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MONOOXYGENASE-LIKE OXIDATIONS OF OLEFINS AND ALKANES CATALYZED BY MANGANESE PORPHYRINS : COMPARISON OF SYSTEMS INVOLVING EITHER O_2 AND ASCORBATE OR IODOSYLBENZENE

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Abstract - A biphasic system using a manganese porphyrin as a catalyst and sodium ascorbate as a reducing agent is able to activate dioxygen and to oxidize olefins selectively into epoxides and alkanes into alcohols and ketones. Its properties and specificities are shown to be different from those of the manganese porphyrin-iodosylbenzene system, suggesting that a manganese-oxo complex is not involved in these O_2-dependent oxidations.

INTRODUCTION

Cytochrome P-450-dependent monooxygenases catalyze the reductive activation of dioxygen by NADPH and the insertion of one oxygen atom into organic compounds[1].

$$S + O_2 \xrightarrow[\text{Cyt P-450}]{\text{NADPH}} SO + H_2O$$

They are able to hydroxylate alkanes and epoxidize olefins. Under anaerobic conditions, they catalyze the reduction by NADPH of several substrates such as halogenated compounds, tertiary N-oxides, arene-oxides and nitroarenes[2]. The desire to understand the mechanisms of cytochrome P-450-catalyzed reactions and the need for selective and effective synthetic oxygenation or reduction catalysts have recently motivated some investigators to study heme model systems either for reduction or oxidation reactions. We have described a biphasic heme model system able to perform in anaerobic conditions, most of the cytochrome P-450-dependent microsomal reductions of organic substrates[3]. This system uses sodium ascorbate as a reducing agent in water, an iron-porphyrin as a catalyst of electron transfer to the substrate in benzene and a catalytic amount of a phase transfer agent. Under aerobic conditions, this system is unable to perform oxidation of substrates such as alkanes or olefins. One must note that no heme model system using an iron-porphyrin as a catalyst has been shown so far able to activate dioxygen and to hydroxylate alkanes or to epoxidize olefins. However, we found very recently that, simply by replacing the iron-porphyrin by a manganese-porphyrin, the biphasic system becomes able, in the presence of dioxygen, to perform the oxidation of many substrates[4]. Very few systems using dioxygen, a reducing agent and a metalloporphyrin as a catalyst have been so far reported to be able to hydroxylate alkanes or epoxidize olefins. Two such systems using manganese-porphyrins as catalysts and either a borohydride[5] or H_2 (in the presence of Pt)[6] as reducing agents have been recently described. The first system performs the oxidation of cyclohexene to cyclohexanol and cyclohexenol[5a] and the oxidation of terminal olefins to methylketones[5b]. The second system performs the epoxidation of cyclohexene and the hydroxylation of adamantane[6]. Very recently, a rhodium-porphyrin has been used as a catalyst for the oxidation of olefins by dioxygen in the presence of $NaBH_4$ in excess[7], leading eventually to alcohols of the "anti-

Markovnikoff" type.

Many studies have implicated that high-valent oxo-iron-porphyrin species are key oxidizing intermediates in the catalytic cycle of cytochrome P-450[1,8]. This was supported by the fact that a number of single oxygen atom donors such as hydroperoxides, peroxyacids and iodosylbenzene, effect oxygen transfer in a manner similar in many respects to the enzymatic system working with O_2 and NADPH[9]. Model studies have demonstrated that metalloporphyrins can catalyze various hydrocarbon oxygenation processes by using iodosylbenzene as oxidant[10,11,12].

More particularly, manganese-porphyrins have been shown to produce, by reaction with iodosylbenzene, an oxo-manganese species Mn(V) = O able to transfer very efficiently its oxygen atom to alkanes[12]. However, only few data are available in the literature on reactions of this Mn(III)-C_6H_5IO system with olefins. They concern the non stereospecific epoxidation of cis- and trans-stilbenes[12b] and the relative reactivities of some olefins towards this system, estimated from competition experiments[6].

In this paper, we describe the properties and specificities of the biphasic Mn(TPP)(Cl)-O_2-ascorbate system and, in particular, we show that it is able to perform the selective epoxidation of a variety of olefins under very simple and mild conditions. In order to get information on the nature of the active oxidizing species involved in this system and to compare it with the species involved in the Mn(TPP)(Cl)-C_6H_5IO system (Mn^V = O), we had to further precise some properties of the latter concerning its reactivity towards olefins and its reactions with alkanes in the presence of O_2 which were not available in the literature. The present results strongly suggest that different oxidizing species are involved in the two systems.

RESULTS

Description of the Mn(porphyrin)-O_2-ascorbate system

The reductive activation of dioxygen can be performed by a system using Mn(III)(TPP)(Cl),[13] dioxygen and a reducing agent[5,6]. We used the biphasic system schematically represented in Fig. 1. Catalytic amounts of Mn(TPP)(Cl), 2.5 mM, are dissolved in a mixture of the hydrocarbon substrate (1 ml) and C_6H_6 (1 ml). The reducing agent is sodium ascorbate, 250 mM, in an aqueous buffer (pH 8.5) containing a phase transfer agent, trioctylmethylammonium chloride (TOMA), 5 mM. Reactions are performed in the presence of O_2 (1 atm). Ascorbate has been found as the most appropriate reducing agent for dioxygen activation and substrate oxidation. Effectively, by studying the oxidation of styrene by the same biphasic C_6H_6-H_2O system but with 250 mM sodium dithionite (Table 1) or sodium cyano-borohydride as reducing agents, one found respectively less or no formation of styrene oxide. Moreover, heterogenous systems using a metallic powder (manganese or iron) as a reducing

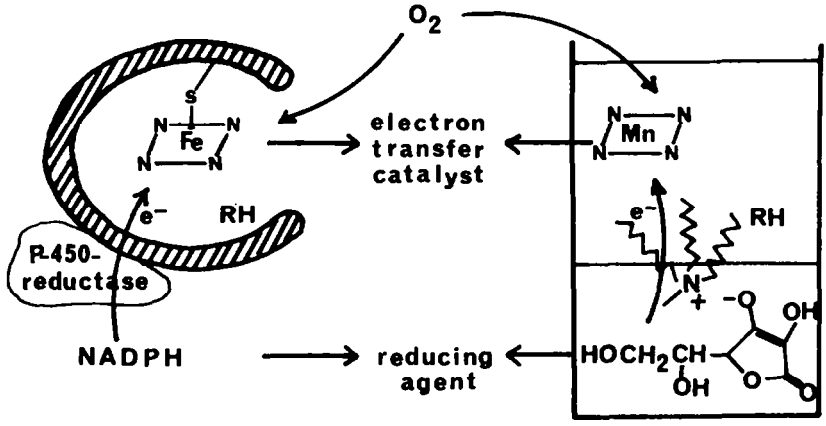


Figure 1 : Schematic representation of the Mn(TPP)-O_2-ascorbate system and comparison with the cytochrome P-450 system.

agent and a mixture of styrene and benzene, in the presence of dioxygen (1 atm), were found unable to oxidize styrene into styrene oxide.

