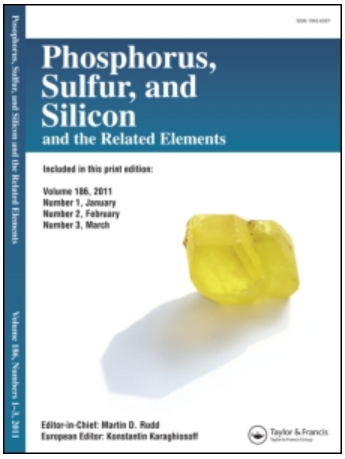

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SELECTIVE OXIDATION OF SULFIDE BY ArIO—METALLOPORPHYRIN SYSTEM-AN ENZYME MODEL *S*-OXIDATION

Toshikazu Takata[a]; Rieko Tajima[a]; Wataru Ando[a]
[a] Department of Chemistry, University of Tsukuba, Sakura, Ibaraki, Japan

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SELECTIVE OXIDATION OF SULFIDE BY ArIO–METALLOPORPHYRIN SYSTEM— AN ENZYME MODEL *S*-OXIDATION*,[1]

TOSHIKAZU TAKATA, RIEKO TAJIMA and WATARU ANDO*

Department of Chemistry, University of Tsukuba, Sakura, Ibaraki 305, Japan

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Various sulfides are easily oxidized selectively to the corresponding sulfoxides in quantitative yields by iodosylarene (ArIO) catalyzed by metalloporphyrin (TPPM(III)Cl (M = Fe, Mn)). The oxidation system is demonstrated to be a possible model for monooxygenase in the study of the stereochemistry of these sulfoxides. Metalloporphyrin–iodosylarene can initially equilibrate with the oxometalloporphyrin (TPPM(V)=O · Cl) formed *in situ*. The initial process may involve one-electron transfer from the sulfide to the intermediate oxometalloporphyrin followed by coupling of two resulting charged products, and/or nucleophilic attack of sulfide on oxometalloporphyrin oxygen. The overall reactions are depicted by paths with different electron demands from the results of Hammett plots.

INTRODUCTION

Cytochrome P-450 enzyme is a special hemoprotein that catalyzes the oxygenation of a wide variety of organic compounds, i.e., hydroxylation of hydrocarbons, epoxidation of olefinic functions, hetero-atom oxidations, etc.[2–4] The enzyme is recognized to activate molecular oxygen by binding and an ensuing two-electron reduction by NADPH followed by O—O bond scission.[2–4] The active species for the oxidizing function has been proposed to be an oxenoid, i.e., oxene, formed at an iron-porphyrin active center of the enzyme.[2–4]

Ullrich *et al.* in 1976 have demonstrated that cytochrome P-450 mediated hydroxylation can occur in the presence of iodosylbenzene[5] as well as organic peroxides[6–8] without the requirement for molecular oxygen and NADPH.

Oxometalloporphyrins (TPPM(V)=O) as models of active intermediates in the catalytic oxygenation cycles of monooxygenase such as cytochrome P-450, have long been proposed and have recently been prepared with appropriate metalloporphyrins (TPPM(III)X) and monooxygen donors, such as iodosylbenzene,[9–14] *m*-chloroperbenzoic acid (MCPBA),[11] hydrogen peroxide (with imidazole),[15] sodium hypochlorite,[20] superoxide anion (with alkyl halide),[21] and also molecular oxygen (with reducing agents) in elegant systems.[22,23] More extensive investigations however, have not been found for the reactivity of the oxometalloporphyrins toward substrates, especially hetero compounds, despite the fact that the cytochrome P-450 enzyme can readily catalyze the oxygenations of nitrogen and sulfur compounds.[3] Bruice *et al.* have recently reported an application of these systems to the model reaction of

*Cordially dedicated to Professor Shigeru Oae on the occasion of his retirement from University of Tsukuba.

oxidative *N*-dealkylation of *N*,*N*-dimethylaniline with a system of TPPFe(III)Cl and PhIO, as a model of a function of cytochrome P-450.[24] No report has appeared for the reaction of sulfur compounds with these model systems, in spite of the recent extensive investigations by Oae *et al.* in the enzymatic oxygenation of sulfur compounds with cytochrome P-450.[25-28]

Use of sulfides as substrates is expected to lead to a simple oxidation system which allows a search of the reactivity and nature of the intermediate oxometalloporphyrins proposed in monooxygenases. Because of our interest in models for biological oxidations,[29,30] we examined the oxidation of sulfides with the metalloporphyrins and iodosylarenes systems, and found that the systems are capable of catalyzing selective oxygen transfer to sulfides to form the corresponding sulfoxides.

