Mono-oxygenase-like Oxidation of Hydrocarbons using Supported Manganese–Porphyrin Catalysts: Beneficial Effects of a Silica Support for Alkane Hydroxylation

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A supported Mn–porphyrin catalyst was prepared by strong adsorption of the tetracationic Mn[*meso*-tetra(4-*N*-methylpyridiniumyl)porphyrin](Cl)$^{4+}$4Cl$^-$ on silica, and was found very efficient for cyclo-octene epoxidation (95% yield, 13 turnovers per min) and for alkane hydroxylation, with alcohol yields and alcohol : ketone ratios remarkably higher than those obtained with corresponding soluble Mn–porphyrins.

Very efficient systems for alkene epoxidation and alkane hydroxylation, mimicking cytochrome P-450-dependent mono-oxygenases, using iron or manganese–porphyrins as catalysts, and various oxygen atom donors such as PhIO, ClO$^-$, or H_2O_2 have been reported.[1] High yields and rates have been obtained with these biomimetic systems making them useful for complete conversion of various substrates and thus potentially useful for preparative oxidations in organic chemistry.

Immobilisation of metalloporphyrins on inorganic supports appears to provide a method of obtaining catalysts which are easier to handle and possibly exhibiting an improved selectivity because of the support environment.

In this Communication we report our results, describing a simple and easy preparation of a supported Mn-catalyst by strong adsorption of a cationic porphyrin on silica and showing the particular efficacy of this heterogeneous catalyst for alkane hydroxylation when compared to similar homogeneous catalysts.

Mn–porphyrin catalysts were immobilized on silica by taking advantage of a very strong interaction between silica and tetracationic porphyrins. In a typical experiment a suspension of silica (0.5 g) (Kieselguhr 60, Merck, 40—63 µm) in MeOH (10 ml), containing Mn^{III} [*meso*-tetra(4-*N*-methylpyridiniumyl)porphyrin](Cl)$^{4+}$4Cl$^-$, [Mn(T4MPyP)-Cl],[2—4] (0.05 M), was stirred for 1 h at 20 °C. After filtration

Table 1. Oxidation of alkanes by PhIO catalysed by Mn(T4MPyP)Cl supported on silica [compared to Mn(T4MPyP)Cl alone].[a]

	Product yields (%)[b]			
Alkane	Alcohol(s)[c]	Ketone(s)[d]	Ol/one	Total yield[d]
Cyclohexane	26	4	6.5	34
	(4)	(2)	(2)	(8)
Cyclo-octane	34	6.5	5.2	47
	(5)	(6)	(0.8)	(17)
Heptane	32	3.5	9	39
	(1)	(1)	(1)	(3)
Adamantane	37	1		39
	(7)	(0.5)		(8)

[a] Conditions; alkane : PhIO : Mn = 800 : 20 : 1 ('equivalent concentration' of supported catalyst, 1.5 mM) in 1 ml MeCN : CH_2Cl_2 = 2 : 1, 2 h at 20 °C under argon. In reactions using Mn(T4MPyP)Cl alone, 10% MeOH was added to solubilize the metalloporphyrin. Results obtained with this homogeneous catalyst are given in parentheses. [b] Yields based on starting PhIO determined as indicated in caption to Figure 1. For total yields, it was assumed that 2 moles of PhIO were necessary for ketone formation. [c] Alcohols formed; cyclohexanol from cyclohexane, cyclo-octanol from cyclo-octane, 2-, 3-, and 4-heptanols from heptane (relative yields in Table 2), adamantan-1- and -2-ol (32.5 and 4.5% respectively). [d] Ketones formed; cyclohexanone, cyclo-octanone, 2-, 3- and 4-heptanone (relative yields in Table 2) and adamantan-2-one respectively.