The transfer of the reducing equivalents of ascorbate to dioxygen occurs in three steps :

1) Transfer of ascorbate into the organic phase owing to a catalytic amount of a phase transfer agent.

2) Reduction of the manganese-porphyrin catalyst Mn(III)(TPP)(Cl) to Mn(II)(TPP) by ascorbate in the organic phase.

3) Electron transfer from Mn(II)(TPP) to dioxygen.

In figure 1, we have compared this biphasic system to cytochrome P-450 itself, where, in a similar manner, the reducing equivalents of NADPH are transferred to dioxygen both by cytochrome P-450-reductase and by cytochrome P-450-heme. As it will be shown in Tables 2 and 4, the biphasic Mn(TPP)(Cl)-O_2-ascorbate system is able to oxidize differently substituted olefins into the corresponding epoxides and to oxidize alkanes into a mixture of alcohols and ketones. However, one found that it cannot oxidize aromatic compounds such as phenanthrene or benzene into epoxides or phenols. This explains why C_6H_6 could be added into the system to enhance the dissolution of the porphyrin catalyst in the organic phase. In order to illustrate the various factors which are important for the oxidations performed by this system, its reaction with styrene as substrate is described in the following paragraph.

Oxidation of styrene by the Mn(TPP)-O_2-ascorbate system

Under the aforementioned conditions, the oxidation of styrene gives mainly styrene oxide and also minor amounts of phenylacetaldehyde . The formation of these products is linear with time for 2 hours, the rates of formation of styrene oxide and phenylacetaldehyde being respectively 0.6 and 0.08 mol per mol of Mn(TPP)(Cl) and per hour (Tables 1 and 2). Actually, at pH 8.5, under 1 atm of dioxygen, the reaction stops after about 2 hours (Figure 2) because sodium ascorbate is

Table 1 : Rates of formation of styrene oxide in the oxidation of styrene by the Mn(TPP)-O_2 ascorbate system, under various conditions

Conditions	v mol/mol Mn(TPP)/h
Complete System (a) : Mn(TPP)(Cl) 2.5 mM, ascorbate 250 mM, pH 8.5, t = 20°C, TOMA 5 mM, pO_2 = 1 atm	0.6
Dithionite 250 mM (b)	0.52
pH 7.4 (c)	0.26
pO_2 = 0.2 atm (d)	0.06
t = 70°C	0.005
TOMA 25 mM	0.6
Complete System (a)	0.6
+ pyridine 62.5 mM	0.2
+ 4-methylpyridine 62.5 mM	0.18
+ pyridine 250 mM	0.08

(a) Conditions for complete system are indicated in the experimental section. The modification of one factor is precised in the Table, and the reactions carried out as described in the experimental section. (b) Ascorbate was replaced by sodium dithionite (500 µmol). (c) 1 M phosphate KH_2PO_4/K_2HPO_4 buffer. (d) Aerated solvents were used and the system opened to the air.

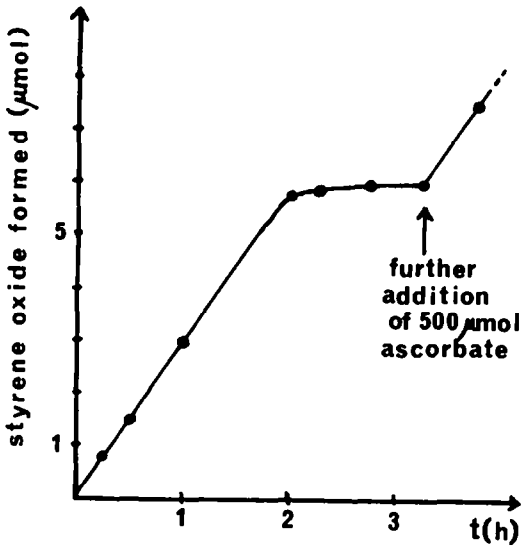


Figure 2 : Time courses of styrene oxide formation upon oxidation of styrene by the Mn(TPP)-O_2-ascorbate system. Conditions : Mn(TPP)(Cl) 5 μmol, ascorbate 500 μmol, styrene 1 ml, in C_6H_6 (1 ml)/H_2O (2 ml), pH 8.5, pO_2 = 1 atm.

Table 3 : Relative reactivities of olefins in the Mn(TPP)-O_2-ascorbate system

Olefin	Relative Reactivity based on competition experiments (a)	Relative Reactivity based on results of table 2 (b)
Hex-1-ene	1	1
trans-hex-2-ene	1.7	1.3
Cyclohexene	9	8
cis-hex-2-ene	8	8.6
2,3-dimethyl-but-2-ene	12.5	11.5
Styrene	25	20

(a) Reactions were performed as indicated in the experimental section. (b) The relative reactivities were calculated from the yields of epoxides indicated in Table 2.

completely consumed not only for substrate oxidation but also for secondary reactions such as its direct reaction with O_2, which is known to be very efficient at high pH. This explains why yields based on the reducing agent are very low ($\simeq$ 1.5 %). After a new addition of sodium ascorbate, the reaction starts again with the same rate (Figure 2). When one works at lower pH or lower dioxygen pressure, the reducing agent is consumed more slowly (after about 4 hours) but the rate of styrene oxidation is lower (Table 1). For example, the rate of formation of styrene oxide is decreased to 0.26 mol per mol of Mn(TPP)(Cl) and per hour by using a phosphate buffer, pH 7.4 and 0.06 mol per mol of Mn(TPP)(Cl) and per hour by using a dioxygen pressure of 0.2 atm.

No oxidation takes place if any component of the system (O_2, sodium ascorbate, Mn(TPP)(Cl), TOMA) is omitted. This shows that the observed oxidation is relative to a reductive activation of dioxygen and not to an autoxidation process. Moreover, this shows that both the phase transfer and electron transfer catalysis are absolutely required.

