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Influence of Quaternary Onium Salts, Crown Ethers and Cryptands on Olefin Epoxidations Promoted by $HOCl/ClO^-$ in the Presence of Mn(III)-tetrakis(2,6-dichlorophenyl)porphyrin Chloride

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Abstract. Reaction rates of alkene epoxidations, promoted by aqueous NaOCl and catalyzed by Mn(III)-tetrakis(2,6-dichlorophenyl)porphyrin chloride **1** (P) in the presence of a lipophilic axial ligand (L) (e.g. *N*-hexylimidazole) and carried out under H_2O/CH_2Cl_2 two phase conditions at 0°C, are strongly enhanced by lowering the pH of the aqueous phase from 12.7 to 9.5. Under these conditions, a further relevant increase in the reaction rates can be achieved by adding phase-transfer catalysts (PT), e.g. quaternary ammonium salt **3**, lipophilic crown ether **4** or cryptand **5**, provided that the amount of L is very small (L/P = 1 for very reactive alkenes, e.g. cyclooctene, and 10 for poorly reactive ones, e.g. 1-dodecene). In the case of cyclooctene epoxidation, the use of 0.006–0.03 mol. equiv. of PT completes the reaction in 1–10 min., the initial rates being up to 600 turnovers/min. with $(2.2.2,C_{10})$ cryptand. In the absence of the axial ligand, the quaternary ammonium salt **3** and cryptand **5** show an inhibitory effect. Such an effect is due to the formation of the poorly reactive Mn(P)Cl species, by Cl^- extraction to the organic phase. However, dibenzo crown ether **4** does not show this effect. In the presence of **4**, and with L/P = 1, the 1-dodecene epoxidation reaches 94% in 1 min. The 'unique' behavior of crown ethers can be explained by their ineffectiveness in extracting alkali chlorides, providing a very low concentration of Cl^- in the organic phase and thus avoiding the Mn(III)-porphyrin deactivation.

Key words. Mn(III)-tetraarylporphyrin, olefin epoxidations, $HOCl/ClO^-$, two-phase conditions, influence of phase-transfer catalysts, effect of Cl^-, competitive extraction of Cl^- and ClO^-, quaternary onium salts, crown ethers, cryptands.

1. Introduction

The use of synthetic metalloporphyrins as biomimetic catalysts in organic syntheses has aroused growing interest in recent years [1]. In hydrocarbon oxygenations, a great effort has been made to combine the catalytic efficiency and the chemical stability of the porphyrin. However, in only a few cases have satisfactory turnover numbers been achieved, even when particularly robust porphyrins were used [2, 3].

Aqueous sodium hypochlorite is one of the most versatile of a great variety of oxidants used as single oxygen atom donors. It was first used by Tabushi for alkene

This paper is dedicated to the memory of the late Dr C. J. Pedersen.
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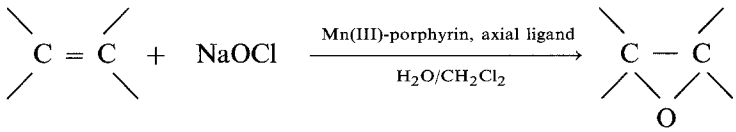
epoxidations under aqueous/organic phase-transfer conditions [4]. Later on, Meunier [5] increased the reaction rates by adding huge amounts of pyridines or imidazoles as axial ligands (Equation 1).



(1)

We have found [2a, b, 6] that a further strong enhancement of the reaction rates is obtained by lowering the pH of the NaOCl aqueous phase from 12.7 to 9.5. At pH lower than 9.5 the concentration of Cl_2 increases [7] so that alkene chlorination becomes unacceptably high [2a, b, 6].

At a pH buffered in the range 9.5–10.5 a significant amount of HOCl ($pK_a = 7.54$) is extracted from the aqueous phase into CH_2Cl_2 where the reaction occurs. HOCl becomes the effective oxygen donor, hence the presence of a phase-transfer catalyst is not strictly necessary [2a, b, 6]. The use of lipophilic axial ligands, such as *N*-hexylimidazole or 4-*tert*-butylpyridine, allowed us to drastically reduce the ligand/porphyrin ratio, and this is very important from the practical point of view [2a, b]. With unhindered electron-rich alkenes, e.g. *cis*-cyclooctene, the reaction proceeds even in the absence of an axial ligand; under such conditions 100 000 overall turnovers were reached without any appreciable degradation of the metalloporphyrin [8]. The results obtained using chemically robust porphyrins with reactive substrates indicate that this catalytic system could be employed on a large scale.

However, in spite of these improvements several aspects still remained unclear:

(i) Other authors [9] found only modest increases of reaction rates by lowering the pH of the NaOCl aqueous phase when working with an excess of imidazole or pyridine with respect to the porphyrin in the presence of quaternary ammonium salts.

