Letter

The oxidation of cyclic alcohols from an aqueous solution by manganese porphyrins embedded in a polydimethylsiloxane membrane

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Abstract

The use of [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato] manganese(III) chloride [TDCPP(Mn)Cl] embedded in polydimethylsiloxane (PDMS) is reported for the oxidation of cyclic alcohols to ketones with t-butylhydroperoxide from an aqueous solution. Two important observations are made which both can be ascribed to the sorption exercised by the polymer. Firstly, compared to a homogeneous set-up much higher activities are reached with the PDMS-system. Secondly, the increase in activity is more pronounced as the ring size of the alcohol increases. The increase in TON going from a five ring to a seven ring is related to the sorption of the respective alcohols in the membrane. Thus, PDMS can be considered as a support with a threefold function. Besides immobilizing and dispersing the complexes, the carrier takes part in the reaction process by selectively sorbing the reagents. Furthermore, the catalyst retained its activity in a second run, proving the stability of this heterogeneous system. The encapsulation of metallo-porphyrins in PDMS creates a heterogeneous selective oxidation catalyst that discriminates among molecules on the basis of their mutual affinity. © 1997 Elsevier Science B.V.

Keywords: Manganese porphyrin; Polydimethylsiloxane; Membranes; Oxidation

1. Introduction

The search for a good support for metallo-complexes is never ending. Recently, chiral Ru–BINAP and Mn–salen complexes have been immobilized in a polydimethylsiloxane (PDMS) membrane, leading to heterogeneous, regenerable chiral catalysts [1]. It was suggested that the synthesis procedure could also be applied to other types of complexes.

It is particularly interesting to wrap metallo-porphyrins in a PDMS polymeric membrane, because of the hydrophobic properties of the polymer matrix, which can change the polarity of the environment of the active site. In general, a hydrophobic carrier will strongly enhance the

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Table 1
The oxidation of cyclopentanol, cyclohexanol and cycloheptanol by t-BHP mediated by TDCPP(Mn)Cl or PDMS–TDCPP(Mn)Cl

Run	Catalyst	TON		
		cyclopentanol	cyclohexanol	cycloheptanol
1 [a]	TDCPP(Mn)Cl	5.5	5.0	10.0
2 [b]	TDCPP(Mn)Cl	3.4	4.3	11.0
3 [a]	PDMS–TDCPP(Mn)Cl	10.7	29.0	72.9
4 [b]	PDMS–TDCPP(Mn)Cl	16.2	27.6	49.4

[a] Separate oxidation of the respective alcohols.
[b] Competitive oxidation reaction.

activity of metallo-porphyrins by providing a better supply of the apolar substrate to the complex [2–5]. In oxidation reactions, the apolar substrate competes for sorption near the active site with polar components of the reaction mixture, such as the products, the oxidant and the solvent. Sorption experiments on PDMS occluded catalytic systems show an enrichment of the apolar molecules in the membrane [6]. When using organic peroxides as oxygen donor a better substrate versus oxidant ratio is achieved near the active site, favoring the oxidation of the hydrocarbon above the decomposition of the peroxide [2–4]. More specifically, sorption effects are extremely important for reactions of hydrocarbons from an aqueous solution, because of the occurrence of recalcitrant organic pollutants in wastewater [7,8] and the ability of metallo-porphyrins or metallo-phthalocyanines to oxidatively dehalogenate organohalides [9–12]. A hydrophobic support is indispensable for concentrating the organic reagents from the diluted aqueous solution near the catalytic complex [13,14].

In this paper we evaluate the performance of PDMS–TDCPP(Mn)Cl [1] in the oxidation of cyclic water soluble alcohols, which serve as test molecules. The chloro substituted complex is used for its good activity and stability [16].

[1] Synthesis procedure for TDCPP(Mn)Cl according to Adler et al. [15].

2. Experimental

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

Prepolymer (General Electric; RTV 615A) and crosslinker (General Electric; RTV 615B) are stirred in dichloromethane in a ratio of 10:1 during 1 h at 40°C (prepolymerization step). A solution of TDCPP(Mn)Cl (loading of 0.37 wt% relative to PDMS) in dichloromethane is then added to the prepolymerization mixture and the whole is 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 prepared.

