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Evidence for parallel destructive, and competitive epoxidation and dismutation pathways in metalloporphyrin-catalysed alkene oxidation by hydrogen peroxide

Ian D. Cunningham,* Timothy N. Danks, John N. Hay, Ian Hamerton and Suthahari Gunathilagan

Department of Chemistry, School of Physics and Chemistry, University of Surrey, Guildford GU2 7XH, UK

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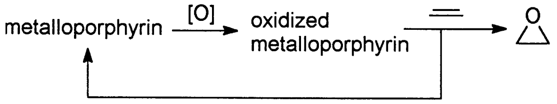
Abstract—A kinetic and product yield analysis of the F$_{20}$TPPFeCl-catalysed H_2O_2 epoxidation of cyclooctene has shown that decomposition is not via either the oxoperferryl intermediate (F$_{20}$TPP$^{+\cdot}$)Fe^{IV}=O or the oxoferryl intermediate F$_{20}$TPPFe^{IV}=O, but appears to involve direct oxidation of the porphyrin in parallel with the catalytic epoxidation cycle. This is in contrast to the reaction of F$_{20}$TPPFeCl in the absence of alkene where decomposition is via F$_{20}$TPPFe^{IV}=O. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Metalloporphyrins have been studied extensively, both as models for the cytochrome P-450 oxidising enzymes and as important oxidation,[1] oxygenation[2] and hydroxylation catalysts[3] in their own right.[4] They have been used with a variety of oxidants, including iodosylbenzenes,[4,5] dioxygen,[6] hydrogen peroxide,[4] hydroperoxides[4] and peracids.[7] Although the general oxidation mechanism shown in Scheme 1 is widely accepted, the fine detail has long been the subject of much debate.

Over the last decade or so, attention has focussed on the nature of the 'oxidised intermediate' especially when formed from reaction with hydrogen peroxide or hydroperoxides (ROOH). One school of thought favours an oxoferryl species por-Fe^{IV}=O formed by homolysis of the peroxide,[8] the other an oxo*per*ferryl species por-Fe^{V}=O, or more likely, (por$^{+\cdot}$)Fe^{IV}=O formed by heterolysis.[1] In addition, there appears to be increasing evidence for 'multiple' active oxidising high-valent intermediates,[9] perhaps formally Fe^{V} but differently ligated.[10] Recently the reactivity of the putative perferryl (por$^{+\cdot}$)Fe^{IV}=O intermediate has been studied; in certain cases, it has been shown to react with H_2O_2[11] and hydroperoxides[11,12] in competition with alkene.



Scheme 1. General pathway for metalloporphyrin-catalysed epoxidation of alkene.

An aspect of metalloporphyrin chemistry that has received less attention is the propensity towards oxidative decomposition (bleaching of the typical Soret band usually ca. 400 nm) with loss of catalytic activity. In published work, this decomposition is often implied, but rarely examined in detail. It is a particular problem with the clean, but powerful, oxidant H_2O_2 and one that we are keen to examine further.

For our study we have chosen the readily-available tetra*kis*(pentafluorophenyl)-21*H*,23*H*-porphine iron(III) chloride (F$_{20}$TPPFeCl) catalyst. It is commercially available, soluble in organic solvents, relatively stable and is an efficient catalyst for use in a range of organic transformations, for example the oxidation of dimethoxyarenes[13] and the epoxidation of hydroxynaphthoquinones.[14] In earlier work we found that the catalyst is rapidly decomposed (bleached) in the presence of H_2O_2 and that decomposition in the absence of a readily-oxidised organic substrate proceeds via an oxo-ferryl species F$_{20}$TPPFe^{IV}=O.[15] In this work we study decomposition during alkene epoxidation and probe the relative reactivity of the heterolysis intermediate (F$_{20}$TPP$^{\cdot+}$)Fe^{IV}=O towards alkene, H_2O_2 and decomposition.