RESULTS AND DISCUSSION

TPPM(III)Cl-Catalyzed Oxidation

When 0.045 mmol of 5,10,15,20-tetraphenylporphynatoiron(III)chloride (TPPFe(III)Cl,[31] *ca.* 1%) as a catalyst was added to a heterogeneous mixture of 5.0 mmol of diphenyl sulfide and 1.0 mmol of iodosylbenzene (PhIO)[32] in dichloromethane at $-18°C$ under argon atmosphere, and the resulting mixture was stirred for 50 min, diphenyl sulfoxide was isolated in 87% yield. No diphenyl sulfone was obtained. In the absence of the catalyst, no diphenyl sulfoxide was obtained, whereas in the absence of sulfide rapid degradation of the catalyst occurred. The yields of diphenyl sulfoxide vs. reaction time, shown in Figure 1, clearly indicate the effectiveness of the catalyst. TPPMn(III)Cl[33] as a catalyst was less effective than TPPFe(III)Cl. Various sulfides were subjected to the oxidation with the

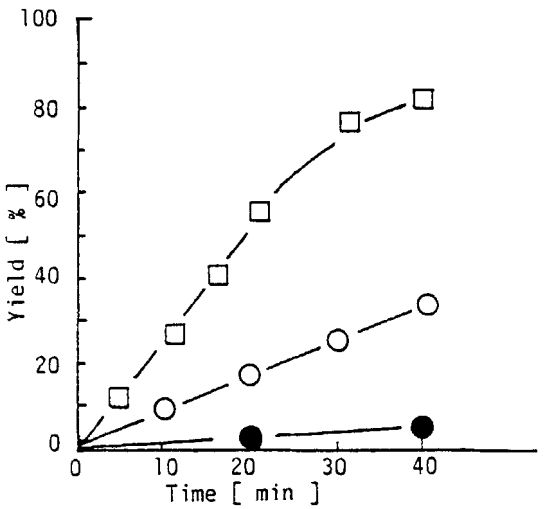
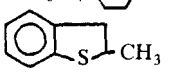


FIGURE 1 Oxidation of diphenyl sulfide (5.0 mmol) with PhIO (1.0 mmol) at $-18°C$ in the presence of catalyst (0.045 mmol) in CH_2Cl_2 (6 ml); □, TPPFe(III)Cl; ○, TPPMn(III)Cl; ●, without catalyst (control experiment). The yields based on PhIO were determined by GC using an internal standard.

TABLE I

Oxidation of sulfides with TPPM(III)Cl–PhIO[a]

Entry No.	Substrate	Catalyst TPPM(III)Cl =	Time	Temp.	Yield of sulfoxide
1	PhSPh	Fe	50 min	−18°C	87% (5%)[b]
2	PhSPh	Fe	3 min	20–23	81[c] (4)[c]
3	p-$NO_2C_6H_4SC_6H_5$	Fe	1 h	20–23	77 (16)
4	$^tBuS^tBu$	Mn	10 min	20	90 (< 5)
5	$PhCH_2SCH_2Ph$	Fe	35 min	−18	94 (13)
6	p-ClC_6H_4- 	Fe[d]	1 h	−18	85 (11)
7		Fe	1 h	−18	70
8		Fe	8 h	21	0[h]
9	BuSBu	Fe	42 min	−18	89 (58)
10	EtSEt	Fe	25 min	−18	90 (90)[e]
11[f]	$PhCH_2SCH_2Ph$ (O)	Mn	20 min	20–23	95[g]

[a] Molar ratio; for PhIO, substrate : TPPM(III)Cl : PhIO = 5 : 0.045 : 1.
[b] Yields parenthesized are obtained in control experiments without TPPM(III)Cl.
[c] GC yield.
[d] 9.2% TPPFe(III)Cl vs. PhIO was used.
[e] Reaction time was 28 min.
[f] Molar ratio; substrate : TPPMn(III)Cl : PhIO = 1 : 0.045 : 1.
[g] NMR yield of dibenzylsulfone.
[h] $PhIO_2$ was used in a molar ratio of substrate : TPPFe(III)Cl : $PhIO_2$ = 1 : 0.085 : 1.

TPPM(III)Cl–ArIO system. The results are summarized in Table I. PhIO itself is capable of oxidizing the sulfides without any catalyst, though its ability is low for aromatic and bulky sulfides, as described in the following section. Molecular oxygen, room light or moisture did not affect the overall reaction and product formation. The bulky and electron-deficient sulfides resistant to normal oxidations were selec-

$$R{-}S{-}R' \xrightarrow[CH_2Cl_2 \text{ or } CHCl_3]{TPPM(III)Cl/ArIO} R{-}\overset{\overset{O}{\|}}{S}{-}R' \text{ quant.} \qquad (1)$$

tively and easily oxidized to the sulfoxides. Although the yields of the sulfoxides were not optimized, they are nearly quantitative and no sulfone is observed under the reaction conditions. Prolonged reaction is required with smaller amounts of the catalyst. Iodoxybenzene ($PhIO_2$)[34] was used as an oxidant instead of PhIO. However, no sulfoxide was obtained.