(ii) Our preliminary data [2a] indicated that, in the absence of axial ligands, quaternary ammonium salts had an inhibiting effect on the reactions, even at low pH and with reactive substrates.

(iii) Using dibenzo-18-crown-6 as the phase-transfer catalyst, we had found [10], at pH 9.5–10.5 and with very small amounts of axial ligand, that poorly reactive alkenes could be epoxidized in a few minutes and with good selectivity. Under the same conditions quaternary ammonium salts once more showed an inhibiting effect.

These aspects prompted us to further investigate alkene epoxidations promoted by $HOCl/ClO^-$ and catalyzed by chemically robust Mn(III)-porphyrins. Particular attention was given to the influence of quaternary ammonium salts, crown ethers and cryptands [11] on reaction rates, both in the presence and absence of the axial ligand.

2. Experimental

2.1. GENERAL

UV–vis spectra were obtained with a Perkin-Elmer Lambda 6 spectrophotometer. Potentiometric titrations were performed with a Metrohm 670 Titroprocessor

equipped with a Metrohm 665 Dosimat. GC analyses were performed on a Varian model 3700 gas chromatograph flame ionization instrument (20×0.125 in OV-101-5% on CHP 100–125 mesh column), with VISTA CDS 401 Varian chromatography data system. Oxidations were carried out in a 10 mL flask equipped with a Teflon-lined screw cap and magnetic stirrer, thermostatted at 0 ± 0.2°C with circulating ethanol by a Colora Misstechnick GMBH Lorch/Württ cryostat. Stirring speed was maintained at 1300 ± 50 rpm. The molarity of the NaOCl aqueous solution was determined by iodometric titration and its pH was measured with a Orion pH meter model SH 250 with pH electrode Model 91–03 (semimicro glass body). The alkenes and the phase transfer catalysts were of the highest purity commercially available and were used without further purification. Mn(III)-tetrakis(2,6-dichlorophenyl)porphyrin chloride **1** was synthesized according to a published procedure [12]. Pyrrole and boron trifluoride etherate were distilled before use. CH_2Cl_2 was distilled from $CaCl_2$ when used as solvent in the synthesis of the porphyrin.

2.2. GENERAL PROCEDURE OF ALKENE EPOXIDATION

The flask was charged with: (a) 1 mL of CH_2Cl_2 solution containing 0.5 mmol (S/P = 200) or 2.5 mmol (S/P = 1000) of substrate and 0.25 mmol (or 1.25 mmol) of decane as internal standard; (b) 1 mL of 0.0025M CH_2Cl_2 solution of Mn(III)-porphyrin **1**; (c) the required amount of *N*-hexylimidazole was added with a microsyringe; 10 μL (0.25M) and 50 μL (1.25M) of CH_2Cl_2 solutions for L/P = 1 and 25, respectively; (d) 50 μL of a 0.3M CH_2Cl_2 solution of phase-transfer catalyst (PT/P = 6). Aqueous 0.40M NaOCl solution (4.4 mL), buffered at pH 10.5 or 9.5 by adding 130 mg or 265 mg of solid $NaHCO_3$ to 20 mL of NaOCl (initial pH = 12.7), was then layered over the organic phase. The mixture was stirred and samples were taken at different times and analyzed by GC.

2.3. STABILITY OF Mn-PORPHYRINS 1

In the epoxidation experiments, a 50 μL sample of the organic phase was withdrawn before the addition of the ligand and diluted in 5 mL of CH_2Cl_2 (zero time). Samples (50 μL) were withdrawn at different times and diluted in 5 mL of CH_2Cl_2. Mn-porphyrin decomposition was followed by UV-vis spectroscopy in the 350–700 nm range, measuring the percentage decrease of the absorbance at the λ_{max} referred to the sample taken at zero time.

2.4. POTENTIOMETRIC ClO^- AND Cl^- TITRATION OF AQUEOUS NaOCl SOLUTION

(a) Two mL of 0.04 NaOCl was diluted with 20 mL of distilled water, acidified with 10% HNO_3 and titrated with 13.42 mL of 10^{-2}M $AgNO_3$ solution. This corresponds to 0.067M Cl^- initially present.

(b) Two mL of 0.04M NaOCl were diluted with 20 mL of distilled water, acidified with 10% HNO_3, treated with 0.14 g (1.2 mmol) of Na_2SO_3 and titrated with 21.37 mL of 10^{-2}M $AgNO_3$ solution. This corresponds to 0.107M Cl^- derived from the reduction of ClO^- plus the Cl^- initially present. The ClO^- concentration

(0.04M) was given by the difference between these two values. The molarity of ClO^- found by this method corresponds exactly to that obtained by iodometric titration.