Table 2. Oxidation of pentane and heptane by PhIO catalysed by Mn(T4MPyP)Cl supported on silica. Comparison with various soluble Mn–porphyrin catalysts.[a]

Catalyst	Alkane[b]	Total yield (%)[c]	Alcohol(s) yield(%)[d]	Ketone(s) yield(%)[e]	Ol : one	Regioselectivity[f]			
						1	2	3	4
Mn(T4MPyP)Cl on SiO_2	H	39	32	3.5	9.1	<2	35	44	21
	P	23	15	4	3.7	3	65	32	
Mn(T4MPyP)Cl	H	3	1	1	1	<2	36	43	21
	P	n.d.	1	n.d.			n.d.		
Mn(TPP)Cl	H	22	15	3.5	4.3	<2	36	42	22
	P	6	2	2	1	5	61	34	
Mn(TDCPP)Cl	H	42	26	8	3.2	5	62	30	3
	P	3.5	1.5	1	1.5	5	73	22	

[a] Conditions as in Table 1 for heptane. Conditions used for oxidation of pentane were identical except for the solvent; pure CH_2Cl_2 was used because of problems in the determination of pentanones by g.c. owing to superimposition with the peak of MeCN. In the case of Mn(T4MPyP)Cl which is insoluble in CH_2Cl_2, 10% MeOH was added. Yields of heptanones could not be determined (n.d.) because of superimposition of their g.c. peaks with MeOH. Product analysis by g.c. as indicated in Figure 1. [b] H = heptane; P = pentane. [c] Yields based on starting PhIO. [d] Total yields of 1-, 2-, 3- and 4-heptanols or of 1-, 2- and 3-pentanols. [e] Total yields of 2-, 3- and 4-heptanones or of 2- and 3-pentanones. [f] Relative proportions of products coming from the oxidation of positions 1, 2, 3, and 4 of heptane, or of positions 1, 2, and 3 of pentane.

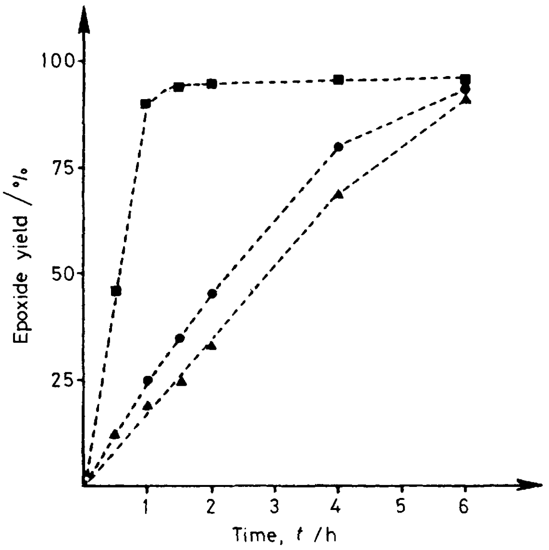

Figure 1. Epoxidation of cyclo-octene by PhIO catalysed by a cationic Mn–porphyrin supported on silica and by anionic Mn–porphyrins supported on alumina. ■: SiO_2–Mn(T4MPyP)Cl; ▲: Mn [tetra(4-carboxyphenyl)porphyrin]$(Cl)^{4-}$, $4Na^+$ on alumina; ●: Mn [tetra(4-sulphonatophenyl)porphyrin]$(Cl)^{4-}4Na^+$ on alumina. *Reagents and conditions*: ratio of Mn : alkene : PhIO = 1 : 10^5 : 10^3; 'equivalent concentration' of Mn in the suspension was 2.2×10^{-5} M in 4.5 ml CH_2Cl_2 : MeCN (1 : 2) at 20 °C. Analysis of products was by gas chromatography on a FFAP (10%) column by comparison with authentic samples; determination of quantity was made using calibration curves with acetophenone as internal standard.

and washing with CH_2Cl_2 and MeCN, the solid obtained was found to retain completely the adsorbed metalloporphyrin when put in suspension in MeCN or CH_2Cl_2, even after several days. Elemental analysis (Mn, N, Cl) of the solid showed that it contained about 10% (w : w) of adsorbed Mn–porphyrin. Analogous supported catalysts were similarly prepared by adsorption of the Na^+ salts of Mn^{III} [*meso*-tetra(4-carboxyphenyl)porphyrin] or Mn^{III} [tetra(4-sulphonatophenyl)-porphyrin] on alumina (Merck, active basic, 63—200 μm) or magnesia (Janssen).