2. Results and discussion

2.1. Preliminary findings

F$_{20}$TPPFeCl-catalysed H_2O_2-oxidation of cyclooctene at 25°C gave 84% yield (GC, relative to standard dodecane) of epoxide based on oxidant, under similar conditions

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Keywords: metalloporphyrin; epoxidation; mechanism; kinetics.

* Corresponding author. Tel.: +44-0-1483-876832; fax: +44-0-1483-876851; e-mail: i.cunningham@surrey.ac.uk

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Table 1. Yields of cyclooctene oxide from the $F_{20}TPPFeCl$-catalysed H_2O_2-epoxidation of cyclooctene in 3:1 MeOH–CH_2Cl_2 at 25°C

Entry	[Cyclooctene]$_0$ (M)	[$F_{20}TPPFeCl$]$_0$[a] (μM)	[H_2O_2]$_0$ (mM)	[Cyclooctene oxide][b] (mM)
1	1.5	0	173	0
2	1.5	25	173	82±12[c,d]
3	1	25	173	98±8
4	0.5	25	173	73±12
5	0.25	25	173	38±13
6	1.5	15	173	73±4
7	1	15	173	57±1
8	0.5	15	173	43±3
9	0.25	15	173	31±5
10	1.5	7.5	173	38±7
11	1	7.5	173	29±3
12	0.5	7.5	173	24±1
13	0.25	7.5	173	16±4
14	1.5	7.5	86	45±3
15	1.5	7.5	173	42±3[e]
16	1.5	7.5	259	34±5

The solvent contained 59 mM dodecane as GC standard, giving typically 44 mM dodecane in the reaction.

[a] Determined by UV–Vis assuming $\epsilon=1.2\times10^5\ M^{-1}\ cm^{-1}$.

[b] Determined by GC after 20 min. UV–Vis showed that all catalyst was bleached after this time.

[c] The yield was ca. 63 mM at 2 min.

[d] Addition of a further 25 μM catalyst gave an increase in [cyclooctene oxide] to ca. 110 mM after a further 20 min (with UV–Vis evidence of unbleached catalyst).

[e] Addition of 2,4-dimethoxyphenol at 0.74 mM gave a cyclooctene oxide yield of ca. 22 mM.

([cyclooctene]$_0$=1.5 M, [H_2O_2]$_0$=0.12 M, [$F_{20}TPPFeCl$]$_0$=0.001 M, in 3:1 MeOH–CH_2Cl_2) to those of Traylor.[2a] However, a reduced yield in a second cycle showed that ca. 50% of the catalyst had been deactivated during the original run.

A repeat of the reaction with a much lower concentration of catalyst ([$F_{20}TPPFeCl$]$_0$=15 μM) gave a UV–Vis spectrum which showed an instantaneous (<ca. 30 s), but small, shift of the Soret band at 402 nm to 405 nm on addition of the H_2O_2 followed by almost complete 'bleaching' of the catalyst spectrum over a few minutes. Importantly, despite the apparent shift in the Soret peak on addition of the H_2O_2, the smaller peaks of $F_{20}TPPFeCl$ at 500 and 580 nm were not noticeably shifted, apart from a very slight increase in the 550 nm region, and decayed in concert with the Soret peak. This pattern of bleaching is different to that observed *in the absence of* alkene substrate where the spectrum of the $F_{20}TPPFeCl$ is replaced, upon addition of the H_2O_2, by one showing a Soret peak at 408 nm (with a shoulder at ca. 395 nm) and a smaller peak ca. 550 nm. We have previously argued that this latter spectrum represents the ferryl species $(F_{20}TPP)Fe^{IV}{=}O$ {or $(F_{20}TPP)Fe^{IV}{-}OH$}.[15]

In the present case the decay of the $F_{20}TPPFeCl$ Soret peak vs. time showed little variation despite a three-fold change in cyclooctene concentration ([cyclooctene]$_0$=0.5, 1.0 and 1.5 M) as shown by the *Abs* vs. *t* plots.

