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Structural effects on the NaOCl epoxidation of styrene in micellar media catalysed by amphiphilised Mn(III)metalloporphyrins

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Abstract

A biomimetic system of cytochrome P450, constituted by [5-(4-(1-methylpyridinium))-10,15,20-triphenylporphyrinato] manganese(III) dichloride (Mn1) included in cetylpyridinium chloride (CPyCl) micellar phase, features good catalytic activity in the NaClO promoted epoxidation of styrene.

A closely related system, i.e. [5-(4-(3-trimethylammonium) propyloxyphenyl)-10,15,20-tryphenyl-porphyrinato] manganese(III) dichloride (Mn2) in cetyltrimethylammonium bromide (CTAB), presents a lower reactivity, similar to that achieved in ethanol–water solvent mixture. A crossover experiment, i.e. that carried out with Mn1/CTAB system, shows intermediate degree of conversion. These findings indicate that the catalytic properties of the investigated systems are deeply influenced by the specific non-covalent interactions established among the catalyst, substrate, and surfactant.

Keywords: Catalysis; Epoxidation reaction; Micelles; Porphyrinoids; Selectivity

1. Introduction

In the fervent arena of the porphyrin chemistry, the development of a porphyrin-based system for the selective oxidation of organic substrates [1–3] represents one of the most challenging tasks devoted to the construction of synthetic systems able to mimic the activity of metalloenzymes involved in many life-sustaining cycles [4,5]. Intriguing porphyrin-based supramolecular architectures, featuring cytochrome P450 biomimetic activity, [6–13] have been realised and their catalytic features, in terms of regioselectivity, shape-selectivity, as well as their robustness toward the degradative action of the oxidants, make the systems investigated, though achievable by demanding synthetic protocols, of great interest and importance. The fact that P450 is a membrane-bound enzyme sparkled the idea of building up a biomimetic tool in which a synthetic heme core is included in a self-organised medium. According to this philosophy, properly tailored membrane-spanning porphyrins [14–16], once embedded in a DMPC bilayer, are able to catalyse the site-selective iodosylbenzene promoted

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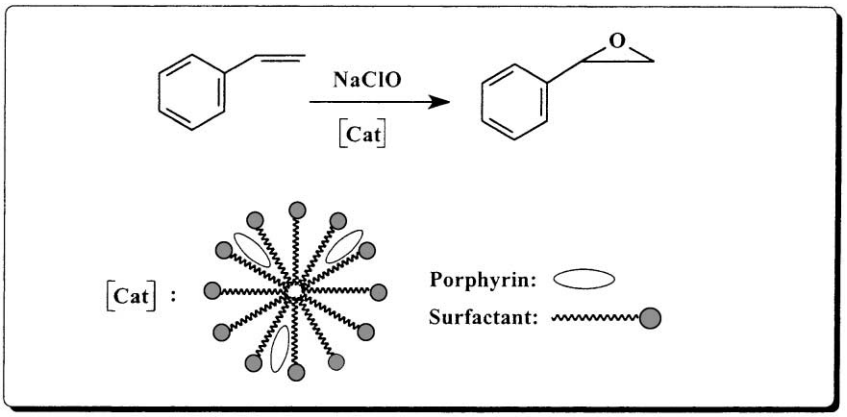
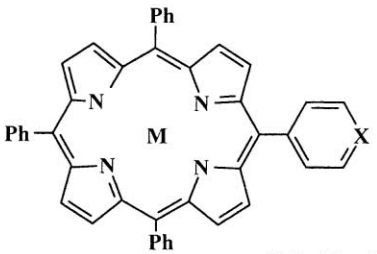
epoxidation of steroid derivatives and of some fatty acids. Other important results were reported by Nolte and co-workers [17–19], who succeeded in the incorporation of all the features of natural cytochrome P450 in liposome bilayer. Recently, a manganese(III) porphyrin incorporated in polydimethylsiloxane synthetic membranes has been reported to act as a selective catalyst for the epoxidation of deactivated allylic alcohols [20].

