

Stability of various metalloporphyrin catalysts during hydrogen peroxide epoxidation of alkene

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Abstract

The ability of certain Fe and Mn metalloporphyrins to catalyse the H₂O₂ epoxidation of cyclooctene is analysed. The ‘efficiency’ of epoxidation is dissected into contributions due to inherent catalyst epoxidation ability, catalyst H₂O₂ dismutation ability, and catalyst stability towards the oxidant. It is shown that catalyst stability is a major factor contributing to apparent catalyst ability. The preparation of a sol–gel encapsulated metalloporphyrin is reported and it is shown to exhibit reduced rate of epoxidation, but a much enhanced stability. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metalloporphyrins have long excited interest as epoxidation and hydroxylation catalysts [1,2], and they continue to do so [3]. Increasingly, attention is being directed to the use of the clean oxidant H₂O₂ [4–10]. It is widely accepted that the metalloporphyrin tetrakis(pentafluorophenyl)-21*H*,23*H*-porphyrin iron(III) chloride (**1**), is an effective catalyst for H₂O₂ epoxidation of alkenes [11–15]. In a recent paper we have re-iterated this efficiency, but have also shown that catalyst degradation plays a key role in the overall oxidation [16]. Furthermore, we have shown that degradation (bleaching) of the catalyst results primarily from direct oxidation of the resting catalyst (Fe^{III}), rather than the high-valent oxo-perferryl ((TF₅PP^{•+})Fe^{IV}=O) or oxo-ferryl (TF₅PPFe^{IV}=O)

intermediates [16]. Clearly, degradation is an important factor in metalloporphyrin-catalysed oxidations, particularly when using H₂O₂, but it is one that is rarely addressed explicitly [17,18].

Examination of the literature shows that there are several strategies commonly employed with the aim of reducing catalyst degradation during oxidation. The first involves use of electron-deficient substituents to the aryl groups of the commonly used *meso*-tetraarylmetalloporphyrins; it has been suggested by Traylor et al. that such substituents favour a *two-electron* reduction of the oxo-perferryl intermediate (e.g. (TF₅PP^{•+})Fe^{IV}=O) back to Fe^{III} [14], thus avoiding the *one-electron* reduction to the ferryl species (e.g. TF₅PPFe^{IV}=O), which is known to be susceptible to oxidative degradation [4]. However, if our ‘direct oxidation’ of the porphyrin ring of the resting catalyst is a general process, this offers an alternative explanation (at least in part) for reduced degradation with electron-withdrawing aryl substituents. The second strategy uses bulky, often

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ortho, groups on the aryl group to reduce intermolecular catalyst interactions and so prevent, for example, oxidation of resting catalyst by the oxo-perferryl intermediate. (This strategy has been an established one since the mid-1980s, see e.g. [19].) The third strategy is to ensure a very large excess of substrate (e.g. alkene) [14], the idea being to ‘trap’ the oxo-perferryl species as efficiently as possible and prevent its destruction via intermolecular reaction with resting catalyst, or with oxidant (involving conversion to the oxo-ferryl intermediate). However, again, if our proposal is general, oxidative destruction is predominantly via direct oxidation of the resting catalyst, and the last two strategies are ineffective [16].

It seems clear, therefore, that for metalloporphyrin-catalysed oxidation, what might be referred to as ‘observed catalyst efficiency’ is in fact a mixed effect of inherent reactivity coupled with a ‘catalyst stability’ effect. Given this, we decided to undertake a brief study to try to dissect observed catalyst ‘efficiency’ into ‘reactivity’ and ‘stability’ factors.

While factors such as the solvent and the nature of the axial ligand(s) are among the many that influence the ‘catalyst efficiency’ [20,21], the main ones are the nature of the metal and the structure of the porphyrin. Therefore, in this study, we have examined the stability, during alkene epoxidation by H₂O₂, of a small range of metalloporphyrins with different aryl substituents and metals. In addition, we have attempted to assess the effect of encapsulation within a silica sol–gel matrix on catalyst efficiency and stability. The use of supported metalloporphyrin catalysts, as opposed to the encapsulated one proposed here, has been widely reported [22,23].