2.5. POTENTIOMETRIC TITRATION OF ClO^- AND Cl^- EXTRACTED IN THE CH_2Cl_2 SOLUTION BY PHASE-TRANSFER CATALYSTS 3–5 AT 0°C

Ten mL of 0.4M aqueous NaOCl at pH 12.7 or 9.5 was stirred together with 25 mL of 8.0×10^{-2}M CH_2Cl_2 solution of PT and after 15 min the phases were separated. Two aliquots of 10 mL of the organic layer were poured into about 30 mL of methanol and titrated with 10^{-2}M solution of $AgNO_3$ in the presence and in the absence of the reducing agent, as described above. Results are reported in Table III.

3. Results

Alkene epoxidations were carried out at 0°C under CH_2Cl_2/H_2O two-phase conditions with 0.35–0.7M aqueous NaOCl (OX) at pH = 9.5–12.7 in the presence of Mn(III)-tetrakis(2,6-dichlorophenyl)porphyrin chloride **1** (P) [3a, 12] and with *N*-hexylimidazole **2** as the axial ligand (L). Three commercially available phase-transfer catalysts (PT) were used: tetrabutylammonium hydrogensulphate **3**, dibenzo-18-crown-6 **4**, and (2.2.2,C_{10}) cryptand **5**. *cis*-Cyclooctene and 1-dodecene were used as model substrates (S) of very reactive and poorly reactive alkenes, respectively.

3.1. CYCLOOCTENE EPOXIDATION (TABLE I)

At pH 12.7, 0°C and in the absence of both phase transfer catalyst and axial ligand, only 30% conversion occurs within 90 min. using 5×10^{-3} mol. equiv. of Mn(III)porphyrin **1** (entry 1). The addition of 3×10^{-2} mol. equiv. of quaternary ammonium salt **3** produces only 7% conversion in 1 h (entry 6). In both cases the presence of *N*-hexylimidazole (L/P = 1 and 25, respectively) brings about a modest increase of the reaction rate (51% and 11% conversion, respectively, in 45 min. [13], entries 2, 6, 7).

Lowering the pH of the NaOCl aqueous phase (9.5–10.5) leads to much faster reaction rates [2a, b, 6] and makes the comparison of the different phase transfer catalysts more reliable.

At pH 10.5 and molar ratios P : L : PT : S : OX = 1 : 1 : 6–10 : 200 : 700 reactions are complete in 2–7 min. at 0°C with very high selectivity (entries 9, 10, 13). Cryptand **5** is the most active PT catalyst and, with S/P = 1000, the epoxidation is over in 3 min. (350 turnovers in the first min., entry 17).

The highest rates are observed at pH 9.5 (entries 10, 11) although generally a lower selectivity is obtained. At this pH the difference in efficiency of PT catalysts **3**–**5** becomes more evident with S/P = 1000, the order being **5** ≫ **4**–**3** ≫ no PT (entries 14–16, 18, and Figure 1). In particular, with cryptand **5**, 600 turnovers are obtained in the first min. A comparison of the 18-crown-6 and its dibenzo-derivative **4** (entries 10, 12) highlights the importance of the liphophilicity of PT catalysts.

Table I. Epoxidation od cyclooctene.[a,b]

No.	pH	L/P	PT	PT/P	S/P	OX/P	React. time (min.)	Conv. (%)	Selec. (%)	Turnovers[c] (at 1 min.)	Residual P (%)[d]
1	12.7	–	–	–	200	700	90	30	100	–	100
2	12.7	1	–	–	200	700	45	51	100	–	100
3	10.5	–	–	–	200	700	50	100	90	4	100
4	10.5	1	–	–	200	700	13	97	95	52	100
5	9.5	1	–	–	200	700	7	100	85	66	95
6	12.7	–	**3**	12	200	700	60	7			
7	12.7	25	**3**	6	200	700	45	11			
8	10.5	–	**3**	6	200	700	5[e]	17			
9	10.5	1	**3**	6	200	700	7	100	96	60	100
10	10.5	1	**4**	10	200	700	7	100	100	60	85
11	9.5	1	**4**	6	200	700	2	96	95	94	79
12	10.5	1	18-C-6[f]	10	200	700	20	95	100	48	77
13	10.5	1	**5**	6	200	700	2	100	100	170	70
14	9.5	1	–	–	1000	2000	50	97	92	170	86
15	9.5	1	**3**	6	1000	2000	15	96	90	220	73
16	9.5	1	**4**	6	1000	2000	10	95	90	210	70
17	10.5	1	**5**	6	1000	2000	3	98	93	350	75
18	9.5	1	**5**	6	1000	2000	2	100	85	600	50

[a]In CH_2Cl_2–H_2O, 2 : 5 v/v, 0°C.
[b]S = cyclooctene, P = Mn(III)-porphyrin chloride **1**, L = *N*-hexylimidazole, PT = phase-transfer catalyst, OX = ClO^-/HOCl.
[c]Based on the converted substrate.
[d]At the end of the reaction.
[e]The reaction stops at this time.
[f]18-crown-6.