Consequently, ArIO with TPPM(III)Cl shows sufficiently selective oxidations. Actually, the sulfoxide formation completely predominated over the sulfone formation even when an equimolar amount of ArIO (vs. substrate) was used. Therefore, this system would be the best one for laboratory preparation of sulfoxides.

On the other hand, when benzyl sulfoxide was oxidized with the TPPFe(III)Cl–PhIO system at 20–23°C, the corresponding sulfone was isolated in 95% yield, but the rate of the reaction was considerably slower than that of the sulfide oxidation under the same conditions.

Oxidation with ArIO Alone

Iodosylbenzene is a reagent that has hitherto been used for the oxidation of only a few sulfides.[35,36] However, the reactivity of PhIO alone toward sulfides has not yet been studied. We realize that dialkyl sulfides are oxidized much faster than aromatic sulfides, where the oxidation with PhIO proceeds by the electrophilic attack of PhIO on the sulfur atom, as expected for the usual sulfide oxidation. In fact, Hammett plots in the competitive oxidations of *p*-monosubstituted diphenyl sulfides with PhIO indicates minus ρ values, in which the electrophilic attack of PhIO on sulfur would be the rate-determining step (Figure 2).

Stereochemistry of Sulfoxide Formation—Comparison with Enzymatic Oxygenation

The reliability of the oxidation with the TPPM(III)Cl–ArIO system as an enzyme model system, is easily recognized by comparing the stereochemistry of the product sulfoxides. Table II lists the diastereomeric ratios of sulfoxides obtained in the oxidations of a few racemic sulfides with various oxidation systems involving cytochrome P-450.[28]

Apparently, TPPM(III)Cl–ArIO shows similar diastereomeric ratios to those of cytochrome P-450 in the oxidations of 2-methyl-2,3-dihydrobenzothiophene and benzyl *s*-butyl sulfide. These ratios were clearly different from those formed by MCPBA and $NaIO_4$ oxidations. However, the stereochemistry of the oxidation of 4-(*p*-chlorophenyl)thiane hardly depends on the nature of the oxidants except for the case of $NaIO_4$ (Table II and table notes). Thus, these stereochemical aspects

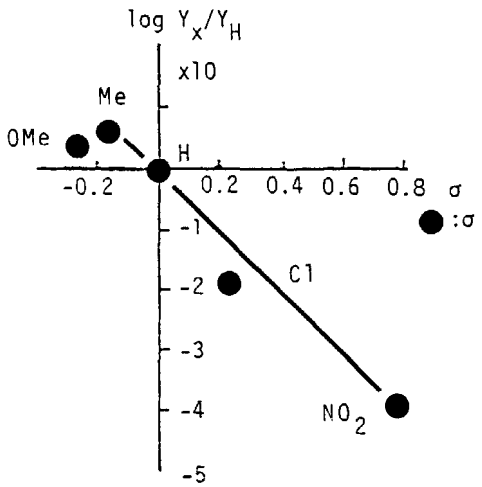
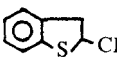
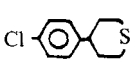


FIGURE 2 Hammett plots of oxidation of *p*-monosubstituted diphenyl sulfides with PhIO alone at room temperature. Y_X/Y_H is a ratio of yield of a substituted diphenyl sulfoxide to that of diphenyl sulfoxide, which was obtained in the competitive oxidation of an equimolar mixture of two sulfides (1 mmol, respectively) with PhIO (1 mmol) in CH_2Cl_2 (6 ml) for 1 h within 20% conversion. The yield was determined by GC technique using fluorenone as an internal standard.

