

Oxidations catalyzed by stable metallo-tetraaryl porphyrins under aqueous-organic two-phase conditions

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Abstract - Factors ruling the epoxidation of internal and of α -olefins, catalyzed by chemically stable Mn(III)tetraaryl porphyrins and promoted by HOCl and/or ClO⁻ and by 30% H₂O₂, are investigated in order to find conditions for large scale practical application. Reactions are carried out in CH₂Cl₂-H₂O at 0°C, and are greatly enhanced by the presence of lipophilic imidazoles or pyridines as axial ligands on the complexed metal. Epoxidation rates and porphyrin stabilities are largely influenced by the pH of the aqueous phase, by the ligand/porphyrin ratio (L/P), and (for HOCl/ClO⁻ promoted reactions) by the presence of a phase-transfer catalyst. The association constants (K_1 , K_2) between Mn(III) porphyrins and the axial ligands have been evaluated in order to rationalize the effect of L/P's on the reaction rates. Imidazole or pyridine "tailed" Mn-porphyrins are very efficient catalysts. Reactions promoted by H₂O₂ are strongly accelerated by lipophilic axial ligands and carboxylic acids, both in equimolecular amounts with respect to the porphyrin.

INTRODUCTION

Metal complexes of synthetic tetraaryl porphyrins, especially Mn(III) and Fe(III) complexes mimicking the biological activity of cytochrome P-450, are efficient catalysts for the epoxidation of olefins and for the hydroxylation of saturated hydrocarbons promoted by several oxidants (ref. 1-4). Oxygenations catalyzed by Mn(III) tetraaryl porphyrins carried out with NaOCl or H₂O₂ under two-phase conditions arouse a special interest from the preparative point of view (ref. 1-7). Reaction rates are greatly enhanced by the presence of heterocyclic bases (imidazoles, pyridines) as electron donating axial ligands coordinated to the metal centre and, in the case of NaOCl, also by a quaternary salt (Q⁺X⁻) as phase-transfer catalyst (ref. 1-4,6,7).

A major drawback is the oxidative demolition of both the porphyrin catalyst (P) and the axial ligand (L), which occur contemporaneously to the substrate oxygenation (ref. 8). These reactions are more relevant for poorly reactive substrates. Other factors, such as the pH of the aqueous phase (ref. 9, 10) and the L/P ratio, make the situation even more complicate.

The availability of a series of porphyrins which are particularly resistant to the oxidative demolition (ref. 10, 11) and the use of lipophilic axial ligands (ref. 11) allowed to define the conditions for efficient large scale epoxidations.

OLEFIN EPOXIDATION WITH NaOCl

In order to get a deeper insight into the effects of aryl substituents on the chemical stability of metallo-tetraaryl porphyrins, a series of Mn(III)porphyrins 1-8 (Fig. 1) has been studied. Catalysts 1-3, combining the presence of electron-withdrawing substituents with the steric protection of the metal centre, turned out to be particularly resistant to the oxidizing agents (ref. 10, 11). If one of these factors is absent, as in 4-8, the chemical stability of porphyrins is strongly diminished.