2. Experimental

2.1. Materials

Cyclooctene (Aldrich), dichloromethane (Fisons), dodecane (KOCH-Light Laboratories Ltd.), 30% hydrogen peroxide (Fisher), methanol (Fisher), 5,10,15,20-tetrakis(*p*-hydroxyphenyl)-21*H*,23*H*-porphyrin iron(III) chloride (Frontier Scientific Inc.), 5,10,15,20-tetrakis(pentafluorophenyl)-21*H*,23*H*-porphyrin iron(III) chloride (Aldrich), 5,10,15,20-tetrakis(*p*-sulfonatophenyl)-21*H*,23*H*-porphyrin manganese(III)

chloride (Aldrich), 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin iron(III) chloride (Aldrich) and 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin manganese(III) chloride (Aldrich) were all used as received.

5,10,15,20-Tetrakis(*p*-hydroxyphenyl)-21*H*,23*H*-porphyrin iron(III) chloride was also synthesised and characterised by ¹H NMR and IR spectroscopy as was 5,10,15,20-tetrakis(*p*-hydroxyphenyl)-21*H*,23*H*-porphyrin manganese(III) chloride.

H₂O₂ was standardised by UV–VIS spectroscopic determination of a diluted sample [24], or by iodometry according to Vogel [25].

2.2. Instrumentation

GC analyses were carried out using a Pye Unicam PU4550 gas chromatograph with a 12 m × 0.25 mm methyl silicone column and an oven temperature which was increased from 50 to 150 °C over 10 min.

For UV–VIS spectroscopy a Phillips PU8700 or a Hewlett-Packard 8452A (diode array) spectrometer was used along with a thermostated circulating water bath.

2.3. Typical epoxidation reaction of cyclooctene in the presence of different catalysts and hydrogen peroxide as the oxidant

A 3:1 methanol:dichloromethane mixture (1524 mm³), containing $59 \times 10^{-3} \text{ mol dm}^{-3}$ dodecane as internal GC standard, was added to a 2 cm³ quartz cuvette using a microsyringe. To this was added via microsyringe cyclooctene (390 mm³) followed by a $1 \times 10^{-3} \text{ mol dm}^{-3}$ solution of the metalloporphyrin in methanol or dichloromethane (40 mm³). The cuvette was allowed to reach 25 °C by use of a thermostated water bath. The reaction was initiated by the injection of sufficient 30% aqueous hydrogen peroxide to yield a 0.12 mol dm^{-3} solution (e.g. 46 mm³ of 5.22 mol dm^{-3}).¹ The decomposition of the catalyst was monitored by following the decay of the Soret band (typically 410 nm), while the yield of cyclooctene oxide was determined by direct injection of the reaction solution into the GC after a given time

¹ The cell concentrations at $t = 0$ were as follows: [dodecane (standard)]: $45 \times 10^{-3} \text{ mol dm}^{-3}$; [cyclooctene]₀: 1.5 mol dm^{-3} ; [catalyst]₀: $20 \times 10^{-6} \text{ mol dm}^{-3}$; [H₂O₂]₀: 0.12 mol dm^{-3} .

interval. The amount of hydrogen peroxide remaining at the end of the reaction was determined by aqueous extraction of the reaction mixture, followed by iodometry [25].

2.4. Epoxidation reaction of cyclooctene in the presence of silica sol–gel encapsulated 5,10,15,20-tetrakis(*p*-hydroxyphenyl)-21H,23H-porphyrin iron(III) chloride and hydrogen peroxide as the oxidant

The same procedure and amounts as above were used, except that the injection of catalyst as a methanol solution was replaced by addition of finely powdered solid sol–gel encapsulated catalyst (SiO₂-2, 1% w/w metalloporphyrin) (0.15 g). The suspension was stirred vigorously at 25 °C and analysed by GC at various time intervals.