TABLE II

Stereochemistry of sulfoxides formed in enzymatic and nonenzymatic oxidations

Oxidation System	 cis/trans[a]	$PhCH_2S^{sec}Bu$ threo/erythro[a,b]	 ax/eq[c]
Cytochrome P-450/O_2/NADPH/37°C[d]	19/81	34/66	33/67
C_6H_5IO/TPPFeCl/CH_2Cl_2/− 18°C	21/79	39/61	28/72
C_6H_5IO/CH_2Cl_2/18°C	34/66	53/47	28/72
$NaIO_4$/H_2O–Acetone/r.t.[d]	48/52	58/42	76/24
MCPBA/CH_2Cl_2/0–5°C[d]	47/53	54/46	33/67[e]
H_2O_2/TPPFeCl/10% Imidazole[f] /$CHCl_3$–H_2O/r.t.	24/76	—	—

[a] The ratio was determined by NMR technique using shift reagent $Eu(dpm)_3$.
[b] It is not clear which is *threo* or *erythro*.
[c] The ratios are those isolated or estimated with GC.
[d] Ref. 30.
[e] Johnson *et al.* have reported a different *ax/eq* ratio of 51/49 for oxidation of 4-(*p*-chlorophenyl)thiane, though the condition is extremely drastic, i.e. refluxing benzene for 12 hr.[37]
[f] Ref. 15.

support the enzyme model behavior of the system of TPPM(III)Cl–ArIO, especially in the *S*-oxidation of a sulfide.

Although cytochrome P-450 generally affords the *S*-dealkylation products as well as the *S*-oxidation products,[25-28] the TPPM(III)Cl–ArIO system could not model the enzymatic *S*-dealkylation since the *S*-oxidation predominated over the *S*-dealkylation even for cyanomethyl phenyl and phenacylmethyl phenyl sulfides. The latter is known to give considerable *S*-dealkylation products in the enzymatic reaction (Table III, Eq. 2).

Similarly, in the model reaction with TPPFe(III)Cl–H_2O_2–imidazole[15] only a small amount of the *S*-dealkylation products was obtained. Thus, there has been no

TABLE III

S-Oxidation and *S*-dealkylation in enzymatic and enzyme model oxidation of cyanomethyl phenyl and phenacylmethyl phenyl sulfides

Substrate	System	*S*-Oxidation (product yield ratio)	*S*-Dealkylation (product yield ratio)
$PhSCH_2CN$	A	100	56
	B	100	1.2
	C	100	0
$PhSCH_2C(=O)Ph$	A	100	100
	B	100	17
	C	100	trace

A; Cytochrome P-450/NADPH/O_2 in H_2O at 37°C (ref. 27).
B; TPPFe(III)Cl/H_2O_2/Imidazole in $CHCl_3$–H_2O at r.t. (ref. 15).
C; TPPFe(III)Cl/PhIO in CH_2Cl_2 at r.t.

suitable example of an enzyme model system accomplishing the *S*-dealkylation efficiently.

$$ArSCH_2X \xrightarrow[NADPH/O_2]{\text{Cytochrome P-450}} \begin{cases} \xrightarrow{O} ArSCH_2X & (S\text{-Oxidation}) \\ \longrightarrow ArSH + XCHO & (S\text{-Dealkylation}) \end{cases} \quad (2)$$

X: electron-withdrawing group

Mechanistic Aspects of TPPM(III)Cl-Catalyzed Oxidation

The visible spectrum of the oxenoid intermediate from TPPFe(III)Cl could not be observed during the reaction with ArIO at room temperature, since the oxenoid intermediate formed is too active to be detected. However, the reaction with ArIO-TPPMn(III)Cl (λ_{max} at 481 nm) showed the visible spectrum of the intermediate TPPMn(V)=O · Cl[16] (λ_{max} at 422 nm) at room temperature as shown in Figure 3,