Preliminary experiments using these supported catalysts for the oxidation of cyclo-octene by PhIO (conditions of Figure 1) led to good to excellent epoxide yields in all cases (80 to 100%). However, higher rates (up to 13 turnovers per min) were obtained with the tetracationic catalyst supported on silica. In fact, almost quantitative epoxide yields were obtained in about 1 h with this catalyst instead of 6 h for the anionic catalysts on alumina (Figure 1). The supported SiO_2–Mn(T4MPyP)Cl catalyst was found to be very resistant to oxidative degradation as 30 successive additions of 1 000 equiv. of PhIO (relative to Mn) (1 addition per h) led to similar rates and yields of cyclo-octene epoxidation.

Owing to its better catalytic activity, the SiO_2–Mn(T4MPyP)Cl catalyst was selected for further experiments of alkane hydroxylation. Reaction of PhIO with various alkanes such as cyclohexane, cyclo-octane, heptane, or adamantane in MeCN : CH_2Cl_2 (2 : 1) in the presence of a suspension of SiO_2–Mn(T4MPyP)Cl led to good yields of alcohols and ketones within 2 h at 20 °C. Under aerobic conditions, total yields based on starting PhIO varied between 45 and 60% with the alcohol : ketone ratio between 1 and 3, as a function of the alkane structure. As found previously for alkane oxidations catalysed by homogeneous Mn-porphyrins,[5] the alcohol : ketone ratio greatly increased when oxidations catalysed by SiO_2–Mn(T4MPyP)Cl were performed under anaerobic conditions. Under these conditions, the alcohol : ketone ratio varied between 5 and 9, the alcohol yield between 26 and 37%, and the total yield between 34 and 47% (Table 1). These yields and alcohol : ketone ratios were much higher than those obtained with the corresponding soluble catalyst, Mn(T4MPyP)Cl,[4] under similar conditions (Table 1).

Table 2 compares the results obtained for the oxidation of two linear alkanes, heptane and pentane (which are generally difficult to activate), by PhIO under anaerobic conditions. The oxidation was catalysed either by the supported catalyst SiO_2–Mn(T4MPyP)Cl, or by various homogeneous Mn–porphyrin catalysts including the robust and reactive Mn-[tetra(2,6-dichlorophenyl)porphyrin]Cl, [Mn(TDCPP)Cl].[6] For both alkanes, the alcohol : ketone ratio and the alcohol yield were higher with the supported catalyst than with the three studied homogeneous catalysts, Mn(TPP)Cl, Mn(TDCPP)Cl, and Mn(T4MPyP)Cl. With both substrates, the alcohol : ketone ratio increased by a factor of between 2 and 12 when passing from one of the soluble catalysts to the supported catalyst. With heptane, a much higher yield of heptanols was obtained with SiO_2–Mn(T4MPyP)Cl than with Mn(TPP)Cl and Mn(T4MPyP)Cl, and this yield was even larger than that obtained with Mn(TDCPP)Cl. This better ability of SiO_2–Mn(T4MPyP)Cl to catalyse the oxidation of linear alkanes was very well illustrated in the case of the less reactive pentane for which the alcohol yield was about ten times higher with the supported catalyst than with the soluble catalysts.

Another possible use of the supported catalyst which we investigated was for oxidation in pure alkanes, which was not possible with homogeneous catalysts because of their poor solubilities in alkanes (total yields of 17 and 26% respectively for heptane and pentane under these conditions). As far as the regioselectivity of oxidation of linear alkanes is concerned, the supported catalyst gave results almost identical to those of the homogeneous catalysts, not hindered in the vicinity of Mn, Mn(TPP)Cl, and Mn(T4MPyP)Cl, whereas the hindered Mn(TDCPP)Cl favoured hydroxylation at position 2 as described previously.[7]

The use of Mn–porphyrin catalysts strongly adsorbed on silica points to four main advantages of these supported catalysts: (i) a very simple preparation from readily available materials and easy recovery at the end of the reactions; (ii) high yields and rates for cyclo-octene epoxidation (about 95% and 13 turnovers per min) as well as a good stability of the catalyst after 30 000 turnovers; (iii) the possibility of using the catalyst even in pure alkane; (iv) unexpectedly higher yields of hydroxylation of linear alkanes with markedly higher alcohol : ketone ratios than with corresponding homogeneous catalysts. Further experiments are required to understand the origin of the effects of the support.

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