As shown by visible spectroscopy, the manganese porphyrin is completely in the Mn(III)(TPP)(Cl) state during styrene oxidation, and no destruction could be detected after 2 days reaction, indicating that the Mn-porphyrin acts as a real catalyst. Table 1 indicates that the rates of styrene oxidation are not changed by increasing the phase transfer agent concentration but are drastically decreased by increasing the temperature to c.a. 70°C certainly because of the lower dioxygen concentration in the organic phase. Finally, we examined if the presence of pyridine enhanced the oxidation rates, as it had been reported for the Mn(TPP)-O_2-H_2 (in the presence of Pt) system in the case of the oxidation of cyclohexene[6]. On the contrary, Table 1 shows that pyridine inhibits the oxidation of styrene by the Mn(TPP)-O_2-ascorbate system. One observed that the more concentrated or the more nucleophilic the base, the more efficient the inhibition. One also observed, by visible spectroscopy, high steady state concentrations of the pentacoordinated Mn(TPP)(Py) complex, λmax = 442 nm[14], during the oxidation of styrene by the biphasic system, in the presence of pyridine. To favour the reaction between the active species and the substrate, we have generally worked with a large excess of substrate relative to the manganese-porphyrin ($\simeq$2000). So, the yield based on the substrate was very low ($\simeq$ 0.3 %). By reducing the concentration of styrene in order to have 100:1 styrene:Mn(TPP)(Cl) molar ratio, all other conditions being unchanged, one ob-

served that the nature and ratio of the products did not change. The formation rates of styrene oxide and phenylacetaldehyde were respectively 0.22 and 0.025 mol per mol of Mn(TPP)(Cl) and per hour, the yields being 2.2 % and 0.25 % based on styrene, after 10 h reaction. It is noteworthy that, under these conditions, the yield of styrene oxide based on consumed styrene (which is difficult to determine precisely because of the error on the styrene concentration) was greater than 75 %.

Oxidation of alkenes by the Mn(TPP)-O_2-ascorbate system

Table 2 records the products formed upon oxidation of differently substituted olefins by the biphasic system as well as the rates of reaction at 20°C. For each olefin, except for styrene and cyclohexene, the only product of the organic phase detected by g.l.c. and mass spectrometry is the corresponding epoxide. No oxidation of the allylic C-H bonds leading to alcohols and ketones has been detected. The oxidation of styrene gives also minor amounts of phenylacetaldehyde. In the case of cyclohexene, whose allylic positions are known to be very sensitive to oxidation, only traces of cyclohexenone are formed. This is a further indication that the reaction does not proceed as a typical autoxidation, since the products distribution typical of cyclohexene autoxidation is very different from that reported here[15,5a]. One should note that this almost exclusive formation of cyclohexene oxide is observed only when all the components of the system are present. In the absence of dioxygen or manganese porphyrin, no oxidation takes place. However, in the absence of either sodium ascorbate or the phase transfer agent, cyclohexenone, cyclohexenol and cyclohexene oxide are formed in a 79/20/1 ratio characteristic of cyclohexene autoxidation catalyzed by metalloporphyrins[15]. These results suggest that sodium ascorbate acts not only as a reducing agent for dioxygen activation as expected but also as an efficient inhibitor of the autoxidation process. For the other olefins of table 2, we also found that the phase transfer and electron transfer catalysts were necessary for the epoxidation to occur. For all olefins, we did not observe, by visible spectroscopy, any characteristic absorption of an intermediate species other than Mn(III)(TPP) or Mn(II)(TPP) and any destruction of the Mn-porphyrin after 2 days reaction.

Table 2 also shows that the epoxidation of aliphatic alkenes by this system is a stereospecific process since trans- and cis-hex-2-ene give only the corresponding epoxide. This is not the case for stilbenes. Effectively, if trans-stilbene gives only the corresponding epoxide, cis-

Table 2 : Oxidation of alkenes by the Mn(TPP)-O_2-ascorbate system (a)

Substrate	Product	v (b) mol/mol Mn(TPP)/h
Styrene	Styrene oxide	0.6
	Phenylacetaldehyde	0.08
cis-stilbene	cis-stilbene oxide	0.14
	trans-stilbene oxide	0.23
trans-stilbene	trans-stilbene oxide	0.07
cis-hex-2-ene	cis-hex-2-ene oxide	0.26
trans-hex-2-ene	trans-hex-2-ene oxide	0.04
Cyclohexene	Cyclohexene oxide (c)	0.24
6-phenoxy-hex-1-ene	6-phenoxy-hex-1-ene oxide	0.07
Hex-1-ene	Hex-1-ene oxide	0.03
2,3-dimethyl-but-2-ene	2,3-dimethyl-but-2-ene oxide	0.34

(a) Reactions carried out as described in the experimental section. (b) The formation of the products is linear with time. (c) Traces of cyclohexenone have been detected (2 % versus epoxide).

Table 4 : Oxidation of C-H bonds by the Mn(TPP)-O_2-ascorbate system (a)

Substrate	Product	v (b) mol/mol Mn(TPP)/h
Cyclohexane	Cyclohexanol	0.04
	Cyclohexanone	0.3
Heptane	Heptan-2-one	0.07
	Heptan-3-one	0.13
	Heptan-4-one	0.03
Methylcyclohexane (c)	1-methylcyclohexanol	0.1
	2-methylcyclohexanols	0.04
	3-methylcyclohexanols	0.02
	4-methylcyclohexanols	0.01
	2-methylcyclohexanone	0.17
	3-methylcyclohexanone + 4-methylcyclohexanone	0.2
Toluene	Benzaldehyde	0.4
Cyclohexanol	Cyclohexanone	1.5
Heptan-4-ol	Heptan-4-one	1.3
Benzyl alcohol	Benzaldehyde	8.7
Anisole	Phenol	0.04

(a) Reactions carried out as described in the experimental section. (b) The formation of the products is linear with time. (c) The used analytical method was unable to separate the stereoisomers of 2-, 3- and 4-methylcyclohexanols, in one hand, and 3- and 4-methylcyclohexanone, in the other hand.

stilbene is oxidized into a mixture of cis-stilbene oxide and trans-stilbene oxide in a 1:1.7 molar ratio .

The relative reactivities of olefins towards the present Mn(TPP)-O_2-ascorbate system were estimated from a series of competition experiments where two olefins were present in the organic phase (Table 3). One observes that the relative reactivity increases with an increase in the number of alkyl substituents of the double bond. Moreover, Tables 2 and 3 indicate that cis-alkenes are more reactive than their trans-isomers. For instance, cis-hex-2-ene was found 4.7 times more reactive than its trans-isomer (Table 3) and cis-stilbene led to much higher yields of epoxide than trans-stilbene (Table 2). It is interesting to note that the relative reactivities of olefins, based on competition experiments, closely resemble those calculated from the rates of epoxide formation reported in Table 2.