2.5. Synthesis of SiO₂-2

Tetraethoxysilane (Lancaster) was purified by treatment with sodium ethoxide followed by distillation. Tetrakis(*p*-hydroxyphenyl)porphyrin iron(III) chloride (0.0064 g, 9.44×10^{-6} mol) was dissolved in ethanol (1.61 g, absolute alcohol 100%) and a maroon colour solution was obtained. To this solution H₂O (2 g) was added and the colour of the solution changed from maroon to green. Then the mixture was stirred for 15 min to get a clear solution. Glacial acetic acid (1.21 g) and TEOS (1.684 g, 8.08×10^{-3} mol) were added and a green turbid mixture was obtained. On standing, the mixture separated into two layers. The mixture was stirred vigorously for 12 h to get a homogeneous liquid and at this point the pH was measured to be 2.65. The sample bottle was covered with perforated foil to allow solvent evaporation. After a gelation time of 7 days at room temperature a dark green, transparent gel was obtained. The wet gel was then dried at 80 °C for 72 h and then dried at 120 °C for 96 h. The whole reaction mix then became a dark green, transparent glassy material (0.49 g) that was washed with ethanol.

2.6. Typical calculation of percentage of porphyrin in the SiO₂-2

Silica sol–gel encapsulated Fe(THPP)Cl (SiO₂-2) (0.5639 g), prepared as above, was stirred in 7 ml

absolute ethanol for 2 days. After this time, the ethanol colour had changed from colourless to green. The ethanol was analysed by UV–VIS spectroscopy and the absorbance of Soret peak (porphyrin peak) was determined. From this was obtained the total amount of ‘washed out’ metalloporphyrin, which gave the amount of metalloporphyrin retained within the sol–gel.

3. Results and discussion

3.1. Results

The catalysts 1–6 were selected for study in this work; in addition a sample of Fe(THPP)Cl (2) encapsulated in a silica sol–gel matrix (here designated SiO₂-2) was tested as a heterogeneous catalyst (Fig. 1).

From amongst the range 1–6 the metalloporphyrin 2 was chosen for encapsulation within the sol–gel matrix partly because the presence of the OH groups allows it to be readily incorporated, probably by hydrogen bonding. Furthermore, although among metalloporphyrins catalysts, compound 2 may ‘traditionally’ be seen as ‘poor’ due to its instability towards H₂O₂; this allows any improved stability to be more clearly seen. Fig. 1 also shows additional metalloporphyrins 7–16 studied by others, and discussed later in this paper.

Reactions were set up involving catalyst, cyclooctene and hydrogen peroxide in methanol:dichloromethane 3:1 at typically, 20×10^{-6} , 1.5 and 0.12 mol dm⁻³, respectively. The decay of the metalloporphyrin Soret peak during the reaction was monitored (UV–VIS), and the final yield of epoxide was determined (GC), as was the residual H₂O₂ (iodometry). Plots of the decay of the Soret peak for catalysts 1–3 are shown in Fig. 2, and epoxide yield, residual H₂O₂, and Soret peak decay half-life results are collected in Table 1.

It is clear that the Fe-containing metalloporphyrins 1–3 are very unstable under these conditions, but that there is during the short lifetime of the catalyst appreciable catalysis of epoxidation, e.g. the turnover number, defined as (epoxide produced)/(catalyst destroyed), is ca. 400 even for the low-yielding Fe(THPP)Cl (2). The Mn-containing metalloporphyrins 4–6 are far more stable, but give low yields of epoxide, even after several days. The silica sol–gel