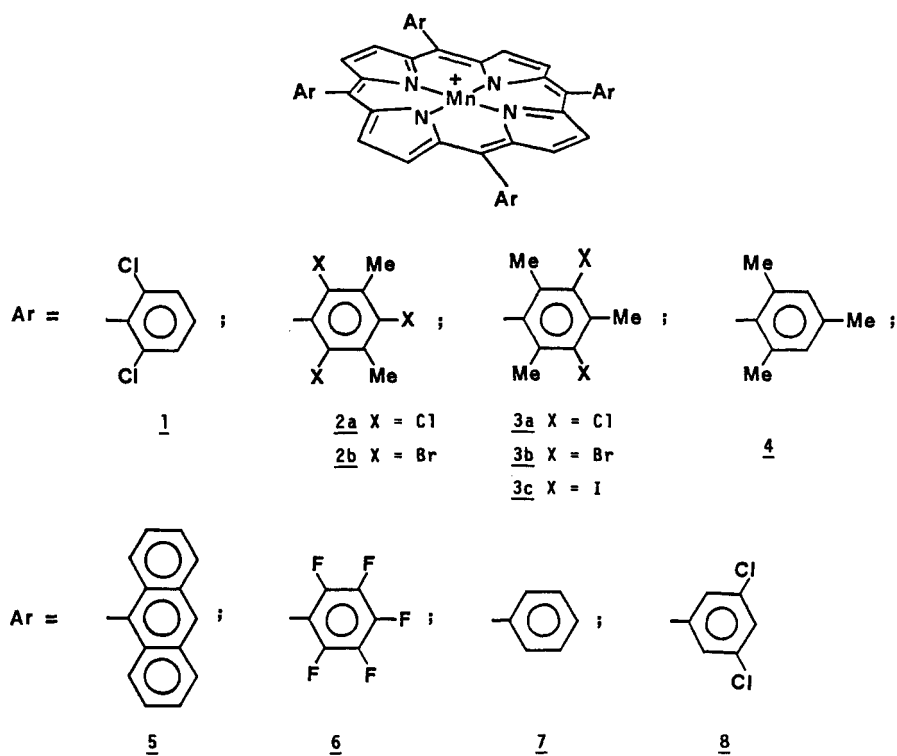


Fig. 1. Mn(III)-tetraaryl porphyrins.

Cyclooctene and 1-dodecene were used as model substrates for most reactions. Oxidations were carried out at 0 and 25°C with 0.35 M NaOCl in $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$, with molar ratios Mn(III)-porphyrin:olefin:oxidant = 1:200:700, and with axial ligand and quaternary onium salt in the range 0-25 and 0-10 mol equiv, respectively (ref. 8, 11). Imidazole 9 and pyridines 10 and 11 were the lipophilic axial ligands (Fig. 2).

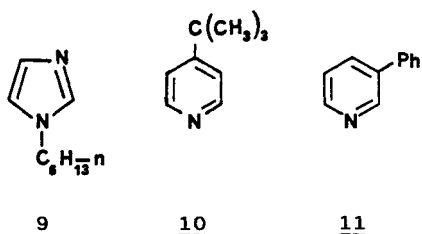


Fig. 2. Lipophilic axial ligands.

It was found (ref. 9-11) that the epoxidation rates progressively increase by lowering the pH of the aqueous NaOCl solution (12.7). Below pH 9.5 the concomitant olefin chlorination becomes unacceptably high. Best pH's are in the 9.5-10.5 range. Under these conditions significant amounts of HOCl (pKa = 7.54) are extracted from the aqueous phase into CH_2Cl_2 , where the reaction occurs. HOCl is now the oxidizing species (Fig. 3), so that a quaternary onium salt for transferring ClO^- into the organic phase is no more necessary (Fig. 4) (ref. 9).

In the NaOCl promoted epoxidations catalyzed by Mn(III)-porphyrins it has been suggested that the reaction intermediate is a high valent oxomanganese complex 13 expressed formally in a +5 oxidation state (ref. 1-4). Its formation from 12 requires electron-donation to the metal by a coordinated nitrogen base. When HOCl is the oxidizing species, the positive charge on the oxygen is the driving force for the conversion of 17 into 16. The reaction is also favoured by electron donation from the axial ligand, which can be now omitted (Fig. 3).