Oxidation of C-H bonds by the Mn(TPP)-O_2-ascorbate system

Table 4 reports the products and rates of oxidation of alkanes, alcohols and anisole, by the biphasic system. It reveals that alkanes are efficiently oxidized, leading mainly to ketones or aldehydes. Minor amounts of cyclohexanol are also formed upon cyclohexane oxidation. With methylcyclohexane as substrate, which contains primary, secondary and tertiary hydrogens, we found 2-, 3-, 4-methylcyclohexanone and 1-methylcyclohexanol as major products as well as minor amounts of 2-, 3-, 4-methylcyclohexanols. The relative reactivity of tertiary to secondary hydrogens of this substrate was c.a 2.3, after statistical correction for the number of hydrogen atoms. No product derived from the oxidation of the primary C-H bonds has been detected. Table 4 also shows that the

Table 5 : Oxidation of alkenes by the Mn(TPP)-C_6H_5IO system, under anaerobic conditions

Substrate	Product	% Yield (a)
Styrene	Styrene oxide	86
	Phenylacetaldehyde	3
cis-hex-2-ene	cis-hex-2-ene oxide	64
	Allylic alcohols (b)	2
trans-hex-2-ene	trans-hex-2-ene oxide	8
	Allylic alcohols (b)	2
Cyclohexene	Cyclohexene oxide	40
	Cyclohex-1-en-3-ol	23
	Cyclohex-1-en-3-one	6
6-phenoxy-hex-1-ene	6-phenoxy-hex-1-ene oxide	45
	6-phenoxy-hex-1-en-3-ol	34
	6-phenoxy-hex-1-en-3-one	8
	6-phenoxy-hexanal	2
Hex-1-ene	Hex-1-ene oxide	29
	Hex-1-en-3-ol	4
	Hex-1-en-3-one	3
	Hexanal	1

(a) % yields based on starting C_6H_5IO after 2 h reaction. Conditions are indicated in the experimental section (Mn(TPP) : C_6H_5IO ≅ 1:5). (b) cis- and trans-hex-2-en-1-ol and hex-1-en-3-ol, the possible products deriving from an oxidation of the primary C-H bonds were not detected. The different possible secondary allylic alcohols (cis- and trans-hex-2-en-4-ol, cis- and trans-hex-3-en-2-ol) could not be separated.

Table 6 : Oxidation of C-H bonds by the Mn(TPP)-C_6H_5IO system

Substrate	Product	% Yield (a) under Argon atmosphere	% Yield (a) under O_2 atmosphere
Cyclohexane	Cyclohexanol	26	22
	Cyclohexanone	5	11
Heptane	Heptan-2-ol	12.5	2.4
	Heptan-3-ol	15	2.5
	Heptan-4-ol	4	1.5
	Heptan-2-one	1	3.4
	Heptan-3-one	1	3.6
	Heptan-4-one	1	1.8
Methylcyclohexane (b)	1-methylcyclohexanol	24	22
	2-methylcyclohexanols	20	2
	3-methylcyclohexanols	3	5
	4-methylcyclohexanols	18	9
	2-methylcyclohexanone	1.5	10
	3-methylcyclohexanone + 4-methylcyclohexanone	1.5	12
Toluene	Benzylalcohol	16	3
	Benzaldehyde	1	29
Anisole	Phenol	2	2

(a) % yields based on starting oxidant after 2 h reaction. Conditions indicated in the experimental section. (b) The used analytical method was unable to separate the stereoisomers of the 2-, 3- and 4-methylcyclohexanols, in one hand, and 3- and 4-methylcyclohexanone, in the other hand.

system is able to perform the demethylation of anisole to phenol and to oxidize very efficiently alcohols to ketones or aldehydes. In order to know if the ketones or aldehydes formed during alkanes oxidation come from the oxidation of intermediate alcohols, we studied the reaction of the complete biphasic system with cyclohexanol and heptan-4-ol, but with starting low concentrations of these alcohols (2.5-10 mM)-i.e. under conditions quite similar to those where one should find these alcohols during the oxidation of cyclohexane and heptane, if they were intermediates in the formation of ketones. Since these alcohols were not found to be oxidized under these conditions, one can conclude that the ketones and aldehydes produced by oxidation of alkanes do not derive from the intermediate corresponding alcohols. In the case of aromatic compounds, no product (methoxyphenols for anisole or methylphenols for toluene) arising from the oxidation of the aromatic ring has been detected.

Oxidation of alkenes by the Mn(TPP)-C_6H_5IO system

As shown in Table 5, Mn(TPP)(Cl) in benzene catalyzes the transfer of the oxygen atom of iodosylbenzene in excess (5 equivalents based on Mn(TPP)(Cl)) to the olefins previously studied (Table 2), under anaerobic conditions, since no oxidation product is detected, by g.l.c. without Mn(TPP)(Cl). Iodosylbenzene is quantitatively converted into iodobenzene, with all the olefins under these conditions. The major product is always the corresponding epoxide, the yields ranging from 8 to 86 %. These yields are unaffected by the presence of dioxygen (even 1 atm) in the reaction medium. In addition to these epoxides, significant amounts of allylic alcohols or ketones are formed, the epoxidation : allylic oxidation ratio being greatly dependent upon the nature of the olefin. Actually, this ratio decreases from 32 for cis-hex-2-ene to about 1 for 6-phenoxyhex-1-ene. No product derived from the oxidation of a primary allylic C-H bond has been detected. With monosubstituted olefins as substrates, one also observed the formation of minor amounts of aldehydes. We have shown that these aldehydes do not derive from an isomerization of the corresponding epoxides that are stable under the reaction conditions.

The results reported in Table 5 indicate that the oxygen transfer from iodosylbenzene to olefins leading to epoxides is a stereospecific process for aliphatic alkenes such as hex-2-ene, since trans- and cis-hex-2-ene give only the corresponding epoxide. The analytical method would have detected the presence of less than 0.5 % of the other epoxide isomer. It has been reported that this was not the case for a non-aliphatic alkene, stilbene[12b].

During the oxidation of olefins by the Mn(TPP)-C_6H_5IO system the manganese-porphyrin catalyst is both in the Mn(III)(TPP) state and in the $\left[(TPP)Mn^{IV}(Cl)(OIPh)\right]_2O$ state as shown by the visible spectrum of the solution which exhibits peaks at λ= 476 nm and λ= 421 nm[12c,d]. The relative concentrations of these complexes depend upon the reactivity of the alkene. For instance, high steady-state concentrations of the 421 nm-absorbing complex (80 % of the starting catalyst) are observed in the case of hex-1-ene whereas only the Mn(III)(TPP) complex is observed in the case of the most reactive substrate, styrene. When C_6H_5IO is completely consumed, the spectrum of the manganese-porphyrin is identical to that of the starting catalyst. Moreover, it is noteworthy that the Mn(III) complex obtained at the end of the reaction retains its full catalytic activity.