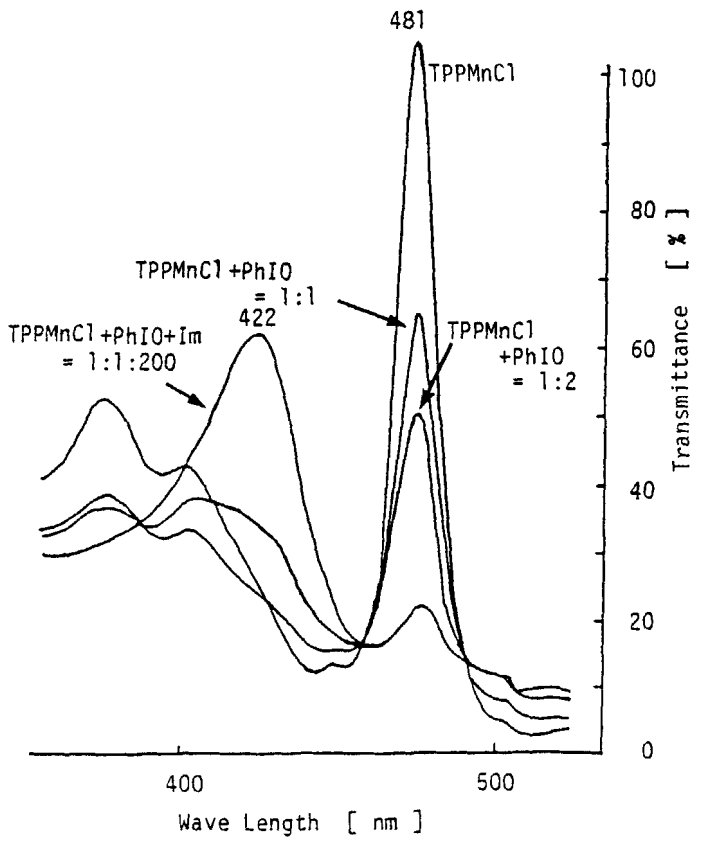


FIGURE 3 Visible spectral change in the reaction of TPPMn(III)Cl with PhIO in CH_2Cl_2 (4 ml) at room temperature. TPPMn(III)Cl (5.0×10^{-8} mol) has a λ_{max} at 481 nm which decreases by the addition of PhIO (5.0×10^{-8} mol) and imidazole (200 equivalents) to produce a new peak at 422 nm which is corresponding to oxometalloporphyrin TPPMn(V)=O · Cl.

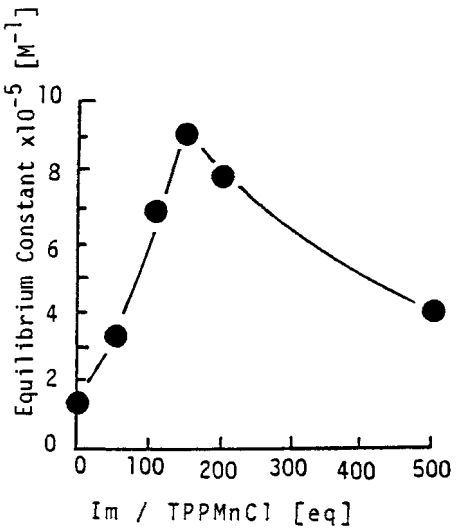


FIGURE 4 Effect of imidazole (0–500 equivalents) added to the reaction of TPPMn(III)Cl and PhIO to the equilibrium constant (see eq. 3), which was calculated based on the absorption at 481 nm of TPPMn(III)Cl in the spectral change by the addition of imidazole to the system of TPPMn(III)Cl (5.0×10^{-8} mol) and PhIO (5.0×10^{-8} mol) in CH_2Cl_2 (4 ml).

which presumably indicates equilibrium between TPPMn(III)Cl–ArIO and TPPMn(V)=O · Cl (eq. 3). The occurrence of the equilibrium is supported by the

$$\text{TPPMn(III)Cl} + \text{ArIO} \overset{K}{\rightleftarrows} \text{TPPMn(V)=O} \cdot \text{Cl(ArI)} \qquad (3)$$

rapid oxygen exchange of TPPMn(V)=O · Cl in the presence of water ($^{18}OH_2$), as reported by Groves.[10]

On the other hand, addition of imidazole largely shifted the equilibrium to the right (Figure 3). The effect of imidazole on the equilibrium is shown in Figure 4. The

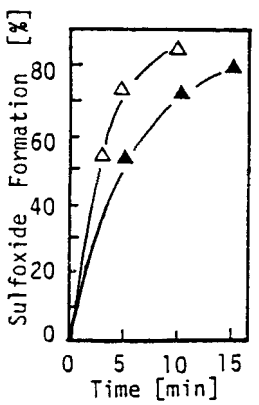
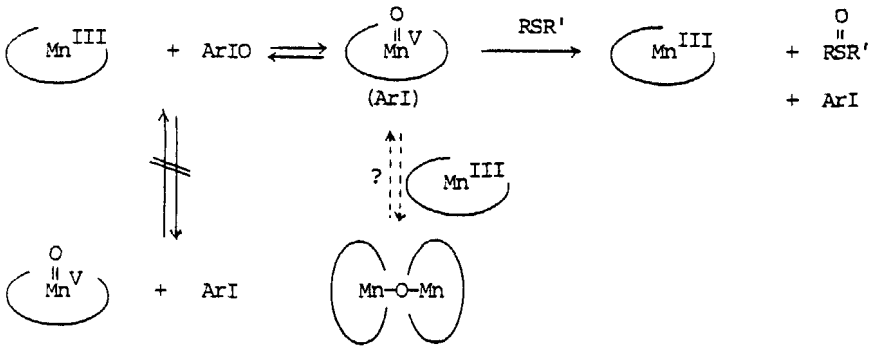


FIGURE 5 Effect of imidazole on the formation of diphenyl sulfoxide in the reaction of diphenyl sulfide (3 mmol) with TPPMn(III)Cl (0.045 mmol) and PhIO (1 mmol) in CH_2Cl_2 (6 ml) at 0°C in the presence (▲) and absence (△) of imidazole (6.8 mmol).