Along this line, we reported [21] on a system based on amphiphilised metalloporphyrins included in micellar media, pointing out how the specificity of the interactions between the macrocycles and the surfactant aggregates strongly affects the catalytic efficiency of these systems in the oxidation of some probe olefins. Subsequently, we found that the diastereoselective course of the epoxidation reaction of chiral probe substrates can be influenced by the microscopic aggregation of chiral surfactants [22]. In the present paper, we wish to report on the results obtained in the NaClO promoted epoxidation of styrene and cyclooctene in micellar solution composed by cetylpyridinium chloride (CPyCl) catalysed by [5-(4-(1-methylpyridinium))-10,15,20-triphenyl-porphyrinato] manganese(III) dichloride (Mn1, Scheme 1), in the presence of imidazole as co-catalyst. The results obtained are compared to those carried out in cethyltrimethylammonium bromide micelle (CTAB), and in homogeneous conditions (ethanol–water). The P450 activity of [5-(4-(3-trimethylammonium)propyloxyphenyl)-10, 15,20-triphenyl porphyrinato] manganese(III) dichloride (Mn2) included in CTAB pseudo-phase was also studied. The results obtained point out, once more, the crucial role played by the microscopic interaction between the substrate, catalyst, and micelle aggregates on the efficiency of the catalytic systems employed.





$H_2$1: X = $N^+CH_3Cl^-$; M = H_2

Mn1: X = $N^+CH_3Cl^-$; M = MnCl

Mn2: X = $COCH_2CH_2CH_2N^+(CH_3)_3Cl^-$; M=MnCl

Scheme 1. Reaction scheme, porphyrin structures and idealised porphyrin-micelle catalytic system.

2. Experimental section

2.1. Instrumentation

GC analyses have been performed on a Carlo Erba HRGC 5160 or on a Varian Vista equipped with a Supelco SPB-35 capillary column. GC–MS runs have been performed on a Varian 3400 matched to a Mass Selective Detector Hewlett & Packard HP-5970. UV–visible spectra were carried out on a Perkin Elmer λ 18 Spectrophotometer equipped with a thermostated cell holder. Mass spectra (FAB) were recorded on a VG Quattro Triple Quadrupole Spectrometer using *m*-nitrobenzyl alcohol (NBA, Aldrich) as a matrix in positive ion mode.

2.2. Materials

Reagents (Aldrich, Merck or Fluka) were of the highest grade available and were used without further purification. Solvents were dried, distilled and degassed prior to use, by using standard procedures [23]. Commercially available surfactants have been purified according to literature methods [24]. Solvents for UV–visible studies are of spectroscopic grade and used as received.

2.3. UV–visible spectroscopic studies

Porphyrin solutions for UV–visible studies of their incorporation in micellar phases were prepared by injection of the required amount of concentrated porphyrin stock solution ($\approx 1 \times 10^{-3}$ M, in 1,4-dioxane) in 0.010 M aqueous CTAB or CPyCl (doubly distilled water). The small fraction of the added organic solvent ($\leq$0.05%) safely does not alter the surfactant microscopic organisation to a detectable extent. The resultant solutions were incubated at 35 °C for 15 min and the electronic spectra recorded. The relative spectroscopic features are reported in Table 1. Notably, the clear solutions obtained were found to be stable in the dark at room temperature and no significant alteration (UV–visible check of the band intensities) or precipitation was observed after several months of storage.

2.4. Synthesis

Porphyrin derivatives $H_2$1 and Mn2 have been synthesised according to published procedures [25]. All the spectroscopic features are in agreement with the reported data and confirm the identity of the compounds. The Mn1 derivative has been prepared by standard $MnCl_2$/DMF metalation method from free-base precursor $H_2$1 [26].

2.5. Manganese [5-(4-(1-methylpyridinium))-10,15, 20-triphenyl-porphyrinato] dichloride (Mn1)

In a 50 ml round-bottomed flask, 56 mg (0.08 mmol) of $H_2$1 and an excess of $MnCl_2 \cdot 4H_2O$ (25 mg, 0.13 mmol) were dissolved in 25 ml of carefully degassed DMF. The reaction mixture was stirred overnight at 80 °C under an inert atmosphere and then left in the open air for 30 min. The solvent was stripped off under reduced pressure and the solid dark green residue dissolved in chloroform (50 ml). The

Table 1
Spectroscopic data of porphyrin catalysts Mn1 and Mn2 in various media[a]