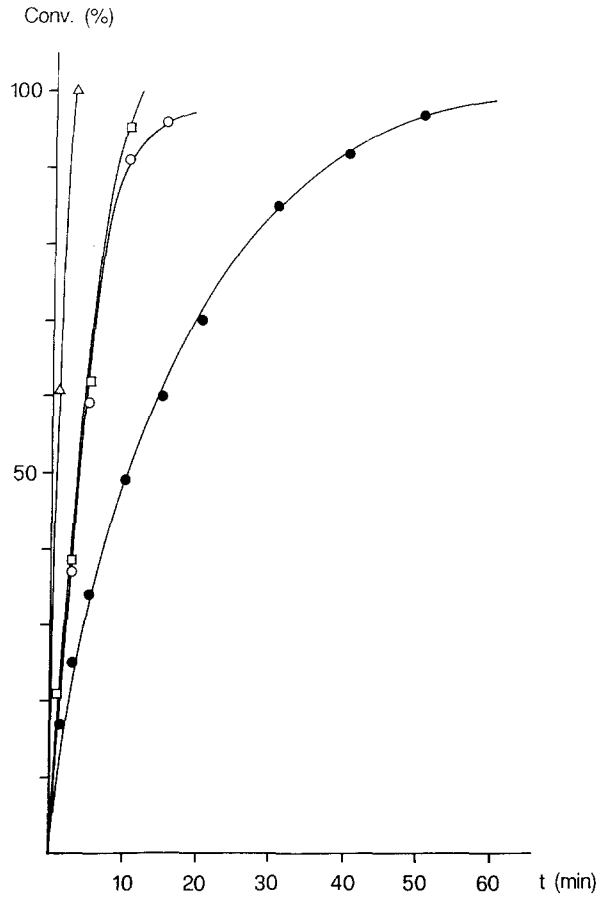


Fig. 1. Influence of phase-transfer catalyst (PT) on the epoxidation of cyclooctene (S) with $HOCl/ClO^-$ (OX), catalyzed by Mn(III)-porphyrin **1** (P) and *N*-hexylimidazole (L) at pH 9.5 and 0°C: absence of PT catalyst (●); $Bu_4N^+ HSO_4^-$ **3** (○); dibenzo-18-crown-6 **4** (□); [2.2.2,C_{10}]cryptand **5** (△). Reagent molar ratio P : L : PT : S : OX = 1 : 1 : 6 : 1000 : 2000.

As previously reported [2a], at pH 9.5 and 10.5 the reactions also proceed in the absence of PT, complete conversion being obtained in 13 and 21 min., respectively (entries 4, 5). In the absence of both axial ligand and PT, the cyclooctene epoxidation is much slower, the reaction being over in 55 min. at pH 10.5 (entry 3). Surprisingly, the addition of the quaternary ammonium salt and cryptand inhibits the reaction (entry 8 and Figure 2). This inhibition is less evident with the crown-ether and complete conversion of cyclooctene is achieved in 70 min. at 0°C, thus the time taken is only slightly longer than that required in the absence of PT.

3.2. 1-DODECENE EPOXIDATION (TABLE II)

At pH = 9.5 in the absence of PT and with molar ratios P : L : S : OX = 1 : 1 : 200 : 700 the reaction is initially very fast, but it suddenly slows down after