Oxidation of C-H bonds by the Mn(TPP)(Cl)-C_6H_5IO system

The oxidation of various alkanes by iodosylbenzene in the presence of catalytic amounts of Mn(TPP)(Cl) has been recently studied and found to give alcohols in good yields[12]. A detailed mechanism that involves the intermediate formation of a Mn^V = O complex as the active species has been proposed for this reaction[12]. In order to know if such an active species is involved in the reactions performed by the above described Mn(TPP)-O_2-ascorbate system, we have studied the oxidation of the alkanes indicated in Table 4 by C_6H_5IO (12.5 mM) in the presence of Mn(TPP)(Cl) (2.5 mM), not only under argon atmosphere, but also under one atmosphere of dioxygen as in reactions performed by the Mn-O_2-ascorbate biphasic system.

The results are summarized in Table 6. They show that the ketone (or aldehyde) : alcohol

ratio largely increases in reactions performed in the presence of O_2. This is particularly clear in the case of toluene and heptane : under an inert atmosphere, benzaldehyde or heptanones are only detected as traces whereas they become the main products under 1 atm of dioxygen. With cyclohexane as substrate, the yields of cyclohexanol and cyclohexanone, obtained under argon, are very similar to those previously reported[12a]. Cyclohexanol remains the main product even under 1 atm of dioxygen. The relative reactivity of tertiary to secondary hydrogens of methylcyclohexane was c.a 5.8 after statistical correction for the number of hydrogen atoms. No product derived from the oxidation of primary C-H bonds, in the case of heptane or methylcyclohexane, has been detected.

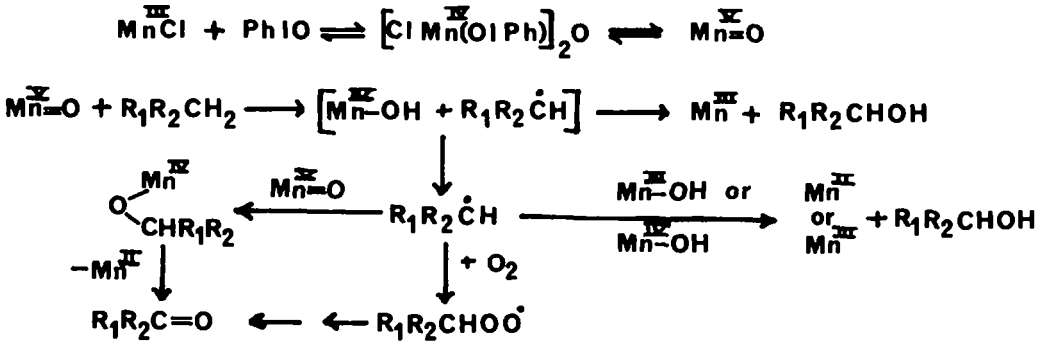
As shown in Table 6, Mn(TPP)(Cl) is not very efficient to catalyze the oxidative demethylation of anisole by iodosylbenzene since only 2 % of phenol is produced. Moreover, as for toluene, no product derived from an oxidation of the aromatic ring could be detected. During these oxidations, the manganese-porphyrin catalyst is both in the Mn(III)(TPP) and in the $\left[(TPP)Mn^{IV}(Cl)(OIPh)\right]_2O$ states, this last complex absorbing at 421 nm[12c,d]. It is noteworthy that after these reactions, using a 5:1 C_6H_5IO : Mn(TPP)(Cl) molar ratio, no irreversible modification of the porphyrin catalyst could be detected by visible spectroscopy.

DISCUSSION

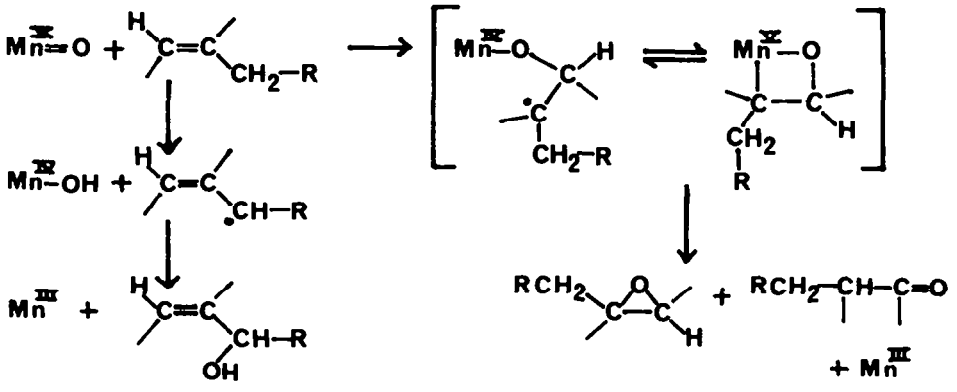
Characteristics and mechanism of the oxidations performed by the Mn(TPP)(Cl)-C_6H_5IO system

Very recently, a detailed mechanism for the oxidation of alkanes into alcohols by C_6H_5IO catalyzed by Mn(III)-porphyrins has been presented[12d]. The species active in these reactions has been proposed to be a Mn(V) = O monomer complex[12b] which is in equilibrium with the isolated

Scheme 1



Scheme 2



$[(TPP)Mn^{IV}(Cl)(PhIO)]_2O$ dimer[12d]. As its Fe(V) = O equivalent formed upon reaction of C_6H_5IO with Fe(III)-porphyrins[10], this species is believed to abstract an hydrogen atom from alkanes $R_1R_2CH_2$ leading to the corresponding free radical $R_1R_2CH^\bullet$ and a Mn(IV)-OH species (Scheme 1). In this mechanism, alcohols are formed by an oxidative OH ligand transfer either inside the $[Mn^{IV}\text{-}OH, R_1R_2CH^\bullet]$ caged radical pair, or between $R_1R_2CH^\bullet$ radicals escaped from this cage and Mn(IV)- or Mn(III)-OH species[12d] (scheme 1). Our results confirm that alcohols are the main products derived from the oxidation of several alkanes in anaerobic conditions and establish a relative reactivity of tertiary to secondary hydrogens of methylcyclohexane toward the active species of 5.8. They also show an important increase of the yields of ketones (or aldehydes) when alkanes are oxidized in the presence of dioxygen (Table 6). This is consistent with the general mechanism of scheme 1 if one admits that the intermediate free radical $R_1R_2CH^\bullet$ reacts with dioxygen and that the resulting peroxy radical $R_1R_2CHOO^\bullet$ reacts with the Mn(III)-porphyrin catalyst leading to the ketone R_1R_2CO (scheme 1). The fact that one found the formation of lower but significant amounts of ketones, under strictly anaerobic conditions (Table 6) suggests that these ketones could be formed by oxidation of the $R_1R_2CH^\bullet$ radicals by the Mn(V) = O species as indicated in Scheme 1. Concerning the oxidation of alkenes by the Mn(III)-C_6H_5IO system, it had been shown that epoxides were formed, the electron rich olefins being more reactive[6], and that stilbenes were epoxidized in a non-stereospecific manner[12b]. The mechanism proposed for these epoxidations[12b] is very similar to that proposed for similar reactions performed by C_6H_5IO in the presence of iron(III)-porphyrin[10]. The high-valent Mn^V (or Fe^V) = O species which has a free radical character, adds to the double bond leading to a Mn^{IV} (or Fe^{IV}) species bearing a carbon-centered free radical (scheme 2). The intramolecular oxidation of this radical by Mn(IV) eventually leads to the epoxide. However, although cis- and trans-stilbene epoxidation by the Fe(III)-C_6H_5IO system is stereospecific[10], their epoxidation by the Mn(III)-C_6H_5IO system is not[12b]. This has been explained by a less efficient control of the intermediate radical by the Mn(IV) species than by its Fe(IV) equivalent[12b].

