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Letter

Manganese porphyrins incorporated in polydimethylsiloxane membranes: selective catalysts for the epoxidation of deactivated alkenes

P.E.F. Neys [a,*], A. Severeyns [a], I.F.J. Vankelecom [a], E. Ceulemans [b], W. Dehaen [b], P.A. Jacobs [a]

[a] *Centrum voor Oppervlaktechemie en Katalyse, Departement Interfasechemie, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, B-3001 Heverlee, Belgium*

[b] *Laboratorium voor Organische Synthese, Departement Scheikunde, Katholieke Universiteit Leuven, Celestijnenlaan 200-F, B-3001 Heverlee, Belgium*

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Abstract

The use of [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato] manganese(III) chloride (TDCPP(Mn)Cl) in the presence of an axial ligand and embedded in a polydimethylsiloxane (PDMS) membrane is reported for the epoxidation of an enol with aqueous H_2O_2. Unlike the homogeneously catalyzed reaction, no ketone product is formed with the PDMS resident catalyst. The PDMS support immmobilizes and disperses the porphyrin molecules, but also steers the reaction by providing for a more balanced reagent composition near the active site. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the presence of an electron-donating axial ligand, good catalytic yields can be achieved in the epoxidation of unfunctionalized alkenes with manganese-porphyrins [1–3]. However, until now the greater part of the described systems operates optimally with an excess of substrate with respect to the oxidant and with a high amount of catalyst. These drawbacks can be by-passed by choosing the proper support material, that is able to tune the supply of the respective reagents to the active site.

Polydimethylsiloxane (PDMS), a dense hydrophobic elastomer, has been applied successfully to the immobilization of oxygenation catalysts, such as Fe-phthalocyanines in zeolite Y [4–6] and metallo-porphyrins [7,8], and epoxidation catalysts, such as Mn-salen [6,9] and Mn-bipyridines in zeolites [6,10]. With every

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[*] Corresponding author. Tel.: +32-16-32-16-10; Fax: +32-16-32-19-98; E-mail patricia.neys@agr.kuleuven.ac.be

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complex, the activity and peroxide efficiency are raised on encapsulation in PDMS, because the hydrophobicity of the polymer favors the sorption of apolar components. In this way, the reagent mixture in the polymer phase becomes enriched in the substrate in comparison with the bulk solution, resulting in the suppression of the oxidant decomposition. Especially in the case of substrates with low reactivity, where the oxidant strongly competes for reaction, it is crucial to properly adjust the substrate to oxidant ratio at the active site. Additionally, membrane-resident catalysts offer the possibility to perform reactions in aqueous solution. Under such conditions, a hydrophobic support is indispensable for concentrating the organic reagents near the catalytic complex [7,8].

In this paper, the capacities of PDMS–[5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato] manganese(III) chloride (TDCPP(Mn)Cl) are checked for the epoxidation of hydroxy-alkenes with H_2O_2 from an aqueous solution and in the presence of an axial ligand.

2. Experimental

2.1. Synthesis of PDMS–TDCPP(Mn)Cl and unfilled PDMS

Prepolymer (General Electric; RTV 615A) and crosslinker (General Electric; RTV 615B) are stirred in dichloromethane (Biosolve) in a ratio of 10:1 for 1 h at 40°C (prepolymerization step). A dichloromethane solution of TDCPP-(Mn)Cl, synthesized according to the method of Adler et al. [11], containing 0.0925 wt.% of complex relative to PDMS is added to the prepolymerization mixture and stirred at room temperature for 1 h. The suspension is cast on a petri dish and kept overnight at room temperature. Finally, the polymerizing mixture is cured under vacuum at 150°C for 1 h. The final membrane thickness is 150 μm, except for the sorption measurements where unfilled PDMS membranes with a thickness of 750 μm are used.

2.2. Spectroscopic characterization of encapsulated complexes

UV-Vis spectra were recorded on a Perkin Elmer lambda 12 UV-Vis spectrophotometer. The catalytic membranes were fixed at the outside of the sample holders, while a PDMS membrane was used as reference. The spectra of the complexes in solution were recorded in dichloromethane (Janssen Chimica, 99.5%), using a quartz cell with 10 mm path length.

2.3. Sorption measurements

The sorption mixtures are aqueous solutions (50 ml) of (1) 3-penten-2-ol (20 mM) (Aldrich, 96%) and H_2O_2 (80 mM) (Acros, 35% in water); (2) 3-penten-2-ol (80 mM); (3) imidazole (20 mM) (Aldrich, 99%); and (4) 1-butylimidazole (20 mM) (Aldrich, 98%). About 1 g of PDMS with a thickness of 750 μm is added to the mixture after pretreatment at 150°C for 1 h under vacuum to remove the sorbed water. For each experiment, a reference mixture without membrane is prepared with the same composition. The mixtures are allowed to stand for 24 h under constant stirring. After removing the membrane from the sorption mixtures, 1 mmol of 2-butanol is added as an internal standard for GC analysis. The H_2O_2 concentration is determined by cerimetric titration.