	Medium	λ_{max}, nm (Log ε)
Mn1	$CHCl_3$	378 (4.6), 406 (4.3), 424 (4.1), 480 (4.8), 583 (3.9), 621 (3.8)
	CPyCl	382 (4.5), 403 (4.4), 424 (4.3), 470 (4.9), 564 (3.9), 600 (3.5)
	CPyCl[b]	380 (4.4), 406 (4.3), 427 (4.0), 472 (5.0), 584 (3.8), 622 (3.6)
	EtOH/H_2O[c]	376 (4.3), 398 (4.4), 420 (4.3), 468 (5.0), 568 (3.8), 602 (3.6)
Mn2	$CHCl_3$	378 (4.6), 403 (4.6), 425 (4.4), 478 (5.0), 583 (3.9), 620 (4.1)
	CTAB	383 (4.6), 403 (4.5), 425 (4.4), 472 (4.9), 573 (3.8), 606 (3.5)
	CTAB[b]	381 (4.5), 406 (4.5), 425 (4.2), 472 (4.9), 586 (3.6), 624 (3.4)
	EtOH/H_2O[c]	379 (4.5), 400 (4.7), 420 (4.3), 467 (5.0), 567 (4.0), 601 (3.5)

[a] [Surfactant] = 0.01 M; T = 25 °C.
[b] In the presence of imidazole, 5×10^{-3} M.
[c] EtOH/H_2O (80:20, v/v) solvent mixture.

resulting solution was filtered from the solid residues constituted by the excess of metal salts and washed with a 5% HCl aqueous solution (50 ml), then with brine until neutrality. The organic phase was dried (Na_2SO_4) and the solvent removed under reduced pressure. The residue, constituted by virtually pure Mn1, was recrystallised from CH_2Cl_2/hexane to give 50 mg (0.06 mmol, 82% yield) of the title porphyrin derivative as a green microcrystalline powder.

UV–visible($CHCl_3$); λ_{max}:
378, 406, 424, 480, 583, 621 nm

FAB-MS(NBA); m/e: 683$[M + H - 2Cl]^+$,
668$[M - 2Cl - CH_3]^+$

2.6. Epoxidation reactions

The solutions for the epoxidation experiments, containing surfactant, catalyst, imidazole, oxidant, and substrate in a 1/0.05/1/10/0.5 molar ratio, were prepared as follows. In a 3 ml vial equipped with a magnetic stirring apparatus, the required amount of porphyrin catalysts (1Mn or 2Mn) and imidazole were co-dissolved in 400 μl of dichloromethane. The resulting solution is briefly sonicated to homogeneity and the solvent removed by gentle warming with the aid of an argon stream. The appropriate surfactant solution (2 ml, 0.01 M) containing the required amount of olefin was then added, and the resulting mixture stirred to homogeneity. The reaction mixture was incubated at 35 °C for 15 min, then cooled to 25 °C. Aliquots of the oxidant solution, e.g. buffered (solid $NaHCO_3$, pH ca. 10) NaClO [27], were added and the resulting mixture vigorously stirred for 10 min. An internal standard (*n*-decane or *n*-dodecane) was then added and an aliquot (200 μl) of the reaction mixture was taken, quenched with methanol (100 μl) to disrupt the micellar aggregates, filtered from the eventually precipitated salts and extracted with petroleum ether. The organic phase was analysed by GC and GC–MS. Runs were triplicate and were reproducible within 5%. The reaction products have been characterised by comparisons (GC and GC–MS) with authentic samples. As far as the reactions in $EtOH/H_2O$ solvent mixture are concerned, the oxidant was added to a 2 ml solution of catalyst, imidazole and olefin, held in the appropriate molar ratios as above described. The reaction mixture was then extract (petroleum ether) and analysed (GC and GC–MS).