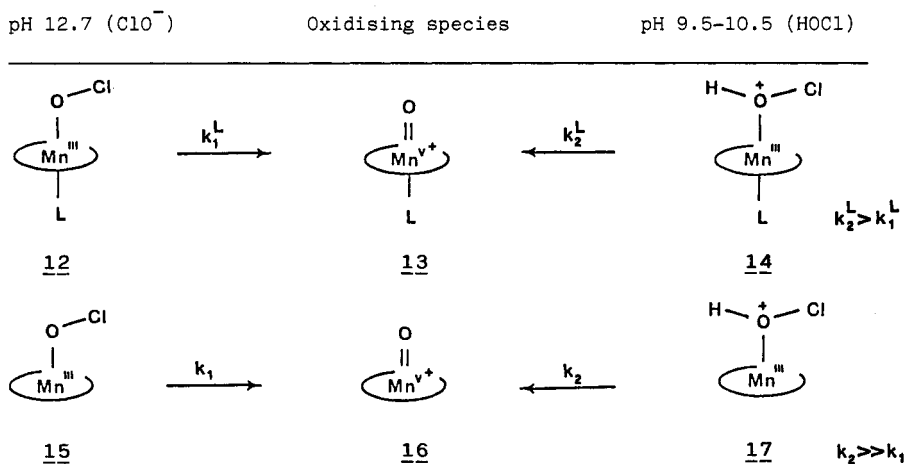
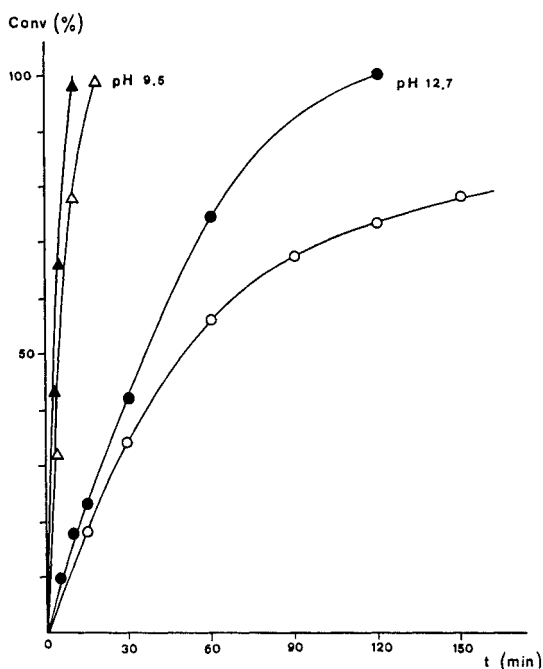
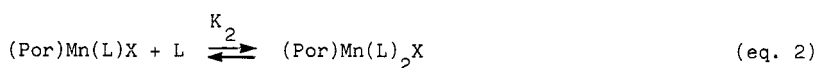


Fig. 3. Formation of oxomanganese complexes.

Fig. 4. Influence of pH on the oxidation of cyclooctene catalyzed by Mn-porphyrin 7 and 3-methyl pyridine at 25°C: presence (full symbols), absence (empty symbols) of phase-transfer catalyst.

Both the axial ligand and the quaternary salt play an intriguing role in the epoxidations, which can be accelerated, slowed down or even inhibited by them. In the equilibria expressed by eq. 1-3, K_2 is always higher than K_1 :



$$\beta_2 = K_1 K_2 \quad (\text{eq. 3})$$

e.g., for $(\text{Por})\text{MnX} = \underline{1}$ and $\text{L} = \text{N-hexyl imidazole } \underline{9}$, K_1 and β_2 values measured following the Walker's method (ref. 12), are $1.18 \pm 0.2 \times 10^3 \text{ M}^{-1}$ and $8.91 \pm 0.25 \times 10^6 \text{ M}^{-2}$, corresponding to

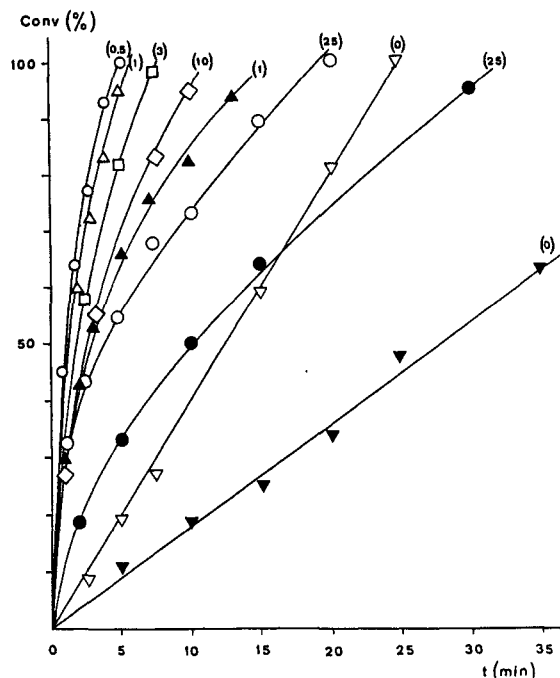


Fig. 5. Influence of ligand/porphyrin ratio (L/P) on the epoxidation of cyclooctene catalyzed by Mn-porphyrin 1 and N-hexyl imidazole 9 at 0°C: pH 9.5 (empty symbols) pH 10.5 (full symbols); L/P in parenthesis

a K_2/K_1 ratio of about 6.5. As a consequence the maximum amount of the mono-ligated species $(\text{Por})\text{Mn}(\text{L})\text{X}$, calculated from eq. 4, occurs at $L/P = 0.30$ (ref. 8).