equilibrium constant K gradually increased up to the addition of *ca.* 200 equivalents of imidazole but in turn decreased over 200 equivalents. One possibility for this effect is that the TPPMn(V)=O · Cl may be stabilized by the coordination with imidazole. Another is that TPPMn(III)Cl may be deactivated by the coordination with imidazole to prevent TPPMn(V)=O · Cl formation. Addition of imidazole shifted the equilibrium largely to the product side (Figures 3 and 4), but caused a rather smaller effect on sulfoxide formation to yield the sulfoxide at a slightly *slower* rate than that without imidazole (Figure 5). These results, coupled with the previous spectral study (Figure 3), may be consistent with the stabilization of TPPMn(V)= O · Cl by imidazole.

The reaction scheme is illustrated below (Scheme 1).



SCHEME 1

In the first equilibrium step, TPPMn(V)=O · Cl[17] is considered to form a complex with residual ArI.[10,18,35] The complex seems not to dissociate to free TPPMn(V)=O · Cl and ArI in solution, since the visible spectra did not change by addition of ArI to the system of TPPMn(III)Cl–ArIO, whereas further addition of TPPMn(III)Cl increased the formation of TPPMn(V)=O · Cl(ArI).

ArIO, therefore, may also affect the formation (or equilibrium) of TPPMn(V)= O · Cl(ArI). As seen in Figure 6, since an electron-rich iodosylarene (*p*-$MeOC_6H_4IO$) reacts with TPPMn(III)Cl faster than a less electron-rich homologue (C_6H_5IO) does, TPPMn(III)Cl has considerable electrophilic nature. However, the addition of excess diethyl sulfide to TPPMn(V)=O · Cl(ArI) prepared from TPPMn(III)Cl and *p*-$MeOC_6H_4IO$ or C_6H_5IO, respectively, caused a nearly *similar* increase of the absorption of TPPMn(III)Cl (Figure 6). Consequently, in the subsequent step of the equilibrium, the oxidation of sulfide with TPPMn(V)=O · Cl(ArI) is little affected by the Ar group of ArIO.

In the visible spectra shown in Figure 7, the maximum peak at 481 nm of TPPMn(III)Cl decreases with addition of PhIO to a certain equilibrium point. In the absence of substrate, the intermediate TPPMn(V)=O · Cl formed slowly decomposes to TPPMn(III)Cl with an increase of the absorption at 481 nm. The addition of some sulfides shows a rapid increase of the peak at 481 nm and sulfoxide formation was observed. The oxidation of diphenyl sulfide was clearly faster than that of diethyl sulfide, suggesting that the reaction is not simply electrophilic, unlike the PhIO oxidation described above.

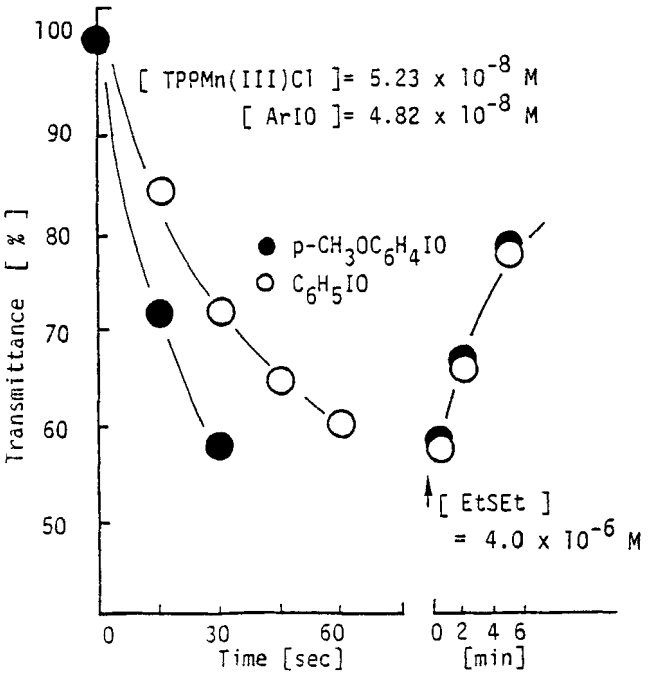


FIGURE 6 Changes of absorption at 481 nm of λ_{max} of TPPMn(III)Cl (5.23×10^{-8} mol) in the reaction with PhIO (○) and *p*-$MeOC_6H_4IO$ (●) (4.62×10^{-8} mol, respectively) and by the addition of Et_2S (4.0×10^{-6} mol) in CH_2Cl_2 (4 ml). The absorption at 481 nm decreases by a different magnitude by the addition of ArIO depending on the Ar group (left of the figure), and reaches a certain equilibrium point, to which the addition of excess Et_2S causes nearly the same increase of the absorption in the cases of both PhIO and *p*-$MeOC_6H_4IO$.