Our results confirm that epoxides are the main products of olefins oxidation by the Mn(III)-C_6H_5IO system, as shown for all the olefins tested. They establish that aliphatic olefins such as hex-2-enes are epoxidized in a completely stereospecific manner (Table 5) contrary to stilbenes. They also show that other oxidation products are formed such as allylic alcohols as soon as allylic hydrogens are present, and aldehydes in the case of monosubstituted olefins. The epoxide : allylic alcohols ratio is high in the case of electron-rich reactive olefins such a cis-hex-2-ene but considerably decreases in the case of monosubstituted olefins, the two kinds of products being formed in nearly equal amounts with 6-phenoxy-hex-1-ene (Table 5). The aldehydes observed upon oxidation of monosubstituted olefins are not derived from the corresponding epoxides since treatment of these epoxides by the Mn(III)- C_6H_5IO system under identical conditions failed to give aldehydes (data not shown). The formation of these aldehydes has also been recently observed upon oxidation of the corresponding olefins by Fe(III)-porphyrin-C_6H_5IO systems[16] and by cytochrome P-450[16]. Moreover, the formation of aryl-ethanals upon oxidation of styrenes by C_6H_5IO and iron-porphyrins has been very recently reported[10h]. The formation of aldehydes and allylic alcohols as well as epoxides upon olefin oxidation by the Mn(III)-C_6H_5IO system can be easily explained by considering scheme 2. The Mn(V) = O species can either add to the double bond or abstract allylic hydrogens. The intermediate free radical formed by the first reaction can lead either to the epoxide or to the aldehyde by migration of a hydrogen atom. Actually, these two reactions could also occur inside a four membered metallocycle deriving from the combination of the intermediate free radical with the metal (Scheme 2)[17]. Abstraction of an allylic hydrogen atom leads to the finally observed allylic alcohol by the general mechanism proposed for C-H bonds hydroxylation (Scheme 1). In the case of monosubstituted olefins, allylic hydrogen abstraction efficiently competes with the addition to the double bond whereas with more electron-rich olefins which can easily approach the porphyrin catalyst[10g] such as cis-hex-2-ene, the addition pathway leading to the epoxide becomes predominent (Table 5).

It is interesting to compare the characteristics of the Mn(III)(TPP)-C_6H_5IO system to those previously reported for the Fe(III)(TPP)-C_6H_5IO system[10]. Oxidations by both systems seem to

involve the same general mechanism. Both systems provide an active species reacting as an oxygen-centered free radical[10,12] and exhibiting a marked electrophilic character[6,10,12]. In both systems, the intermediate free radicals derived from the substrates are fastly enough controlled and oxidized by the Mn(IV) or Fe(IV) intermediate complex to give satisfactory yields of alcohols from alkanes and stereospecific epoxidation of hex-2-enes (tables 5,6 and ref.10). However, this control is less efficient in the case of Mn(IV) as previously underlined in the case of the non-stereospecific epoxidation of stilbenes, the intermediate relatively stable benzylic radical having time to undergo a rotation around its C-C bond[12b]. The important increase of ketones yields upon alkane oxidation in the presence of O_2 observed in this study (Table 6) is a further indication of the relatively less efficient control of intermediate free radicals by the Mn(III)-C_6H_5IO system. This is certainly the main advantage of the Fe(III)-C_6H_5IO system over its Mn(III) analogue ; however, one must note that the latter system gives higher yields of alkane hydroxylations and is considerably less limited by an irreversible oxidative degradation of the catalyst[18].

Characteristics and mechanism of the Mn(TPP)-O_2-ascorbate system

This O_2-activating system exhibits several analogies with the Mn(III)-C_6H_5IO system. Both systems perform olefins epoxidation and alkane oxidation, give poor yields of anisole dealkylation and fail to hydroxylate aromatic rings (at least of benzene, anisole and 6-phenoxy-hex-1-ene). Both systems react preferentially on tertiary C-H bonds of alkanes, the relative ratios of reactivity of tertiary over secondary C-H bonds being 2.3 and 5.8 for the O_2- and C_6H_5IO-dependent systems. These ratios are compatible with a free radical reactivity of the active species[19]. Both systems working in aerobic conditions lead to high yields of ketones from alkanes and this could be explained by the involvement of free radicals and their reactions with O_2. The orders of reactivity towards various olefins observed for the two systems (Tables 2 and 5) are very similar suggesting the involvement of electrophilic active species which are able to epoxidize cis-and trans-hex-2-enes, but not cis-and trans-stilbenes, in a completely stereospecific manner. Finally, both systems are considerably more reactive toward cis-1,2-disubstituted olefins than toward the corresponding trans-olefins. This has been observed for hex-2-enes and stilbenes (Tables 2 and 5). A similar result has been reported in the case of Fe(III)-porphyrins-C_6H_5IO systems and interpreted by a much greater hindrance for the approach of trans-olefins to the porphyrin plane[10g].

However, the two systems exhibit also major different characteristics : (i) the Mn-O_2-ascorbate system is totally regioselective for olefin oxidation leading exclusively to epoxides (Table 2) whereas the Mn-C_6H_5IO system also leads to various amounts of allylic alcohols and ketones (Table 5), (ii) the two systems exhibit slightly different reactivity ratios of tertiary versus secondary C-H bonds (2.3 and 5.8 respectively), (iii) the Mn-O_2-ascorbate system gives higher ketone : alcohol ratios for alkane oxidation than the Mn-C_6H_5IO system working under the same O_2 pressure (Tables 4 and 6). For instance, with cyclohexane as substrate, one found a 88:12 cyclohexanone : cyclohexanol ratio, with the Mn(TPP)-O_2-ascorbate system and a 34:66 ratio, with the Mn(TPP)-C_6H_5IO system, under 1 atm of O_2. These major differences strongly suggest that different active oxidizing species are involved in the two systems and therefore that the active species involved in the Mn-O_2-ascorbate system is not a Mn(V) = O complex.