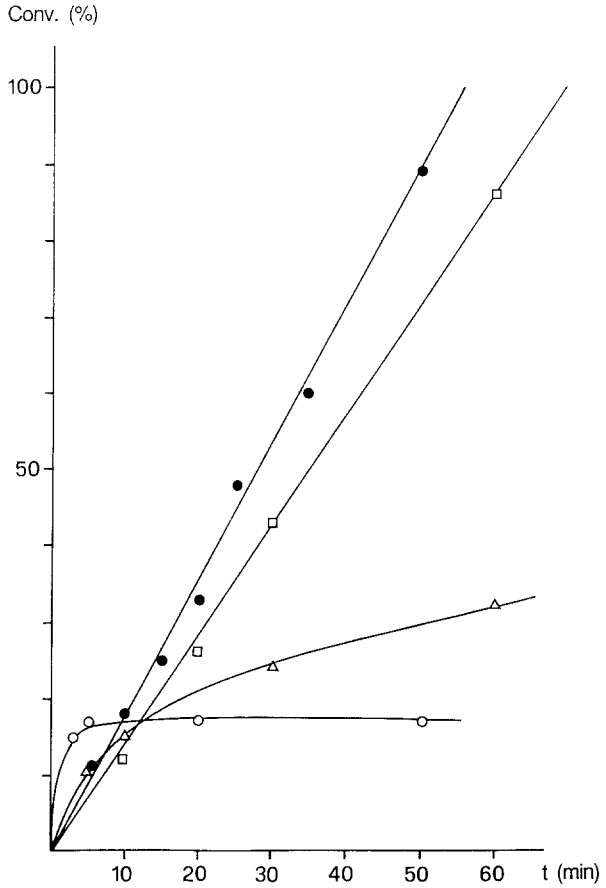


Fig. 2. Influence of phase-transfer catalyst (PT) on the epoxidation of cyclooctene (S) with HOCl/ClO^-(OX), catalyzed by Mn(III)-porphyrin **1** (P) in the absence of the axial ligand at pH 10.5 and 0°C: absence of PT catalyst (●); $Bu_4N^+HSO_4^-$ **3** (○); dibenzo-18-crown-6 **4** (□); [2.2.2,C_{10}] cryptand **5** (△). Reagent molar ratio P : PT : S : OX = 1 : 6 : 200 : 700.

5 min. at about 50% conversion, due to the oxidative destruction of the axial ligand [2a]. As already shown, only an excess of ligand (L/P = 25) allows complete conversion in 5 min. (148 turnovers in the first min.) and good selectivity (entries 1, 2). The catalytic activity decreases on adding the ammonium salt, but with 0.03 mol. equiv. of crown ether **4** 94 and 92% conversion is obtained in 1 and 3 min. at pH 9.5 and 10.5, respectively (188 and 106 turnovers in the first min., entries 3–7). Under these same conditions, cryptand **5** was found less efficient than **4**; however, when L/P = 10, the catalytic efficiency of **4** and **5** is the same and the reaction is nearly complete in 1 min. (entries 8–10 and Figure 3). At pH = 9.5, with **4** and S/P = 1000, 53% conversion is reached in 10 min., with initial rate of 440 turnovers/min. Without PT catalyst, conversion is 33% in 50 min. (entries 11, 12). As previously noted for cyclooctene epoxidation, the absence of the heterocyclic

Table II. Epoxidation of 1-dodecene.[a,b]

No.	pH	L/P	PT	PT/P	S/P	OX/P	React. time (min.)	Conv. (%)	Selec. (%)	Turnovers[c] (at 1 min.)	Residual P (%)[d]
1	9.5	1	–	–	200	700	30	67[e]	90	66	93 (30)
2	9.5	25	–	–	200	700	5	100	89	148	70 (30)
3	10.5	1	**3**	6	200	700	20[f]	49	85	40	75 (30)
4	9.5	1	**3**	6	200	700	1[f]	30	80	60	
5	9.5	10	**3**	6	200	700	1[f]	84	89	168	
6	10.5	1	**4**	6	200	700	3	92	98	106	68 (5)
7	9.5	1	**4**	6	200	700	1	94	100	188	78 (1)
8	9.5	10	**4**	6	200	700	3	96	93	182	
9	10.5	1	**5**	6	200	700	10	81	95	60	75 (10)
10	10.5	10	**5**	6	200	700	1	90	97	180	
11	9.5	1	–	–	1000	2000	50[f]	33	73	140	45 (50)
12	9.5	1	**4**	10	1000	2000	10[f]	53	86	440	0 (10)

[a]In CH_2Cl_2–H_2O, 2 : 5 v/v, 0°C.
[b]S = 1-dodecene, P = Mn(III)-porphyrin chloride **1**, L = *N*-hexylimidazole, PT = phase-transfer catalyst, OX = ClO^-/HOCl.
[c]Based on the converted substrate.
[d]Time (min.) in parentheses.
[e]50% conversion after 5 min.
[f]The reaction stops at this time.