3. Results

3.1. UV–visible spectroscopic studies

UV–visible spectroscopic studies on the porphyrin derivatives Mn1 and Mn2 were carried out in order to investigate the behaviour of such species in mixed aqueous solvent and micellar solutions. Ethanol/water (8:2, v/v) solvent mixture was safely taken as reference solvents for CTAB and CPyCl micellar phases [28]. The porphyrin derivatives were soluble in chlorinated solvents, ethanol, or 1,4-dioxane. The incorporation of porphyrin derivatives in micellar phases (0.01 M) has been accomplished by the injection method (see Section 2), from the relative 1,4-dioxane concentrated stock solutions (Fig. 1). The inclusion in micellar phases results in a peculiar shift of the absorption maxima (Table 1). In particular the LMCT band [29], at about 480 nm in chloroform, is blue-shifted by 7–10 nm in micellar phase, toward the values observed in EtOH/water solution. The inclusion of porphyrin derivatives Mn1 and Mn2 in the micellar phases has been found to be complete even at values of porphyrin/surfactants ratio as high as 0.05, in CPyCl and CTAB respectively, without the occurrence of a detectable degree of aggregation (UV–visible). This is indicated by the excellent degree of linearity of the relative Lambert–Beer curve (e.g. porphyrin LMCT or Soret band), within the examined concentration window, well above 5×10^{-4} M. These concentration ratios are consistently used in the epoxidation experiments (vide infra). The coordination of imidazole to the micelle-included metalloporphyrin is witnessed by the typical red shift of the LMCT band (Table 1). The role of the added ligand is to mimic the cysteine axial ligand of P450 in vivo enzyme [5]. Notably, the simple addition of imidazole to Mn1 or Mn2 included in micelle hardly results in the axially coordinated species, owing to the low degree of binding of the nitrogen base to the micelle pseudo-phase. The axial ligation is then effectively achieved by co-solubilisation of the species prior to surfactant addition (see Section 2).

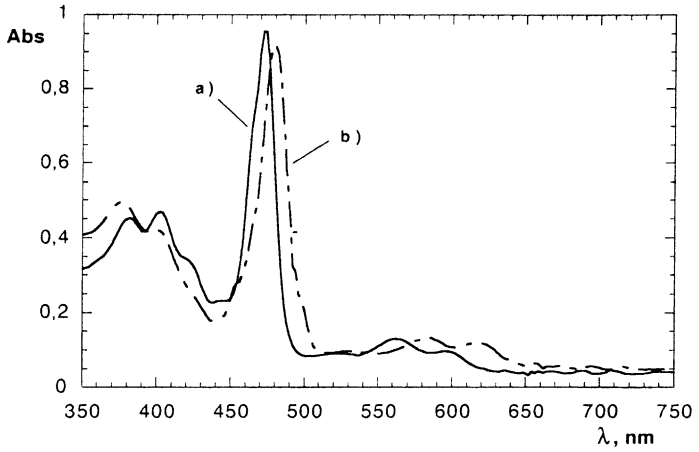


Fig. 1. UV–visible spectra of Mn1 (1×10^{-5} M) in (a) CPyCl, 0.01 M and (b) $CHCl_3$.

3.2. Reactivity studies

Epoxidation reactions of olefins by using NaOCl as oxygen atom donor were carried out at 25 °C in micellar aggregates formed by CPyCl or CTAB surfactants in the presence of catalytic amounts of Mn1 or Mn2, respectively, and an excess of imidazole as co-catalyst. The choice of the surfactant was made on the bases of previous results [21,22], showing that the optimal performance of a catalytic system is achieved when the porphyrin and the surfactant were characterised by polar heads of like structure.

The concentration of the surfactants was fixed at 1×10^{-2} M, a value at least 1 order of magnitude above the cmc (9.0×10^{-4} and 8.0×10^{-4} M for CPyCl and CTAB, respectively), in order to safely exclude any contribution of the surfactant monomeric form [30]. The concentration of the catalyst was consequently held at 5.0×10^{-4} M, so that a minimum average value of two molecules of porphyrin per micelle can be estimated, being the aggregation number of CPyCl and CTAB about 90 and 60, respectively [31,32]. This ensures both the complete incorporation of the catalysts in the micellar phase, and a high probability of the productive encounter event between the reactants and the catalyst. The reactions were stopped at a fixed time, 10 min, and analysed by GC and GC–MS (see Section 2). As far as the Mn1/CpyCl system is concerned, styrene was smoothly converted to the epoxide, and only traces of ring opening derivatives (1,2-diols) or chlorohydrine were detected. Conversely, the reaction carried out on cyclooctene gave only moderate yield of epoxide product. Blank experiments, carried out in the absence of catalyst, yielded chlorohydrine, as major products, and small amounts of other not identified products. The reactions carried out in the reference ethanol/water solvent mixture yielded a substantially

Table 2
NaOCl promoted epoxidation reaction of styrene in various aqueous media[a]

Entry	Catalyst	Medium	Yield (%)[b]
1	Mn1	CPyCl	90
2[c]	Mn1	CPyCl	10
3	Mn1	CTAB	25
4	Mn1	EtOH/H_2O[d]	25
5	None	CPyCl	[e]
6	Mn2	CTAB	20
7	Mn2	EtOH/H_2O[c]	23
8[f]	Mn2	CTAB	8

[a] [catalyst] = 5.0×10^{-4} M, [imidazole] = 0.01 M, [NaOCl] = 0.10 M, [surfactant] = 0.01 M, [olefin] = 5.0×10^{-3} M, T = 25 °C.