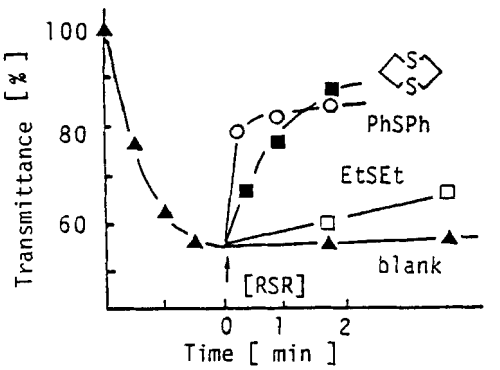


FIGURE 7 Absorption change at 481 nm of λ_{max} of TPPMn(III)Cl in the reaction with PhIO followed by the reaction with various sulfides. The absorption decreases by addition of PhIO to a certain equilibrium point and increases slowly if no substrate (▲) is added. On the other hand, an excess sulfide (100 equivalents vs. TPPMn(III)Cl) added to the equilibrium (eq. 3) recovers the absorption, depending on sulfide; □, EtSEt; ○, PhSPh; ■, $S(CH_2CH_2CH_2)_2S$.

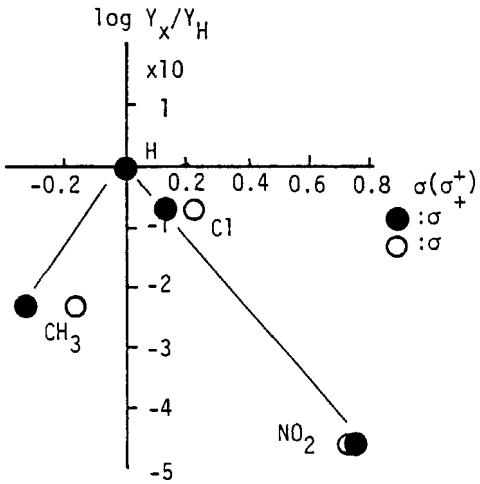
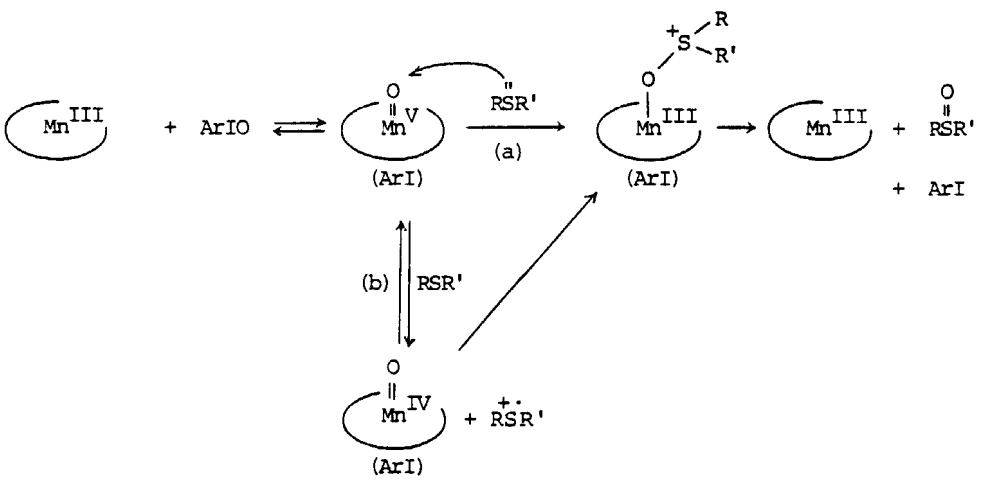


FIGURE 8 Hammett plots of the oxidation of *p*-substituted thioanisole with *p*-$MeOC_6H_4IO$–TPPMn(III)Cl at −71°C. Y_X/Y_H is a ratio of yield of *p*-substituted thioanisole *S*-oxide to that of thioanisole *S*-oxide, which was determined by an NMR method in the oxidation of sulfide (1 mmol) with TPPMn(III)Cl (0.0063 mmol) and *p*-$MeOC_6H_4$ (0.5 mmol) in a mixed solvent of CH_2Cl_2 (10 ml) and MeOH (5 ml) within 20% conversion.