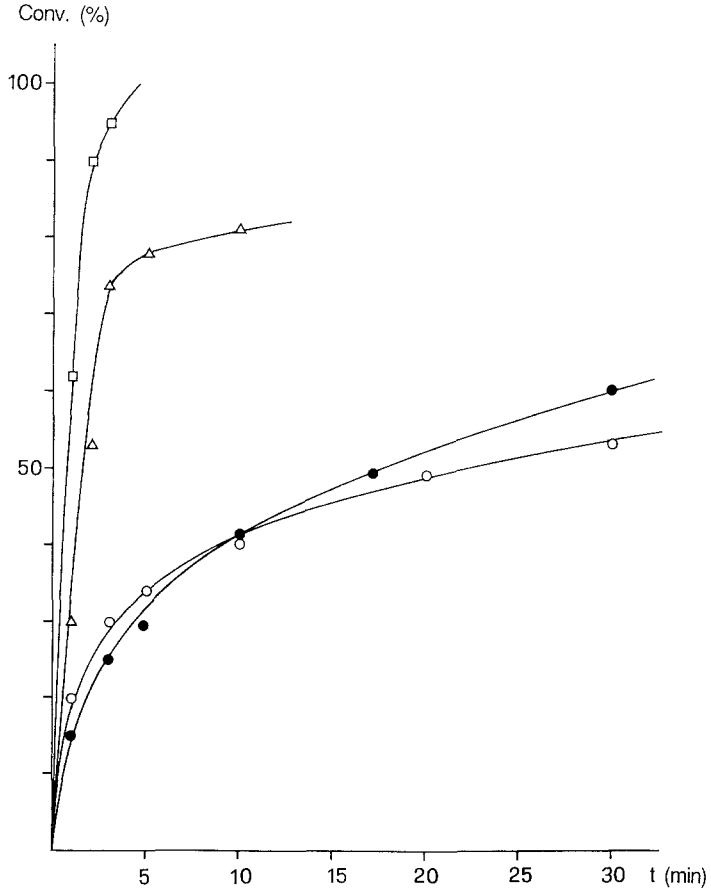


Fig. 3. Influence of phase-transfer catalyst (PT) on the epoxidation of 1-dodecene (S) with $HOCl/ClO^-$ (OX), catalyzed by Mn(III)-porphyrin **1** (P) and *N*-hexylimidazole (L) at pH 10.5 and 0°C: absence of PT catalyst (●); $Bu_4N^+HSO_4^-$ **3** (○); dibenzo-18-crown-6 **4** (□); [2.2.2,C_{10}]cryptand **5**(△). Reagent molar ratio P : L : PT : S : OX = 1 : 1 : 6 : 200 : 700.

nitrogen base causes the reactivity of Mn(III)-porphyrin to be inhibited by all the PT catalysts.

3.3. COMPETITIVE EXTRACTION OF $HOCl/ClO^-$ IN THE ORGANIC PHASE BY PT CATALYSTS 3–5

Extraction experiments were performed by stirring the aqueous NaOCl solution at pH 12.7 and 9.5 at 0°C, with the CH_2Cl_2 solution of PT catalyst **3–5**. After 10 min., two aliquots of the organic phase were titrated potentiometrically, one without and one with Na_2SO_3 as the reducing agent. Titration in the absence of Na_2SO_3 allows the direct determination of the (Cl^-PT^+) complex; titration of the second aliquot after its reduction with Na_2SO_3 gives $HOCl/ClO^-$ and Cl^-. The amount of $HOCl/ClO^-$ is obtained by the difference between the two values. Results are reported in Table III.

Table III. Competitive extraction of $HOCl/ClO^-$ and Cl^- in the organic phase by PT-catalysts **3–5**.[a,b]

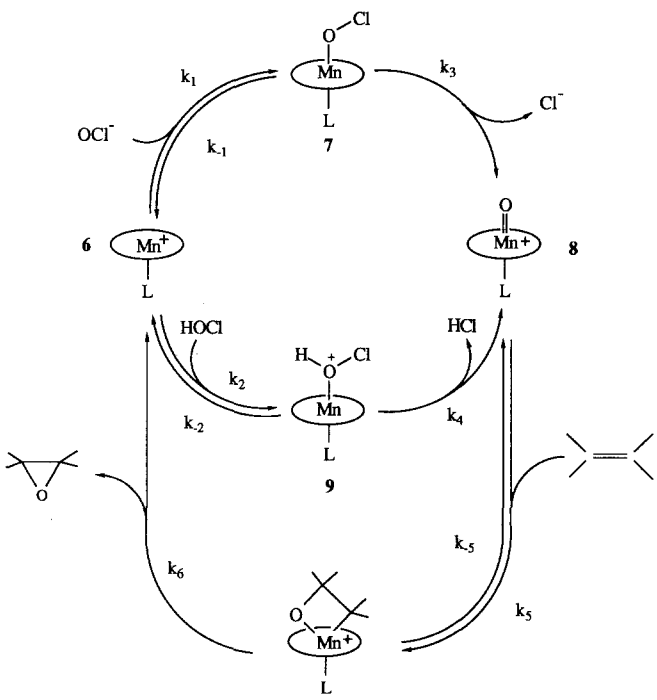
PT[c]	pH	$HOCl/ClO^-$	Cl
3	12.7	70.3	11.6
3	9.5	106.3	20.6
4	9.5	2.5	1.5
5	9.5	117.0	31.5

[a]Ions % with respect to $(PT)^+$.
[b]Values measured after 10 min. stirring at 0°C of the aqueous solution of sodium hypochlorite (0.40M in NaOCl and 0.67M in NaCl) with CH_2Cl_2 (10 : 25 v/v).
[c]8×10^{-3}M in CH_2Cl_2.

4. Discussion

The proposed mechanism for the epoxidation catalyzed by Mn(III)-porphyrins and promoted by NaOCl either at pH = 12.7 or pH = 9.5–10.5 is depicted in Scheme 1.