2.4. Reaction conditions

Whereas the homogeneous reactions are done in a (1:1) dichloromethane-acetonitrile (Fisher Scientific) mixture (5 ml), the heterogeneous reactions are performed in water (20 ml). The complex:axial ligand:substrate:oxidant ratio

Table 1
The position of the UV-Vis absorption bands for TDCPP(Mn)Cl in dichloromethane and for PDMS–TDCPP(Mn)Cl in the presence or absence of an axial ligand

Run	Catalyst	Axial ligand	Wavelength (nm)		
			CT-band	Soret band	Q-band
1	TDCPP(Mn)Cl	–	370	478	580
2	TDCPP(Mn)Cl	imidazole	368 (392)	467	571
3	TDCPP(Mn)Cl	1-butylimidazole	370 (393)	470	570
4	PDMS–TDCPP(Mn)Cl	–	373	480	580
5	PDMS–TDCPP(Mn)Cl	imidazole	374	477	582
6	PDMS–TDCPP(Mn)Cl	1-butylimidazole	374 (393)	475	582

amounts either to 1:150:2500:10000 with 0.4 μmol complex in PDMS or to 1:10:40:20 with 40 μmol of TDCPP(Mn)Cl in solution. The homogeneous reactions are performed in a fed-batch mode, the H_2O_2 oxidant being added over a period of 0.5 h. All reactions are carried out at room temperature, sampling is done after 1 and 24 h, respectively. 2-butanol is used as external standard. The membrane is first stirred in an aqueous solution containing the axial ligand (imidazole or 1-butylimidazole) and then the membrane is transferred to the reaction mixture.

3. Results and discussion

Electron donors in the axial ligand position of the metallo-porphyrin facilitate the het-

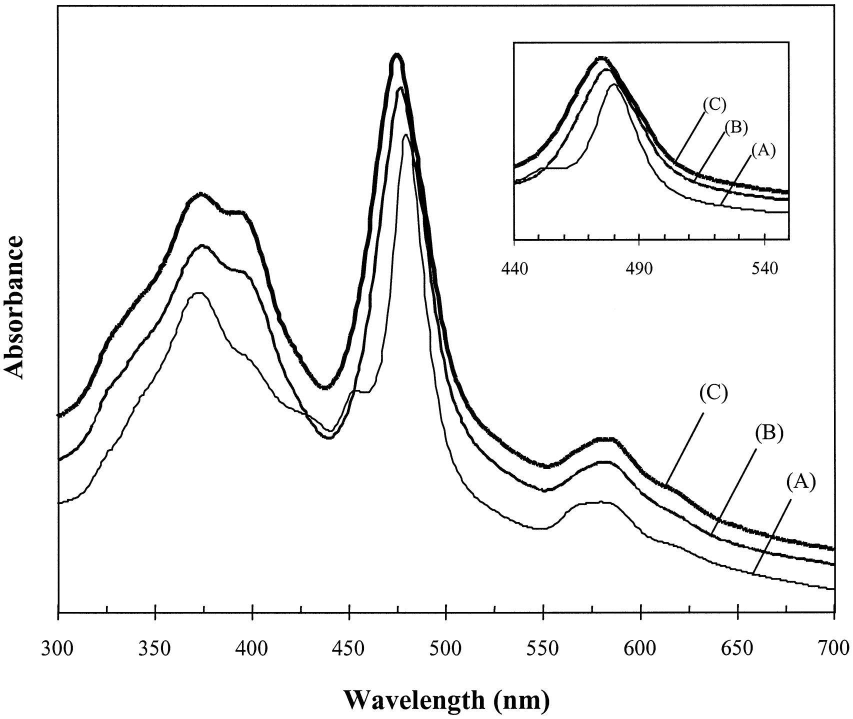

Fig. 1. The UV-Vis spectrum of PDMS-TDCPP(Mn)Cl in the absence and presence of an axial ligand: (A) non-coordinated (————), (B) imidazole (————) and (C) 1-butylimidazole (———).

Table 2
The competitive and separate sorption values for 3-penten-2-ol and H_2O_2 and the values for imidazole and 1-butylimidazole, all measured from an aqueous solution

Run	Substrate	Sorption (mmol g^{-1})
1	3-penten-2-ol	0.182 (0.204)[a]
2	H_2O_2	0.165
3	imidazole	0.019
4	1-butylimidazole	0.023

[a] The number between brackets is the sorption value of the substrate in absence of oxidant.

erolytic cleavage of the O–O bond of the peroxide oxidant, leading to the formation of the active Mn(V)-oxo species [12]. The coordination of the axial ligand with the manganese-porphyrin is verified with UV-Vis spectroscopy. Both the UV-Vis absorption spectra of the complex in solution and of the analogous membrane resident system, show a typical blue shift of the Soret-band as the result of the coordination with imidazole and 1-butylimidazole (Table 1, Fig. 1). With TDCPP(Mn)Cl, the shift is observed immediately after the addition of the ligand to the solution. In the case of the PDMS-encapsulated complex, the coordinative link between the ligand and the central metal-ion is established after sorption of the ligand in the polymer phase. The polarity of the ligand determines the rate and the extent of the sorption. 1-Butylimidazole is succesfully coordinated after stirring the catalytic membrane vigorously for 20 min in the aqueous ligand solution. With imidazole, the same effect is only achieved after 2 h. The faster coordination of the alkyl-substituted imidazole is related to its higher hydrophobicity, that results in a higher sorbed amount at equilibrium (Table 2, run 2 + 3).