Hammett plots of the oxidation of *p*-substituted thioanisoles with TPPMn(III)Cl–*p*-$MeOC_6H_4IO$ at −71°C clearly suggested that two different electron-demand steps are involved in the reaction (Figure 8).[19] Thus, the oxidation of sulfide with the TPPM(III)Cl–ArIO system does not correlate well with either nucleophilicity or oxidation potential.

The following Scheme 2 is proposed from the data obtained here for the reaction of TPPMn(V)=O · Cl with sulfide. The sulfonium intermediate is produced via either an initial nucleophilic attack of sulfide on the oxygen of TPPMn(V)=O · Cl,



SCHEME 2 (a) Nucleophilic attack of sulfide, (b) an electron transfer (reversible) from sulfide.

or a fast electron transfer followed by coupling of two charged products. Presumably, in the initial step, electron-donating substituents on sulfide favor the formation of the sulfonium intermediate, and in the subsequent step, the decomposition of this intermediate may be accelerated by electron-withdrawing groups. An initial electron-transfer process has been suggested for the oxidation of *N,N*-dimethylaniline[40] with TPPFe(III)Cl–PhIO[24] and for the enzymatic oxygenation of sulfides[21-23] and amines.[4,37] Reversible electron transfer is also possible, although there has been no evidence up to now for such a process. There is no distinguishable data for the two possible pathways, since Hammett plots for both σ and σ^+ as well as other observations are complicated.

EXPERIMENTAL

Materials. Both 5,10,15,20-mesotetraphenylporphynato-iron(III)[27] and manganese(III)-chlorides were prepared by literature method.[33] Iodosylbenzene[32] and iodoxybenzene[34] were obtained by known preparative methods. Substrate sulfides and product sulfoxides are all known and the authentic sulfoxides and sulfone were prepared according to the usual oxidation methods from commercially available compounds. Extra-pure solvents used in this study were commercially available.

Oxidation of Sulfide with TPPM(III)Cl–ArIO. In a typical run, a heterogeneous mixture of diphenyl sulfide (5.0 mmol), iodosylbenzene (1.0 mmol) and TPPFe(III)Cl (0.045 mmol) was stirred in 6.0 ml of CH_2Cl_2 at $-18°C$ under an argon atmosphere. After stirring for 50 min, the mixture was quenched by adding $Na_2S_2O_3$ solution and subjected to the usual work-up. The residue after evaporation was chromatographed over silica gel using benzene as an eluent to give diphenyl sulfoxide in 87% yield.

When an equimolar amount of PhIO vs. sulfide was used, the sulfoxide was obtained in a similar procedure in nearly the same yield.

Reaction of Sulfide with TPPFe(III)Cl–PhIO$_2$. A heterogeneous mixture of 2-methyl-2,3-dihydrobenzothiophene (1.25 mmol), TPPFe(III)Cl (0.0085 mmol) and $PhIO_2$ (1.56 mmol) in 3 ml of $CHCl_3$ was stirred at room temperature for several hours. No product other than starting materials appeared on TLC.

Oxidation of Dibenzyl Sulfoxide with TPPMn(III)Cl–PhIO. In a similar manner, a heterogeneous mixture of dibenzyl sulfoxide (1.0 mmol), PhIO (1.0 mmol) and TPPMn(III)Cl (0.045 mmol) in 5 ml of CH_2Cl_2 was stirred at room temperature for 20 min, while monitoring the complete disappearance of the sulfoxide. The resulting mixture was subjected to the usual work-up. From the integration ratio in a NMR spectrum of the residual organic layer, the yield of dibenzyl sulfone was 95%.

Kinetic Method. Kinetic conditions and methods are given in the figure notes.

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16. The valence of the central metal is believed to be +5 for both Mn[10] and Fe in the PhIO oxidation of TPPMn(III)Cl and TMPFe(III)Cl (tetramesitylporphynatoiron(III)chloride),[33] but to be +4 for Fe in the MCPBA oxidation of TMPFe(III)Cl.[33]
17. Formation of μ-oxo dimer in the reaction with TPPMn(III)Cl[34] has recently been reported, presumably because of the absence of Mn=O absorption in the IR spectrum.[10] However, the active species for the oxidation should be TPPMn(V)=O · Cl.
18. The exact structure of the complex into which ArI is believed to be included is still uncertain.[10,35] Usually, TPPM(V)=O · Cl(ArI) is abbreviated as TPPM(V)=O · Cl.
19. Similarly, the oxidation of *p*-substituted thioanisole *S*-oxides with TPPFe(III)Cl–*p*-$MeOC_6H_4IO$ at −72°C showed a bell-shaped Hammett plot. Clearly, there are also two different electron-demand steps in this reaction.
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