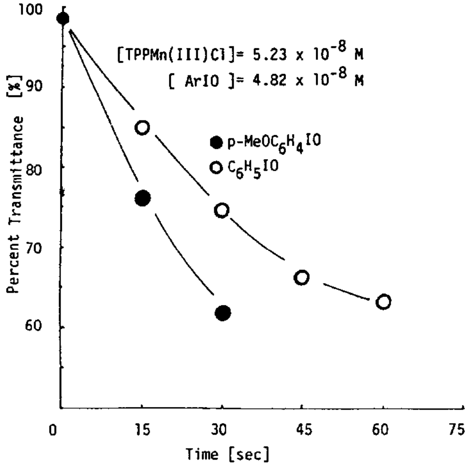
Besides diphenyl sulfide, various mono-p-substituted diphenyl, aryl alkyl and dialkyl sulfides were easily oxidized to the corresponding sulfoxides in high yields in this system. The results are shown in Figure I and Table I. Sulfone, as a further oxidation product, was not detected at all under the conditions. However, when sulfoxide(dibenzyl sulfoxide, 1 mmole) was used as a substrate, the corresponding sulfone was obtained in high yield(95 % by NMR) in the oxidation with TPPMn(III)Cl(0.045 mmole) - PhIO(1 mmole) at room temperature. This reaction was considerably slower than that for the corresponding sulfide(sulfoxide: ca 20 min. at room temperature; sulfide: 35 min. at -18°C), but this oxidation system(i.e. TPPM(III)Cl - ArIO) was intrinsically much stronger than usual peracids. Namely, somewhat oxidation-resisting sulfides such as nitro-substituted diphenyl and di-tert-butyl sulfides and dibenzyl sulfoxide, were readily converted to the corresponding oxides (Table I). Catalytic cycles were ca 20 but could rise up to more than 100 if increasing sulfide and decreasing catalyst concentration. This method of

Figure I



Time Conversion of Sulfoxide Formation in the Oxidation of Various Sulfides with TPPFe(III)Cl - PhIO at -18°C under Argon.

Figure II

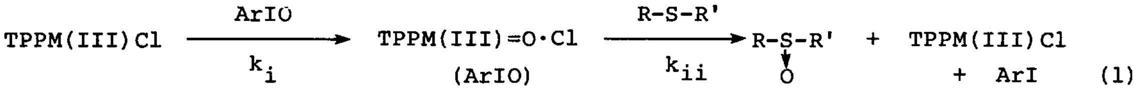


Change of Percent Transmittance at 481 nm (λ_{max} of TPPMn(III)Cl) in Electronic Spectra in the Reaction of TPPMn(III)Cl with ArIO in CH_2Cl_2 at 20°C.

oxidation, therefore, should be useful for sulfides and sulfoxides resisting for normal oxidations. Other substrates such as disulfide and thioketone were also oxidized in the system of TPPM(III)Cl - ArIO to give thiosulfinate and sulfine.

Catalyst TPPFe(III)Cl accelerated the oxidation faster than TPPMn(III)Cl as shown in Figure I, however, the yield of sulfoxide in TPPFe(III)Cl-catalyzed oxidation was slightly lower than that in TPPMn(III)Cl-catalyzed one, especially at room temperature, presumably because of less stability of oxo-TPPFe(III)Cl as suggested.[1b,c)]

Difference of reactivity toward sulfide between C_6H_5IO and p-$MeOC_6H_4IO$ was small in the oxidation with ArIO without the catalyst, but so large in the catalytic oxidation with TPPM(III)Cl that the TPPFe(III)Cl-catalyzed oxidation of diphenyl sulfide with p-$MeOC_6H_4IO$ completed within 10 min. even at -18°C (with C_6H_5IO: ca 40 min, see Figure I). The difference can be explained by the fact that the reaction of TPPMn(III)Cl with p-$MeOC_6H_4IO$(i.e. formation of oxo-TPPMn(III)Cl) in the absence of sulfide is faster than that with C_6H_5IO, as shown in Figure II.4) Thus, this suggests that the rate of the oxidation depends definitely on that of the reaction of TPPMn(III)Cl with ArIO(k_i), but not on that of the reaction of oxo-TPPMn(III)Cl5) with sulfide(k_{ii}), which should be faster process(see equation 1).