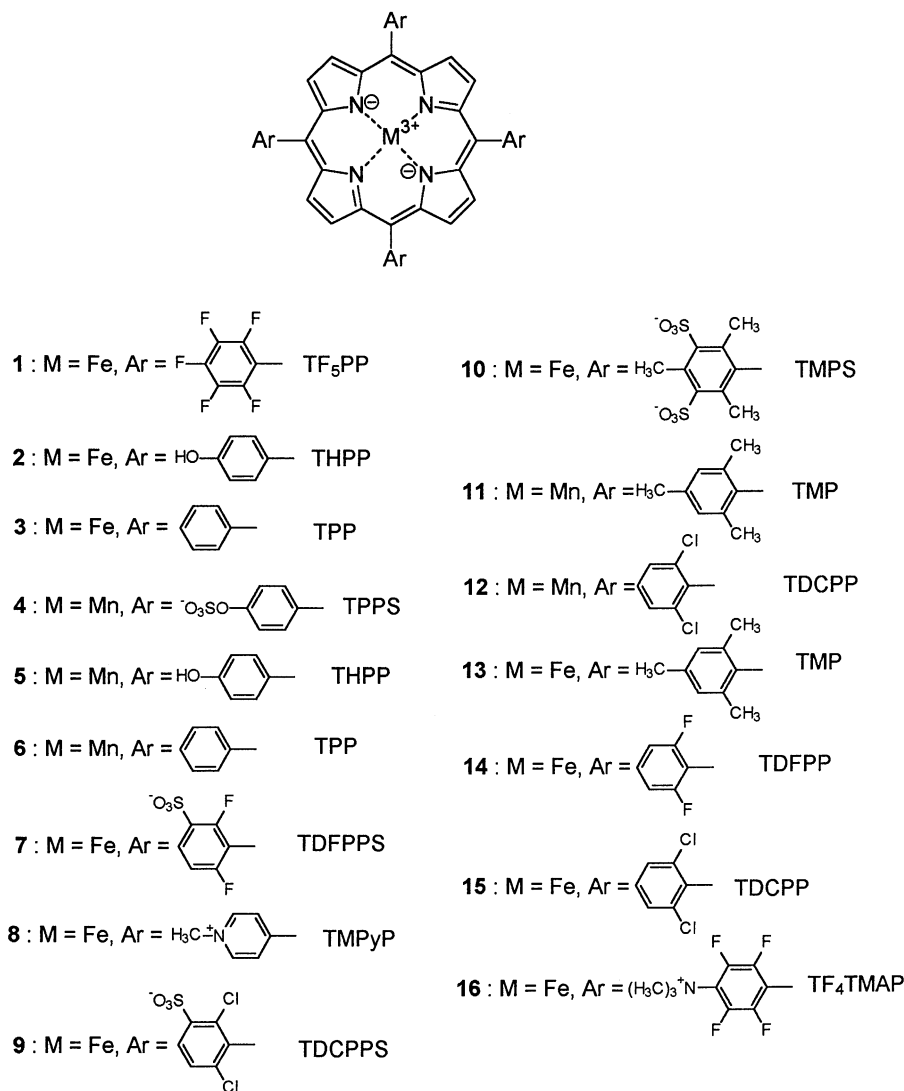


Fig. 1. Structures of metalloporphyrins.

encapsulated catalyst, SiO₂-2 was determined (see Section 2) to comprise ca. 1% w/w of metalloporphyrin **2**; 0.15 g of the catalyst was added to the reaction mixture (2 cm³) as a heterogeneous catalyst, giving a nominal metalloporphyrin level of ca. $1000 \times 10^{-6} \text{ mol dm}^{-3}$. This reaction produced $3 \times 10^{-3} \text{ mol dm}^{-3}$ cyclooctene oxide after 1 day, lower than the $8 \times 10^{-3} \text{ mol dm}^{-3}$ found for the homogeneous reaction using Fe(THPP)Cl (**2**). However,

the reaction catalysed by SiO₂-2 continued after 1 day, giving $11 \times 10^{-3} \text{ mol dm}^{-3}$ of oxide after 3 days.

3.2. Discussion

It is generally accepted that electron-deficient metalloporphyrins are "... effective catalysts in the epoxidation of olefins by H₂O₂ and ROOH..." (see for e.g. [26]). However, such statements are

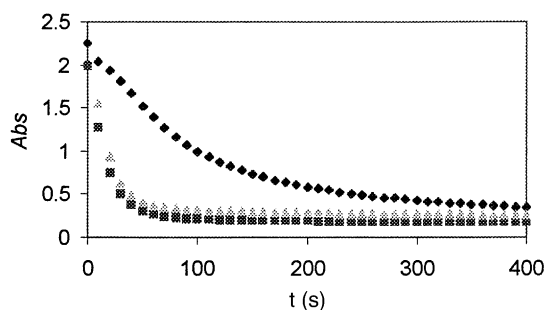
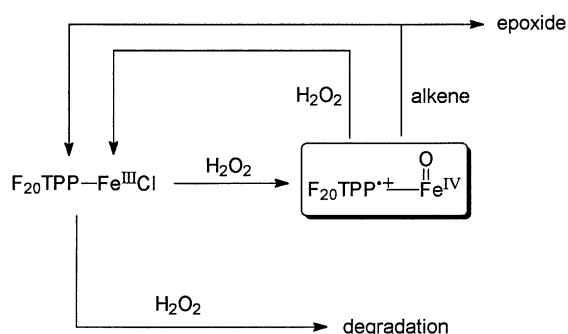