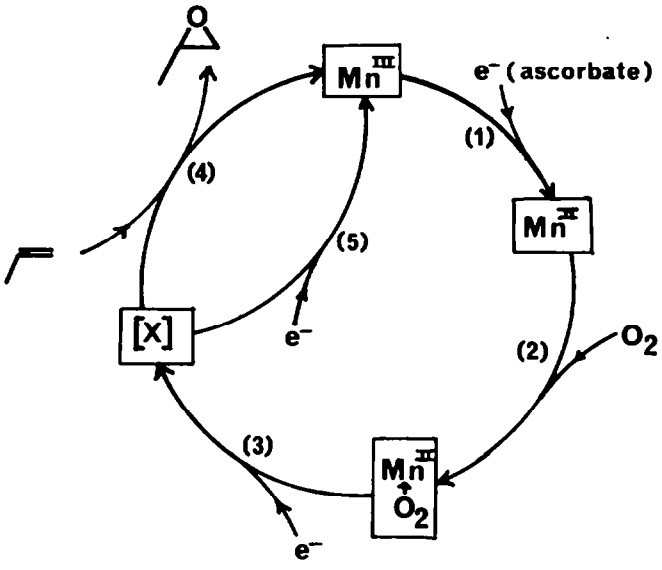
Another possible active species could derive from compounds such as O_2^- and H_2O_2, coming from dioxygen reduction by ascorbate which has been shown to be important in the reaction conditions (see for instance Fig. 2). In order to test this hypothesis, experiments have been done with the complete system (Table 1) where ascorbate has been replaced either by H_2O_2 or by KO_2 (from 2.5 to 250 mM) (data not shown). In the case of KO_2, similar experiments have been performed in the absence of the aqueous phase in order to limit its fast dismutation but in the presence of a crown ether (dibenzo-18-crown-6-ether) to solubilize KO_2 in the organic phase. Under none of these conditions using KO_2 or H_2O_2 instead of O_2 and ascorbate, styrene was epoxidized or cyclohexane oxidized into cyclohexanol or cyclohexanone. This result indicates that reduced dioxygen species such as O_2^- and H_2O_2 are not involved in the oxidations performed by the Mn-O_2-ascorbate system. Moreover, it has been previously shown that alkylhydroperoxides in the presence of catalytic amounts

of Mn(TPP)(Cl) were very poor oxidizing agents toward hydrocarbons and, particularly, were unable to epoxidize olefins[10e]. This is not in agreement with but does not completely exclude an active species of the Mn-O_2-ascorbate system derived from reaction of Mn(TPP)(Cl) with a peroxidic compound formed upon autoxidation of ascorbate.

Another possible origin of the active species is tentatively depicted in scheme 3. The Mn(III) catalyst is first reduced by ascorbate (step (1) of Scheme 3) the resulting Mn(II) complex being able to bind O_2 (step (2)). The involvement of the Mn(II)(TPP)(O_2) complex is supported by the observed inhibition of styrene oxidation upon addition of pyridine (Table 1). It is well known that Mn(II)-porphyrins can bind only one ligand,because in five-coordinated complexes, the metal ion is displaced from the porphyrin plane towards the ligand[20]. Thus, pyridine competes very efficiently with dioxygen for coordination to Mn(II)(TPP) since it has been shown that the affinity for O_2 is far less than that for nitrogenous ligands[14]. This explains why one observed by visible spectroscopy high concentrations of Mn(II)(TPP)(Py) during the oxidation of styrene by the biphasic system in the presence of pyridine. Since dioxygen cannot bind to the metal ion trans to pyridine, only a very low part of the manganese porphyrin acts as a catalyst for the activation of dioxygen under these conditions. The oxidizing species could derive from a one-electron reduction of the Mn(II)(TPP)(O_2) complex (step (3)) and could have been either a Mn(III)-peroxo complex or a Mn(V)-oxo complex after cleavage of the O-O bond[21]. Whatever the structure of its active species may be, the Mn-O_2-ascorbate system exhibits properties very similar to those of the previously described Mn(TPP)(Cl)-O_2-H_2-Pt system (same regioselectivity for olefin epoxidation and similar order of reactivity of olefins)[6]. In that regard, it is noteworthy that the characteristics of these systems are very different from those of the Mn(TPP)(Cl)-O_2-NR_4BH_4 system[5b] which was described to oxidize monosubstituted olefins to the corresponding methylketones. Actually we found no methylketone formation upon oxidation of styrene, hex-1-ene and 6-phenoxy-hex-1-ene by the Mn-O_2-ascorbate system.

The major problem of the Mn(TPP)(Cl)-O_2-ascorbate system, in its present form, is its low yields of oxidation products based on the consumed reducing agent. Actually, sodium ascorbate is not only consumed for the formation of the active oxidizing species but also by reaction with O_2 itself and with the oxidizing species (step (5) of scheme 3). The above results could be explained by a competition at the active oxidizing species level between substrate and ascorbate itself (step (4) and (5)). As this active species is oxidizing enough to activate alkanes, it should be easily reduced by ascorbate itself. This active species is thus mainly consumed by reduction by

Scheme 3 : Proposed mechanism for substrate oxidation by the Mn(TPP)(Cl)-O_2-ascorbate system



ascorbate, only a very low part of it being used for substrate oxidation. This is a general problem for chemical models of monooxygenases which must produce a highly oxidizing species in a medium where high concentrations of a reducing agent are required for reductive dioxygen activation. Despite this problem which limits presently both the rates of substrate oxidation and the yields of oxidized products based on the reducing agent, the above described Mn(TPP)(Cl)-O_2-ascorbate system is interesting at least from two points of view. First, it oxidizes alkanes and olefins in very mild and simple conditions (room temperature, pH 8.5), which are close to those used for monooxygenases. Second, it leads to a completely regioselective oxidation of olefins with the exclusive formation of epoxides, differing in that point with cytochromes P-450 and most of their metalloporphyrins based models. It would be very interesting to determine the nature of the oxidizing species which does not seem to be a Mn(V) = O complex, responsible for these reactions.