$$[(\text{Por})\text{Mn}(\text{L})\text{X}] = \frac{K_1 [\text{L}] [(\text{Por})\text{MnX}]}{1 + K_1 [\text{L}] + \beta_2 [\text{L}]^2} \quad (\text{eq. 4})$$

$$[(\text{Por})\text{MnX}] = \text{Mn-porphyrin employed}$$

As it is shown in Fig. 5, the maximum rate for the epoxidation of cyclooctene is found for $L/P = 0.5$, which means that the mono-ligated species $(\text{Por})\text{Mn}(\text{L})\text{X}$, $\text{X} = \text{HOCl}$, is by far the most reactive among the species involved in eq. 1,2.

TABLE 1. Degradation of Mn-porphyrins during the epoxidation of cyclooctene.

Porphyrin	Percentage of residual Mn-porphyrin (reaction time, min.)		
	A	B	C
<u>1</u>	100 (120)	100 (120)	100 (300)
<u>2a</u>	100 (120)	100 (120)	100 (300)
<u>2b</u>	100 (120)	100 (120)	100 (300)
<u>3a</u>	—	100 (60)	—
<u>3b</u>	—	96 (60)	—
<u>3c</u>	—	96 (60)	—
<u>4</u>	91 (10) 62 (30)	100 (60)	100 (300)
<u>5</u>	80 (10) 50 (20)	—	—
<u>6</u>	41 (5) 16 (10)	73 (10) 51 (40)	70 (300)
<u>7</u>	24 (5) 9 (10)	57 (10) 28 (40)	64 (300)
<u>8</u>	40 (5) 0 (15)	70 (60)	20 (300)

Reaction conditions: A = pH 9.5, 0°C, $L/P = 25$, $Q^+X^-/P = 10$
 B = pH 10.5, 0°C, $L/P = 1$, $Q^+X^-/P = 0$
 C = pH 10.5, 0°C, $L/P = 0$, $Q^+X^-/P = 0$

Reaction rates progressively diminish by increasing the L/P ratio, but they are even more slowed down in the absence of the axial ligand. The latter must be used in much higher amounts in the case of α -olefins (L/P = 10-25), otherwise the reaction stops, or becomes extremely slow, towards the end. This is due to the oxidation of the axial ligand, a competitive reaction which is particularly important with poorly reactive substrates, like α -olefins. Imidazole 9 is entirely demolished, whereas pyridines 10 and 11 are first converted into the corresponding N-oxides, which can also act as efficient axial ligands (ref. 8).

Both the axial ligand and the quaternary salt strongly decrease the chemical stability of Mn-porphyrins. This is shown in Table 1, which reports the data on the degradation of Mn-porphyrins 1-8 during the epoxidation of cyclooctene, carried out with L/P = 25 and $Q^+X^- = 10$ (ref. 11), and with L/P = 0-1 and $Q^+X^-/P = 0$ (ref. 8), respectively.

As shown in Fig. 5, internal olefins are oxidized even in the absence of the axial ligand, provided that particularly robust porphyrins are used. The phase-transfer catalyst must be also absent, otherwise it inhibits the reaction. These conditions are the best ones for the chemical stability of porphyrins, since also 4 can be used without appreciable demolition, and up to 60,000 turnovers are realized with very high selectivities (ref. 8).

In order to get more efficient catalysts, imidazole or pyridine "tailed" Mn-porphyrins 18-21 have been prepared (ref. 8, 9) (Fig. 6).