Fig. 2. Plots of absorbance vs. t for the decay of metalloporphyrins **1** (\blacklozenge), **2** (\blacktriangle) and **3** (\blacksquare) ($[\text{cyclooctene}]_0$: 1.5 mol dm^{-3} ; $[\text{metalloporphyrin}]_0$: $20 \times 10^{-6} \text{ mol dm}^{-3}$; $[\text{H}_2\text{O}_2]_0$: 0.12 mol dm^{-3}).

not always unambiguously supported by experimental evidence. For example, stilbene epoxidation with 2-methyl-1-phenylpropan-2-yl hydroperoxide ($\text{PhCH}_2\text{CMe}_2\text{OOH}$) as oxidant and the iron porphyrins **7–10** shown in Fig. 1 as catalysts (see for e.g. [26]), gave the lowest yield (2%) with for the electronegatively substituted $\text{Fe}(\text{TMPyP})^{5+}$ (**8**). A similar trend is seen in the work of Mansuy and co-workers for manganese porphyrins **6**, **11** and **12** [7,10].

The importance of oxidation catalysis versus stability was illustrated by our earlier work, where the catalyst $\text{Fe}(\text{TF}_5\text{PP})\text{Cl}$ (**1**) was shown to undergo oxidative destruction in parallel with the epoxidation cycle (Scheme 1) [16]. In the same work we also



Scheme 1. Degradation via direct oxidation of the porphyrin ring.

noted a competition between alkene (cyclooctene) and oxidant (H_2O_2) for the high-valent oxo-perferryl intermediate ($(\text{TF}_5\text{PP}^{\bullet+})\text{Fe}^{\text{IV}}=\text{O}$).

A similar competition between alkene (cyclohexene) and H_2O_2 has been studied for a range of oxo-perferryl metalloporphyrins derived from **13–16** by Goh and Nam [27]. Their results show that the oxo-perferryl intermediates from iron porphyrins with electron-deficient aryl groups prefer reaction with alkene, but those with electron-donating groups react readily with H_2O_2 (and $t\text{-BuOOH}$) in competition with alkene. Thus, under certain conditions, a metalloporphyrin, which appears to be ‘stable’ and which is readily converted to the oxo-perferryl intermediate, gives a low yield of epoxide.

Table 1
Epoxide yields, residual H_2O_2 , and metalloporphyrin decay rates

Catalyst	$[\text{Cyclooctene}]_0$ (mol dm^{-3})	$[\text{Catalyst}]_0 \times 10^6$ (mol dm^{-3})	$[\text{H}_2\text{O}_2]_0 \times 10^3$ (mol dm^{-3}) ^a	$[\text{Cyclooctene oxide}]$ $\times 10^3$ (mol dm^{-3})	$[\text{H}_2\text{O}_2]_f \times 10^3$ (mol dm^{-3}) ^b	$t_{1/2}$ for decay of catalyst (s) ^c
$\text{Fe}(\text{TF}_5\text{PP})\text{Cl}$ (1)	1.5	20	120	55 ^d	27	110
$\text{Fe}(\text{THPP})\text{Cl}$ (2)	1.5	20	120	8 ^d	112	20
$\text{Fe}(\text{TPP})\text{Cl}$ (3)	1.5	20	120	Trace ^d	118	15
$\text{Mn}(\text{TPPS})\text{Cl}$ (4)	1.5	20	120	6 ^e	110	NC ^f
$\text{Mn}(\text{THPP})\text{Cl}$ (5)	1.5	20	120	Trace ^e		
$\text{Mn}(\text{TPP})\text{Cl}$ (6)	1.5	20	120	0 ^d	112	NC ^f
$\text{SiO}_2\text{-2}$	1.5	1000 ^g	120	3 ^h and 11 ^e		

^a Levels of H_2O are typically 2% v/v (ca. 1.3 mol dm^{-3}).