The formation of the metal-oxene **8**, which is the oxidising species of the catalytic cycle [1], is favored by electron donation of the coordinated nitrogen base. When HOCl is the oxygen donor, the positive charge on the oxygen is the driving force for



Scheme 1

the conversion of **9** into **8**. Also in this case, the presence of the axial ligand improves the reaction rate but it is not really necessary for the reaction to take place [2a].

The role of the axial ligand on the epoxidation rate can be rationalized through equilibria (2) and (3).

$$\mathrm{Mn(P)} + \mathrm{L} \overset{K_1}{\rightleftharpoons} \mathrm{Mn(P)L} \tag{2}$$

$$\mathrm{Mn(P)L} + \mathrm{L} \overset{K_2}{\rightleftharpoons} \mathrm{Mn(P)L_2} \tag{3}$$

$$\beta_2 = K_1 \cdot K_2 \tag{4}$$

The values of K_1 and β_2 are obtained by spectrophotometric measurements [2a, 6d, 14].

The concentration of Mn(P)L, which is by far more active with respect to the non-coordinated and bis-coordinated species Mn(P) and $\mathrm{Mn(P)L_2}$, can be calculated by Equation (5).

$$\mathrm{Mn(P)L} = \frac{K_1[\mathrm{L}][\mathrm{Mn(P)}]_0}{1 + K_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2} \tag{5}$$

When the first derivative of Equation (5) with respect to [L] is equal to zero, $[\mathrm{L}]_{max}$ is obtained from Equation (6). $[\mathrm{L}]_{max}$ is the concentration of the free ligand at the equilibrium at the maximum Mn(P)L concentration.

$$[\mathrm{L}]_{max} = \sqrt{\frac{1}{\beta_2}} \tag{6}$$

Hence the optimum L/P initial ratio can easily be calculated in order to avoid an excess of axial ligand in the reaction medium. In fact, the non-coordinated nitrogen base behaves as a competitive substrate and its oxidation by the metal-oxene **8** is well documented [2a].

In this context phase-transfer catalysts play an intriguing role in the olefin epoxidations catalyzed by Mn(III)-porphyrin **1** and promoted by NaOCl; in fact, depending on the reaction conditions, quaternary ammonium salt and cryptand can either promote or inhibit the reaction, while the crown ether displays a particular behavior.

The epoxidations of cyclooctene and 1-dodecene with the aqueous NaOCl solution buffered at pH 9.5–10.5 indicate that quaternary salt **3** and the lipophilic cryptand **5** increase the reaction rate only if a heterocyclic nitrogen base is also present, the amount required depending on the reactivity of the substrate (L/P = 1 and 25 for cyclooctene and 1-dodecene, respectively; Tables 1 and II and Figure 1). However, in the absence of the axial ligand, the phase-transfer catalysts **3** and **5** show an evident inhibiting effect (Fig. 2).

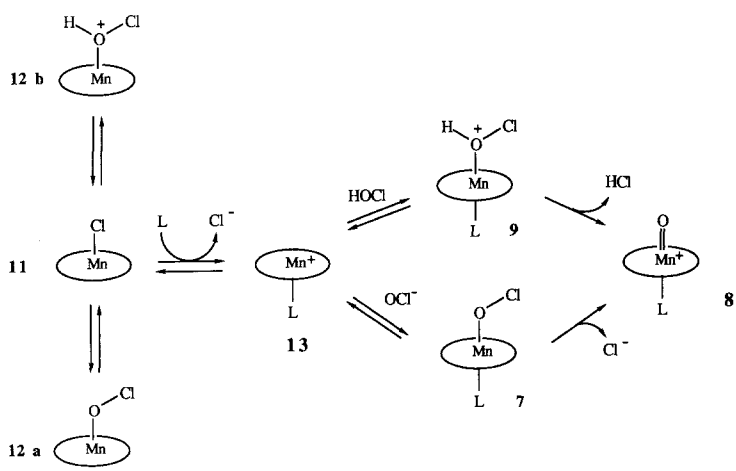
On the other hand, in the presence of the axial ligand (L/P = 1), the crown ether **4** favors both the cyclooctene and 1-dodecene epoxidations, the effect with the former being similar to that of the quaternary salt **3**. With 1-dodecene, the crown-ether **4** is noticeably more effective than cryptand **5**, whereas with the same L/P ratio the quaternary salt **3** again displays an inhibiting effect (Figure 3). Only with L/P = 10 do cryptand **5** and crown ether **4** behave in a similar way (Table II).

The possible reason underlying the intriguing effect of catalysts **3–5** is to be found in the extraction values of Cl^- and ClO^- from NaOCl aqueous phase into CH_2Cl_2 at 0°C (Table III).