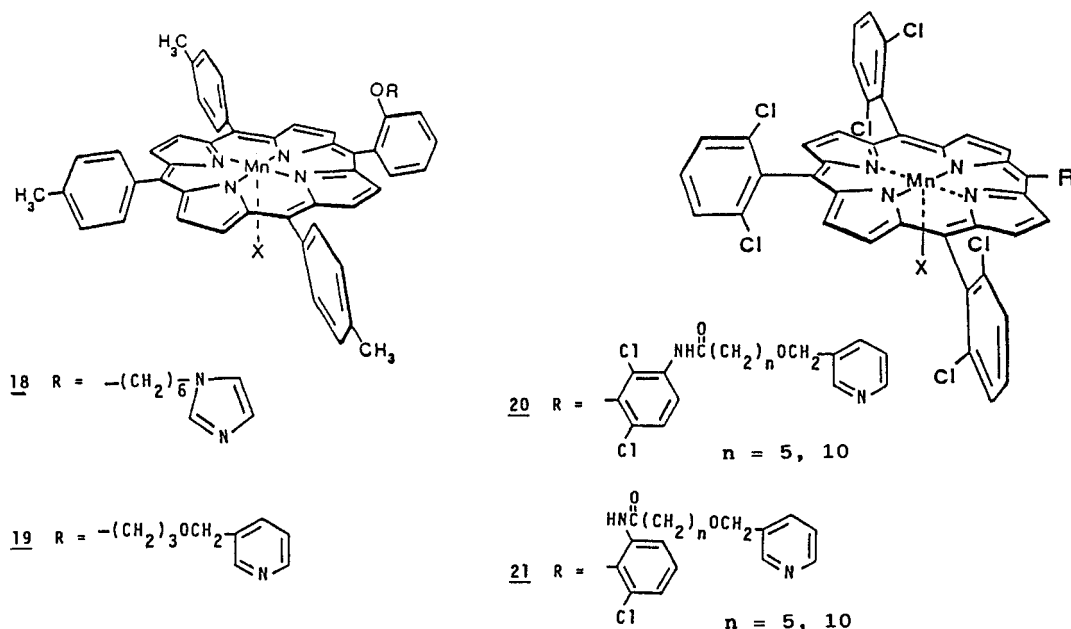


Fig. 6. "Tailed" Mn-porphyrins.

Porphyrins 18 and 19 catalyze the epoxidation of internal olefins in a few min and with very high selectivity, but they are demolished during the reaction. Better results were obtained with the more robust terms 20 and 21 (especially with 20, $n = 5$). The behaviour of the latter is very similar to that shown by 1 in the reactions carried out with equimolecular amounts of ligand and porphyrin. Unfortunately, a slow demolition of the "tail" is unavoidable, particularly in the epoxidation of α -olefins.

OLEFIN EPOXIDATION WITH H_2O_2

Mansuy has described the H_2O_2 olefin epoxidation catalyzed by Mn-porphyrins and carried out under $CH_2Cl_2-H_2O$ two-phase conditions, or in homogeneous phase in the presence of CH_2CN as a co-solvent (ref. 4, 13). Required conditions are the use of robust Mn-porphyrins, as 1, and of a large excess of imidazole as axial ligand.

We have found that under two-phase conditions reactions are extraordinarily accelerated by addition of 1-4 mol equiv of a carboxylic acid with respect to the porphyrin (e.g. acetic, benzoic, *m*-chlorobenzoic acid, etc.). The pH of the aqueous phase is kept at 4.5-5.0, and a small excess of 30% H₂O₂ is required. As for the HOCl promoted oxidations, very small amounts of $\frac{9}{9}$ (L/P = 0.5-1.0) must be also added. With 0.5% of Mn-porphyrins with respect to the olefin reactions are completed at 0°C in about 10 and 20 min for internal and α -olefins, respectively. Further lowering of pH slows down or inhibits the reaction, whereas higher pH's lead to a fast decomposition of H₂O₂ (ref. 8).

The present state of knowledge does not allow any reasonable definition of the reaction mechanism, but it is important to emphasize that in the absence of the Mn-porphyrin no reaction occurs, and that catalytic activity of carboxylic acid roughly increases by increasing its lipophilicity (ArCOOH > CH₃COOH >> HCOOH), thus indicating that fast formation of peroxy acids in the organic phase might be involved.

CONCLUSION

Both olefin epoxidations by HOCl and by 30% H₂O₂, carried out under aqueous-organic two-phase conditions and catalyzed by chemically stable Mn(III)porphyrins, can be easily extended for large scale applications. In the case of internal olefins, reactions promoted by HOCl do not necessarily require the presence of the axial ligand, thus not only allowing a simpler methodology, but also increasing the chemical stability of the porphyrin. Unfortunately, under these same conditions, the oxidation of α -olefins is very slow, and needs the presence of the axial ligand. The latter is also oxidized together with the olefin, which is a disappointing drawback. Reactions promoted by 30% H₂O₂-ArCOOH can be equally applied to internal and to α -olefins, although at least 1 mol² equiv of axial ligand with respect to the porphyrin must be used. Since small amounts of solvent and the inexpensive and not polluting H₂O₂ are required, this methodology displays a particular interest, at least for α -olefin epoxidation.

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