$$\mathrm{TPPM(III)Cl} \xrightarrow[k_i]{\mathrm{ArIO}} \underset{(\mathrm{ArIO})}{\mathrm{TPPM(III){=}O\cdot Cl}} \xrightarrow[k_{ii}]{\mathrm{R{-}S{-}R'}} \mathrm{R{-}}\underset{\mathrm{O}}{\underset{\downarrow}{\mathrm{S}}}\mathrm{{-}R'} + \mathrm{TPPM(III)Cl} + \mathrm{ArI} \qquad (1)$$

Stereochemistry of diastereomeric sulfoxides formed in the oxygenation of sulfides(5 and 6) with cytochrome P-450[6] was nicely traced in this study.[7] The system of TPPM(III)Cl - ArIO may be recognized as a model of cytochrome P-450 in the oxidation of sulfides, because of the high reactivity[8] and the above stereospecificity.

Detail investigation on mechanistic feature of this reaction is now under way in this laboratory.

REFERENCES AND FOOTNOTES

1)a) Groves,J.T. and Kruper,W.J., J. Am. Chem. Soc., 1979, 101, 7613. b) Groves,J.T., Kruper,W.J., and Haushalter,R.C., ibid, 1980, 102, 6375. c) Groves,J.T., Haushalter,R.C., Nakamura,M., Neo,T.E., and Evans,B.J., ibid, 1981, 103, 2884.

2)a) Guilmet,E. and Meunier,B., Tetrahedron Lett., 1980, 21, 4449. b) Tabushi,I. and Koga,N., J. Am. Chem. Soc., 1979, 101, 6456. c) Chin,D.-H., LaMar,G.N., and Blach,A.L., ibid, 1980, 102, 5947. d) Hill.C.H. and Schardt,B.C., ibid, 1980, 102, 6357. e) Shannon,P. and Bruice,T.C., ibid, 1981, 103, 4580. f) Ledon,H.J., Durbut,P., and Vzrescon,F., ibid, 1981, 103, 3601. g) These two systems of oxidations for sulfides have recently been developed: i) TPPFe(III)Cl - H_2O_2 - Imidazole(in $CHCl_3$ - H_2O): Oae,S., Watanabe,Y., and Fujimori,K., Tetrahedron Lett., in press; ii) TPPFe(III)Cl - $\dot{O}_2^{-}$(from KO_2 - 18-crown-6)(in CH_2Cl_2 or $CHCl_3$): Oae,S., Fujimori,K., and Takata,T., Bull. Chem. Soc. Jpn., in contribution.

3) Only two reports have appeared on the reactions of sulfides[a] and thiol[b] with PhIO alone: Ford-Moore,A.H., J. Chem. Soc., 1949, 2126; b) Takaya,T., Hiroji,E., and Imoto,E., Bull. Chem. Soc. Jpn., 1968, 41, 1032.

4) No study on reactivity of iodosylbenzene alone toward sulfide has been demonstrated yet.[3] The control experiments without TPPM(III)Cl showed that iodosylaromatics oxidized alkyl sulfide more easily than aryl sulfide(Table I), suggesting that iodosylaromatics are electrophilic. Interestingly, Figure II indicats that iodosylaromatics seem to act in turn as a nucleophile.

5) Influence of the residue of iodosyl aromatics(i.e. ArI), which is known to be attached to oxo-TPPM(III)Cl, toward reactivity of the oxo-TPPM(III)Cl has been unsolved yet.[1]

6) Takata,T., Yamazaki,M., Fujimori,K., Kim,Y.H., Oae,S., and Iyanagi,T., Chem. Lett., 1980, 1441.

7) Ratio of ax/eq of 5'(sulfoxide) = 29/71(cf. 33/67 by cytochrome P-450[6]). Ratio of cis/trans of 6'(sulfoxide) = 21/79(cf. 19/81 by cytochrome P-450[6]).

8) The yield of sulfoxide has not seriously been affected by variable substituent(even bulky tert-butyl group) in the oxygenation catalyzed by cytochrome P-450.[6]

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