[b] Product yields are based on starting olefin and referred to a reaction time of 10 min. Errors lie within 5% range.

[c] Epoxidation reaction of cyclooctene, in the above reaction conditions.

[d] EtOH/H_2O 80:20 (v/v) solvent mixture.

[e] Epoxide formation was not detected. A 35% chlorohydrine was formed.

[f] Epoxidation reaction of cyclooctene (see [21,22]).

lower degree of substrate conversion. It is worth of noting that, in this latter case, an evident extent of catalyst bleaching is found on increasing the amount of NaClO. In the case of the reaction carried out with the Mn2/CTAB system a lower degree of substrate conversion, similar to that achieved by performing the reaction in aqueous ethanol is observed. A comparative run of Mn1 in CTAB has been made, to give a moderate conversion to styrene epoxide. The results have been summarised in Table 2.

4. Discussion

The Mn1/CpyCl system shows enhanced catalytic activity in the NaOCl promoted oxidation of styrene, compared to that observed in homogeneous condition. High styrene conversion is usually achieved, in fact, in the presence of more elaborate porphyrin derivatives such as, e.g. polyhalogenated [33] or sterically hindered [34] macrocycles. Moreover, the increased stability of the catalyst underlines the beneficial effect exerted by the surfactant microenvironment. The comparison to Mn2/CTAB counterpart to crossover Mn1/CTAB system should shed some light on the crucial role which is played by the non-covalent interactions established among the substrate, the catalyst and the organised media, on the features of the reaction. The different reactivity featured by the catalysts should not be attributed to the occurrence of aggregation phenomena, being the porphyrins included in the respective micellar phase in the monomeric form. It is known that the location of the catalysts within micellar phases can be modulated by the different nature of the appended groups that characterise the porphyrin frames [25,35,36]. In the case of Mn1 and Mn2, the presence of a positive charge on the periphery of both of the macrocycles should drive their location in a region of the aggregates close to the water–micelle interface. This is witnessed by the similarity of their spectroscopic features in EtOH/water and surfactant media (Table 1) and by their similar reactivity toward lipophilic substrates, once included in cationic CTAB micelle (Table 2). In this surfactant solution, in fact, hydrophobic substrates [21,22] [2], such as styrene and cyclooctene, are converted to their relative epoxides only to a moderate extent. This can be explained in terms of the nestling of the catalysts in a pocket of the micelle hardly accessible to these substrates, making the probability of their productive encounter event substantially low.

This interpretation does not hold, however, for the higher reactivity observed for Mn1 in CPyCl toward styrene. Different factors, such as the occurrence of specific cation–π interaction [38] between the CPyCl polar head group and the aromatic ring of the substrate, would come into play. These non-covalent interactions are known to play a fundamental role in supramolecular host–guest recognition [39] as well as in important biological systems [40,41]. In our case, these hydrophobic forces may steer the course of the reaction driving the reactants in a mutual close proximity, being the Mn1 catalyst reasonably located in the surfacial region of the micelle aggregates.

5. Conclusions

A biomimetic system of cytochrome P450, constituted by a metalloporphyrin included in a micellar phase, has been described and the properties of the resulting assemblies, in terms of catalytic activity toward the epoxidation of styrene, have been studied. The results obtained point out the fundamental role of the affinity of the tetrapyrrolic macrocycles and the substrate toward the micellar phases. Further studies, aimed at the construction of a biomimetic catalyst with tuneable stereoselective properties, are currently under investigation in our laboratories.

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[2] The hydrophobicity of a given substrate can be quantified by the "log P" value, where P is the partition constants of the substrate between *n*-buthanol and water. Log P: cyclooctene = 2.91; styrene = 2.70. Calculation of log P are carried out according to Viswanadan et al. [37].

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