^b Concentration of H_2O_2 determined by iodometry after 20 min. The H_2O_2 dismutation yield is assumed to be given by $[\text{H}_2\text{O}_2]_0 - [\text{cyclooctene oxide}]_f - [\text{H}_2\text{O}_2]_f$.

^c UV–VIS monitoring of Soret peak.

^d Determined by GC after 20 min.

^e Determined by GC after 3 days.

^f No change in UV–VIS spectrum after 70 s.

^g See text.

^h Determined by GC after 1 day.

It is clear from the above discussion, therefore, that the efficiency of any particular metalloporphyrin as an epoxidation catalyst is a reflection of several competing factors. We believe that the most important competition is that between the substrate oxidation cycle, e.g. $\text{TF}_5\text{PPFe}^{\text{III}} + \text{H}_2\text{O}_2 \rightarrow (\text{TF}_5\text{PP}^{\bullet+})\text{Fe}^{\text{IV}}=\text{O} + \text{alkene} \rightarrow \text{TF}_5\text{PPFe}^{\text{III}} + \text{epoxide}$ in Scheme 1, and degradation, e.g. $\text{TF}_5\text{PPFe}^{\text{III}} + \text{H}_2\text{O}_2 \rightarrow \text{'degradation'}$. Clearly, a catalyst with a very fast oxidation cycle, will be seen to be inefficient in terms of epoxidation yield, if it is rapidly degraded.

In this study, catalyst stability is assessed as the decay of the Soret peak in the UV–VIS spectrum, and epoxidation efficiency as the yield of cyclooctene oxide after a given time. In addition, the difference between the *initial* $[\text{H}_2\text{O}_2]_0$ (0.12 mol dm^{-3}) and that represented by epoxide yield *plus* residual $[\text{H}_2\text{O}_2]_f$ is assumed to be that H_2O_2 lost due to catalysis of dismutation ('catalase' activity). Considering the results for $\text{Fe}(\text{TF}_5\text{PP})\text{Cl}$ (**1**) versus $\text{Fe}(\text{THPP})\text{Cl}$ (**2**) versus $\text{Fe}(\text{TPP})\text{Cl}$ (**3**) shown in Table 1, the *least* efficient in terms of epoxide yield is $\text{Fe}(\text{TPP})\text{Cl}$ with the 'neutral electron demand' phenyl substituent. However, it is clear from Fig. 2 that the increased epoxide yield for $\text{Fe}(\text{TF}_5\text{PP})\text{Cl}$ is due, in part at least, to its greater stability; in other words, it lasts longer allowing more catalytic cycles. The question arises, as to whether the oxidation cycle (e.g. $\text{TF}_5\text{PPFe}^{\text{III}} + \text{H}_2\text{O}_2 \rightarrow (\text{TF}_5\text{PP}^{\bullet+})\text{Fe}^{\text{IV}}=\text{O} + \text{alkene} \rightarrow \text{TF}_5\text{PPFe}^{\text{III}} + \text{epoxide}$ in Scheme 1) is faster or slower for this catalyst compared to the others. A semi-quantitative assessment can be made as follows. The half-life for decay of $\text{Fe}(\text{THPP})\text{Cl}$ (**2**) is ca. 20 s, while that for $\text{Fe}(\text{TF}_5\text{PP})\text{Cl}$ (**1**) is ca. 110 s. Therefore, the latter is some five to six times more stable (under similar conditions—see Table 1), so if we allow for the fact that this stability allows the $\text{Fe}(\text{TF}_5\text{PP})\text{Cl}$ (**1**) to continue to oxidise cyclooctene for six times longer than $\text{Fe}(\text{THPP})\text{Cl}$ (**2**), observed yields of 55 mM versus 8 mM (46 and 7% yields, respectively) suggest that the intrinsic epoxidation reactivities (i.e. the comparative ability to epoxidise assuming no degradation) are not as different for $\text{Fe}(\text{TF}_5\text{PP})\text{Cl}$ and $\text{Fe}(\text{THPP})\text{Cl}$ (46% versus $6 \times 7 = 42\%$) as they at first appear. The apparently greater epoxidation efficiency of $\text{Fe}(\text{TF}_5\text{PP})\text{Cl}$ (**1**) compared to $\text{Fe}(\text{THPP})\text{Cl}$ (**2**) is due mainly to the increased stability of the former. Given our identification of a significant direct