To ensure that during the reaction none of the reagents becomes depletive, the amount of substrate and oxidant in the membrane phase is determined by sorption (Table 2, run 1,2). In the absence of substrate, the uptake of H_2O_2 in PDMS from an aqueous solution is negligible. However, in the presence of an apolar substrate the membrane swells and the sorption of the oxidant is strongly enhanced due to the dragging effect that applies to dense elastomers. The coupled sorption creates an almost 1:1 molar ratio of substrate and oxidant in the inner polymer phase.

Table 3 presents the catalytic results obtained with TDCPP(Mn)Cl and PDMS–TDCPP(Mn)Cl in the epoxidation of 3-penten-2-ol with H_2O_2. The double bond of 3-penten-2-ol, being an allylic alcohol, is strongly deactivated. Under homogeneous conditions, the ketone formation dramatically suppresses the selectivity to the desired epoxide (Table 3, run 1 + 2). In the case of high levels of allylic oxidation products, Gunter and Turner [13] suggested that an oxo-manganese(IV) porphyrin π cation radical is responsible for the side-reaction instead of the ligand stabilized oxo-Mn(V) species. The lack of coordination is a consequence of the competition between the substrate and the ligand for oxidation at the active site. Consequently, the

Table 3
The turnover number and the product distribution of the oxidation of 3-penten-2-ol with H_2O_2 mediated by TDCPP(Mn)Cl or PDMS–TDCPP(Mn)Cl in the presence of an axial ligand

Number	Catalyst	Axial ligand	Yield (%)/[Selectivity (%)][b]		TON
			3-epoxy-2-pentanol	3-penten-2-one	
1	TDCPP(Mn)Cl	imidazole	7.7 [27.9]	19.8 [72.1]	10
2	TDCPP(Mn)Cl	1-butylimidazole	6.9 [30.1]	15.9 [69.9]	6
3	PDMS–TDCPP(Mn)Cl	imidazole	9.3 [100]	nd	231
4	PDMS–TDCPP(Mn)Cl	1-butylimidazole	1.7 [100]	nd	40
5[a]	PDMS–TDCPP(Mn)Cl	imidazole	1.9 [100]	nd	47

[a] Regenerated catalyst.
[b] nd: not detected.

yields reached with 1-butylimidazole are lower than with imidazole as the axial ligand, because the introduction of an alkyl-substituent enhances the electron density on the ring (Table 3, run 1–2 and 3–4). The total absence of the ketone in the reactions catalyzed by PDMS–TDCPP-(Mn)Cl could be rationalized by the lowered mobility of the ligand in the more restricive PDMS-phase, that results in a prolonged coordination, in combination with the different (ligand:alkene) ratio in the polymer compared to the solution, that makes the alkene more available for reaction than the ligand. For the homogeneous reactions the ratio amounts to (1:4), whereas for the heterogeneous reactions the initial ratio of (1:17) is even raised in favour of the substrate thanks to the selective sorption by PDMS (Table 2). Through tuning of the concentration of the respective reaction components, the PDMS support has a positive influence on the selectivity. Furthermore, the homogeneous reactions suffer tremendously from a non-productive decomposition of the oxidant when it is added at once. With PDMS–TDCPP(Mn)Cl, the support itself provides for the gradual supply of the oxidant.

On using PDMS–TDCPP(Mn)Cl in a second run, after stirring in water to remove sorbed reagentia and products, the selectivity remains 100% but the activity drops to one fifth of the initial value. The UV-Vis spectrum of the catalyst after reaction still shows the typical bands of the intact manganese porphyrin and leaching of the complex under reaction conditions is neglectable. The decrease in the activity could be attributed to the incomplete extraction of residual components. Since sorption is an equilibrium process, this could lead to an insufficient supply of fresh reagents.

PDMS–TDCPP(Mn)Cl is an efficient catalyst for the selective epoxidation of deactivated alkenes from an aqueous solution. Besides immobilizing and dispersing the complexes, the PDMS support steers the reaction by providing for a more balanced reagent composition near the active catalyst. Especially in the case of deactivated substrates like hydroxyl-alkenes, where unwanted side-reactions—ketone formation; ligand oxidation and oxidant decomposition—strongly compete with the formation of the epoxide, an interactive PDMS support is indispensable.

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