2.2. Reaction conditions

The catalytic reactions are carried out at room temperature in a batch set-up. The homogeneous reactions are done in dichloromethane whereas the heterogeneous reactions are done in water. The reaction conditions are the following: 1 mmol substrate, 2 mmol t-BHP, 5 μmol TDCPP(Mn)Cl (Table 1, run 1) or 0.2 g PDMS–TDCPP(Mn)Cl (Table 1, run 3). For the competitive reaction, conditions are: 1 mmol of each alcohol, 6 mmol t-BHP, 5 μmol

TDCPP(Mn)Cl (Table 1, run 2) or 0.2 g PDMS–TDCPP(Mn)Cl (Table 1, run 4). Sampling is done after 27 h.

2.3. Procedure for the sorption measurements

1.5 mmol of the alcohol in the non-competitive sorption (run 1) and 0.5 mmol of each alcohol in the competitive sorption (run 2) is dissolved in 30 ml water. 1 g of PDMS (750 μm thickness) is added to the mixture after a 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, t-butanol (0.65 mmol) is added to both sorption and reference mixtures as an internal standard for GC analysis. Subtracting the values of the sorption mixture from those found in the reference gives the sorbed amounts corrected for evaporation.

3. Results and discussion

The results of the heterogeneous system are compared with those obtained in the homogeneously catalyzed reaction (Table 1). However, experimental conditions vary slightly: the latter reaction is carried out in dichloromethane because the porphyrins are insoluble in aqueous media. The reactivity order of the respective alcohols in the homogeneous reaction may be rationalized by invoking the concept of I-strain [17–19]. I-strain stands for the change in internal strain which results from a change in coordination number of a ring atom undergoing a chemical reaction. Oxidation of an alcohol to a ketone involves a change in hybridization from sp^3 to sp^2. According to literature, this transformation is more favorable for five- and seven-membered carbon rings than for six-membered rings [17–19]. A clear improvement of the activity is seen for the immobilized complex (Ta-

Table 2
Sorption of cyclopentanol, cyclohexanol and cycloheptanol by PDMS

Run	Sorption (μl g^{-1})		
	cyclopentanol	cyclohexanol	cycloheptanol
1 [a]	1.9	2.5	6.9
2 [b]	1.3	2.0	3.4

[a] Separate sorption of the respective alcohols.
[b] Competitive sorption experiment.

ble 1, rum vs. run 3), which is more pronounced as the carbon number of the alcohol increases. The larger the alkyl chain, the higher the affinity of the polymer for the alcohol, as is confirmed by the competitive oxidation of the cyclic alcohols by PDMS–TDCPP(Mn)Cl (Table 1, run 4) and the sorption of the alcohols from a diluted aqueous solution by unfilled PDMS (Table 2). The preferred sorption of cycloheptanol over cyclohexanol and cyclopentanol, leads to an enrichment near the active site of cycloheptanol over the other substrates which is at the basis of the higher catalytic turnover number. The membrane is more than a carrier for the complex and plays an active role in the catalytic process by selectively sorbing the reagents. For the competitive oxidation (Table 1, run 4), the difference in TON for the three alcohols is less pronounced compared to their individual behavior (Table 1, run 3). In a mixture, the individual components influence each other's sorption in a polymer. The presence of good sorbing species enhances the intake of the more polar components, which is confirmed by the sorption figures, the so-called 'dragging effect' (Table 2, run 1 + 2). The total amount sorbed in the competitive experiment equals that of the single sorption of cycloheptanol, pointing to the same maximum degree of swelling reached at equilibrium. Under homogeneous conditions, these sorption coupling phenomena are not playing of course. The difference in TON is in those cases even greater for the competitive reaction (Table 1, run 2), because for each alcohol the oxidant–substrate ratio increased, which favors the most reactive alcohol.

The regeneration of the catalyst consists of desorbing the reagents and products from me membrane while stirring overnight in water. Leaching of the complex is verified by AAS. After 24 h, the manganese concentration in the solution amounts to 0.028 ppm, which corresponds to 2% of the manganese content of the membrane. On the other hand, a second competitive reaction is carried out without any significant loss of activity.

The occlusion of metallo-porphyrins in a dense polymer creates a catalytic system which is able to oxidize with improved activity water soluble organic molecules from an aqueous solution. This way, it overcomes the need for using an organic solvent. At the same time, it is the first heterogeneous catalyst where the carrier discriminates among the various substrates on the basis of their mutual affinity.

Acknowledgements

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