H_2O_2 decay pathway (i.e. not via the oxo-perferryl or oxo-ferryl species) for $\text{Fe}(\text{TF}_5\text{PP})\text{Cl}$ (**1**) in the presence of alkene and H_2O_2 , the improved catalyst stability with electron-withdrawing substituents can be readily rationalised.

The trend in H_2O_2 dismutation activity roughly parallels that for epoxidation for **1–3** (38, ca. 0 and $<2 \text{ mM}$ 'dismutation yields', respectively), in that rapid decay of the catalyst (i.e. for **2** and **3**) reduces the total number of $(\text{por}^{\bullet+})\text{Fe}^{\text{IV}}=\text{O}$ cycles possible, thereby reducing both the alkene epoxidation and the H_2O_2 dismutation yield. The same argument as used above can be applied if the total yields of epoxide + dismutated H_2O_2 are compared (i.e. $55 + 38 = 93 \text{ mM}$ for **1** versus $8 + 0 = 8 \text{ mM}$). If allowance is made for the six-fold faster decay of the catalyst **2**, the ability of **1** to form $(\text{por}^{\bullet+})\text{Fe}^{\text{IV}}=\text{O}$ is only twice that of **2**.

We have not studied the manganese catalysts in detail, but consideration of their UV–VIS spectra under conditions similar to those for the iron catalysts showed minimal decay (as measured by the Soret peak) over several days. A Mn^{III} metalloporphyrin is more electron deficient than a Fe^{III} metalloporphyrin, hence the slower direct porphyrin degradation, and the slower Mn oxidation.

The silica sol–gel encapsulated catalyst, $\text{SiO}_2\text{-2}$ does show some activity, but it is much lower than for the equivalent homogeneous system; the yield of cyclooctene oxide for the $\text{SiO}_2\text{-2}$ system is $3 \times 10^{-3} \text{ mol}$ after 1 day, while that for **2**, under homogeneous conditions, is $8 \times 10^{-3} \text{ mol}$ after 20 min. Furthermore, the nominal metalloporphyrin level in the $\text{SiO}_2\text{-2}$ system is equivalent to $1000 \times 10^{-6} \text{ mol dm}^{-3}$, compared to $20 \times 10^{-6} \text{ mol dm}^{-3}$ for the homogeneous system. Despite this low activity, it is clear that the catalyst is far more stable in its encapsulated form. The free catalyst, **2**, has a half-life under the conditions of Table 1 of ca. 20 s, and is completely bleached by the time of GC analysis for cyclooctene oxide after 20 min. The sol–gel encapsulated version, $\text{SiO}_2\text{-2}$, is still active after 1 day and probably after 3 days; even allowing for the nominally 50-fold higher level of metalloporphyrin present when $\text{SiO}_2\text{-2}$ is used, this constitutes a considerable protection of the catalyst. However, whether or not improved stability of the $\text{SiO}_2\text{-2}$ can compensate for the reduced catalytic activity remains to be seen in further studies. It may

be a case of tailoring the porosity and polarity of the support.

4. Conclusion

In conclusion, we have shown that the so-called ‘catalyst efficiency’ or ‘catalyst activity’ is indeed determined by the competing factors of the $(\text{por})\text{Fe}^{\text{III}} \rightarrow (\text{por}^{\bullet+})\text{Fe}^{\text{IV}}=\text{O} + \text{alkene} \rightarrow (\text{por})\text{Fe}^{\text{III}} + \text{epoxide cycle}$, versus the bleaching of the catalyst. The competition between these two factors may help to rationalise the often contradictory comments on metalloporphyrin reactivity found in the literature.

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