At pH 12.7 quaternary salt **3**, in the presence of a high molar excess (about 20 mol. equiv.) of aqueous NaOCl containing NaCl (about 30 mol. equiv.) transfers into CH_2Cl_2 70% of ClO^- and 11.3% of Cl^- with respect to the ammonium cation. At pH 9.5 the overall molar equivalents of the anionic species transported into the organic phase greatly exceed those of PT. At this pH a similar behavior is shown by the lipophilic cryptand **5**. This clearly indicates the presence of the associated species $(PT)^+X^- \cdot (HOCl)_n$ ($X^- = Cl^-, ClO^-$). Similar complexes have already been identified for a relevant number of acids such as HF [15], HCl [16], and CH_3COOH [16]. As far as HOCl is concerned, it was demonstrated by Sasson [17] that the oxidation of aldehydes by NaOCl under PT conditions (quaternary ammonium salt as PT catalyst) proceeds at the maximum rate at pH 9.5–11.0, the range where there is the highest extraction of ClO^- and HOCl into the organic phase [18]. Unlike **3** and **5**, crown ether **4** transfers only a very small amount of Cl^- and ClO^-. This behavior is in agreement with the values already reported for the extraction of halides and pseudohalides by quaternary onium salts, liphophilic crown ethers and cryptands [11, 15].

Based on the anion extraction values, the results of the epoxidations can be tentatively rationalized according to Scheme 2 [26].

In the presence of **3** or **5**, Mn-porphyrin **1**, the amount of which in the organic phase is 6–10 times lower than that of PT catalysts, is complexed by the highly coordinating anion Cl^- [23], and affords species **11**. The equilibria of this species with both **12a** and the corresponding protonated species **12b**, should be noticeably shifted towards **11**, in agreement with the observed very low catalytic activity of the porphyrin. On the contrary, if a lipophilic nitrogen base is present, **11** is easily transformed into **13** due to the electron donation of L on the metal [27].



Scheme 2

The intermediate **13** affords **9** (or **7**), this process being favored by both the increased concentration of HOCl (or ClO^-), due to the presence of PT, and by the irreversible formation of the metal-oxene **8**. As the transformation of **7** into **8** is much slower than that of **9** to **8** ($k_3 \ll k_4$, Scheme 1), the catalytic activity at pH 12.7 is expected to be low, as is experimentally observed (Table 1).

As already observed, the extraction capability of crown ether **4** for ClO^- and Cl^- is very low, but with **4** at pH 9.5–10.5 and L/P = 1, the reactivity of Mn(III)-porphyrin **1** is always very high. Furthermore, at this pH range, **4** does not inhibit cyclooctene epoxidation in the absence of L, the reaction rate being only slightly lower than that observed without PT (Figure 2). These results can be explained by the ineffectiveness of **4** in extracting Cl^- anions into CH_2Cl_2; their concentration in the organic phase remains very low, thus limiting the deactivation of Mn(III)-porphyrin **1**.

Under the epoxidation conditions reported above, Mn(III)-porphyrin **1** can undergo partial demolition, its stability decreasing with the increasing efficiency of the catalytic system (Tables I and II).

A last comment concerns a recent observation [9] that there was only a small increase in reaction rate when the pH of the aqueous NaOCl is decreased. The explanation can be related to the very large excess of axial ligand used (4-picoline, L/P = 520, which is twice the amount of the substrate). This excess causes equilibrium (3) to shift to the right, producing almost exclusively the nonreactive bis-coordinated species $Mn(P)L_2$. In fact, we have measured the binding constants between Mn(III)-porphyrin **1** and 4-*tert*-butylpyridine ($k_1 = 420\ mol^{-1}$, $\beta_2 = 3.0 \times 10^5\ mol^{-2}$), following a previously reported procedure [2a, 6d]. At the porphyrin concentration ($2.5 \times 10^{-3}\ mol\ L^{-1}$) and with the amount of axial ligand (L/P = 520) used [9], the calculated $Mn(P)L_2$ percentage is 99.9. The binding constants between **1** and 4-picoline are most probably similar to those found for 4-*tert*-butylpyridine; even taking into account the partial solubility of 4-picoline in the NaOCl aqueous phases (20% with $CH_2Cl_2/H_2O = 25/75$ v/v, our measurements), the amount of $Mn(P)L_2$ at the equilibrium should still be higher than 99%.

Thus, with such an amount of ligand, the reactivity of Mn(III)-prophyrins is minimized [28], and a lowering of pH will have only a negligible effect on the reaction rate.

5. Conclusions

Conditions have been set up for the NaOCl alkene epoxidations catalyzed by the chemically robust Mn(III)-porphyrin **1** in the presence of catalytic amounts of phase transfer agents. Lipophilic crown ethers and cryptands are particularly efficient.

Reaction rates thus obtained are probably the highest reported to date, especially those found for poorly reactive substrates such as 1-dodecene.

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