ACKNOWLEDGMENTS

We are grateful to J. Leclaire for the synthesis of 6-phenoxy-hex-1-ene and products derived from its oxidation, 6-phenoxy-hex-1-ene oxide, 6-phenoxy-hex-1-en -3-ol, 6-phenoxy-hex-1-en-3-one and 6-phenoxy-hexanal.

EXPERIMENTAL SECTION

Materials. All the substrates used for this study were commercial reagent grade unless otherwise stated and were purified by distillation, column chromatography, or recrystallization. Styrene, cyclohexene, cyclohexane, heptane, toluene, methylcyclohexane and anisole were purchased from Prolabo (France). Hex-1-ene, cis- and trans-hex-2-ene, 2,3-dimethyl-but-2-ene were obtained from Fluka, cis- and trans-stilbene from Aldrich. 6-phenoxy-hex-1-ene was prepared by reaction of 6-bromo-hex-1-ene (from Fluka) with an excess of sodium phenate in DMSO (24 h reflux), extracted into hexane and distilled (75 % yield), bp 69°C (0.2 mm)[16,22]. The elemental analysis and the spectroscopic characteristics of this product is in agreement with the indicated structure[16,22].

The products derived from the oxidation of the substrates were generally commercial samples. Phenol, benzyl alcohol, 1-methylcyclohexanol, 2-methylcyclohexanols, cyclohexanone, benzaldehyde, 2-, 3-, 4-methylcyclohexanone were obtained from Prolabo, cis- and trans-hex-2-en-1-ol, cyclohexenol, hex-1-en-3-one, cyclohexenone from Aldrich, cis- and trans-hex-2-en-4-ol, phenylacetaldehyde, hexanal, heptanols and heptanones from Fluka, cyclohexanol and 4-methylcyclohexanols from Touzart et Matignon, a mixture of cis- and trans-3-methylcyclohexanol from Rhone Poulenc and hex-1-en-3-ol from Janssen. Styrene oxide was purchased from Fluka, trans-stilbene oxide and cyclohexene oxide from Aldrich. The other epoxides were synthesized from the corresponding alkenes with m-chloroperbenzoic acid by a standard procedure[23]. 2,3-dimethyl-but-2-ene oxide, bp 90°C (lit[24] bp 89-91°C), hex-1-ene oxide bp 117°C (lit[25] 116-119°C), cis-stilbene oxide, mp 38°C (lit[23] mp 37°C), cis-hex-2-ene oxide, bp 108°C (lit[26] 108°C), trans-hex-2-ene oxide bp 112°C (lit[26] 113°C). The oxidation products of 6-phenoxy-hex-1-ene, 6-phenoxy-hex-1-ene oxide, 6-phenoxy-hexanal, 6-phenoxy-hex-1-en-3-ol and 6-phenoxy-hex-1-en-3-one were synthesized according to classical procedures ([23,27,28] respectively) and gave satisfactory elemental analysis, ^1H NMR and mass spectra[16] in agreement with the indicated structures. Trioctylmethylammonium chloride was obtained from Fluka and sodium ascorbate from Sigma. Tetraphenylporphyrinato manganese (III) chloride[29] and iodosylbenzene[30] were prepared as previously described.

Procedure for the oxidation of substrates by the biphasic system. The oxidation of alkenes and alkanes by dioxygen catalyzed by a manganese porphyrin was carried out under the following conditions. 5 μmol of Mn(TPP)(Cl) were dissolved into a mixture of benzene (1 ml) and substrate (1 ml). This solution was added to 2 ml of a 1M Tris-HCl aqueous buffer, containing 10 μmol of trioctylmethylammonium chloride (TOMA), in a glass tube capped with a septum. 5 μmol of an internal standard were added in order to determine the yields of the products. Dioxygen was then slowly bubbled through the biphasic system for at least 10 min. The reaction was starting by adding 500 μmol of sodium ascorbate and stirring the system under 1 atm of dioxygen at room temperature (20°C). Every 2 hours, 500 μmol of ascorbate were added. The organic phase was analyzed, in one hand, by visible spectroscopy, in an other hand by g.l.c. and mass spectrometry.

The competition experiments were carried out as described above with 0.5 ml of each substrate in 1 ml of benzene for the organic phase.

Procedure for the oxidation of substrates by the Mn(TPP)-C_6H_5IO system. In a glass tube capped with a septum 5 μmol of Mn(TPP)(Cl) were dissolved in 1 ml of benzene and 1 ml of the substrate. Argon, for anaerobic reactions, or dioxygen were bubbled through the solution for at least 15 min. After addition of 25 μmol of iodosylbenzene, the solution was stirred at room temperature under 1 atm of argon or dioxygen. The solution turned brown indicating the presence of the $[(TPP)Mn^{IV}(Cl)(OIPh)]_2O$ complex, in addition to the Mn(III)(TPP)(Cl) complex. Indeed, the visible spectrum of the solution exhibited two bands, at λ= 421 nm and λ= 476 nm. After c.a 2 h, when all the iodosylbenzene had been consumed, as indicated by the disappearance of the brown color and the formation of the green color of Mn(III)(TPP), an internal standard was added. The mixture was then analyzed by g.l.c. and mass spectrometry.

Physical measurements. For both systems, the manganese porphyrin catalyst was studied by visible spectroscopy of the organic phase, using an AMINCO DW2 Spectrophotometer. The spectra have shown the presence of the Mn(III)(TPP), λmax=476 nm and Mn(II)(TPP), λmax=447 nm complexes for the biphasic system and Mn(III)(TPP) and $[(TPP)Mn^{IV}(Cl)(OIPh)]_2O$ λmax=421 nm[12c,d] complexes, for the C_6H_5IO-dependent system.

The formation of oxidation products in both oxidizing systems was followed by g.l.c. with an Intersmat IG 120 FL equipped with a hydrogen flame ionization detector. The glass columns used for this study were packed with the following materials : 5 % W/W OV 210 on gas chrom Q for methylcyclohexane, 5 % W/W Carbowax on Anachrom SD for styrene, toluene and anisole, 5 % W/W FFAP on chromosorb WAW for the other substrates. For 6-phenoxy-hex-1-ene a fused silica capillary column packed with CPSil was used. The carrier gas was N_2. For combined gas chromatography-mass spectrometry, a Riber R 1010 mass spectrometer and a PDP 8 computer were coupled with a Girdel chromatograph. The temperature of the 3 % SE 52 glass column increased from 80 to 250°C at a rate of 5°C per min, the carrier gas was helium at a pressure of 1 Bar. The retention times and the mass spectra of the oxidation products were compared with those of authentic samples. We have not tried to separate by g.l.c. the cis- and trans-isomers of 2-, 3-, 4-methylcyclohexanols and of secondary allylic alcohols derived from cis- and trans-hex-2-ene.

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