Similar results, lack of significant variation with alkene concentration and a half-life the order of a minute, were found for cyclohexene and styrene. Thus, the rate of catalyst decomposition does not appear to vary significantly with the amount *or* the nature of substrate alkene. In contrast, a three-fold increase in H_2O_2 concentration ([cyclooctene]$_0$=1.5 M, [H_2O_2]$_0$=0.06, 0.12 and 0.18 M) gave a three-fold increase in the rate of catalyst bleaching. The lack of clean pseudo first-order kinetics in the plots is not surprising since, in parallel with catalyst decomposition, there is significant H_2O_2 loss due to catalytic epoxidation of the alkene.

2.2. Epoxide yields

The effects of changes in the various components on the *catalytic cycle* rather than the catalyst decomposition were studied by GC analysis of the product yields under the conditions of Table 1.

It should be noted that only cyclooctene oxide product was detected and that the yield of cyclooctene oxide was always well below quantitative based on the amount of H_2O_2 used (at best 57%), *under these conditions* (micromolar levels of catalyst). The termination of the reaction *prior*to complete consumption of the H_2O_2 was confirmed by the observation: (i) that in all cases the final UV–Vis spectrum of the reaction was bleached in the region of the $F_{20}TPPFeCl$ Soret band, and (ii) that addition of further $F_{20}TPPFeCl$ to a 'terminated' reaction, resulted in further oxide product (Table 1, entry 2 and footnote). *It is clear that the reaction terminates due to destruction of the catalyst.*

Examining the results of Table 1, the following can be noted. (i) An increase in yield of cyclooctene oxide with increase in [cyclooctene]$_0$.[†] (ii) An increase in yield of cyclooctene oxide with increase in [$F_{20}TPPFeCl$]$_0$. (iii) A small decrease in yield of cyclooctene oxide with increase in [H_2O_2]$_0$. The variation of oxide yield with H_2O_2 is less clear than with cyclooctene, but appears to mirror the trend. The variation of yield with [cyclooctene]$_0$ (Table 1, entries 2–13; Table 2, entries 17–20) is clear.

[†] The yield appears to level off or decrease slightly at the highest concentrations of catalyst and cyclooctene. This results was found consistently and may reflect extensive depletion of the oxidant.

Table 2. Combined final epoxide yield and catalyst decay results for the $F_{20}TPPFeCl$-catalysed H_2O_2-epoxidation of cyclooctene in 3:1 MeOH–CH_2Cl_2 at 25°C

Entry	$[\text{Cyclooctene}]_0$ (M)	$[F_{20}TPPFeCl]_0$[a] (μM)	$[H_2O_2]_0$ (mM)	[Cyclooctene oxide][b] (Mm)	$10^4\times k_{obs}$[c] (s^{-1})
17	1.5	3.9	86	25±1	29±1
18	1	3.8	86	23±1	
19	0.5	3.8	86	17±2	
20	0.25	3.8	86	12±3	30±6
21	1.5	4.0	173	20±1[d]	62±4

The solvent contained 59 mM dodecane as GC standard, giving typically 44 mM dodecane in the reaction.

[a] Determined by UV–Vis assuming $\epsilon=1.2\times10^5\ M^{-1}\ cm^{-1}$.

[b] Determined by GC after 20 min. UV–Vis showed that all catalyst was bleached after this time.

[c] Pseudo first order rate constant for decay of $F_{20}TPPFeCl$ determined by monitoring decay of the Soret band at 400 nm.

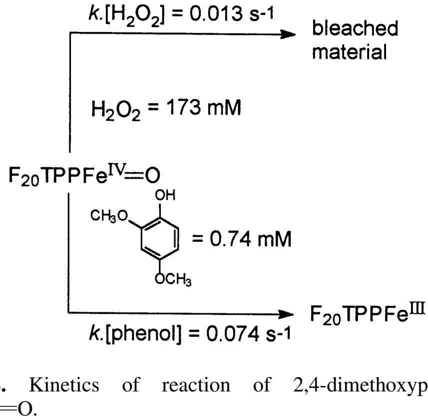
[d] Addition of 2,4-dimethoxyphenol at 0.74 mM gave a cyclooctene oxide yield of ca. 12 mM.

To ensure that the catalyst decomposition data and the product yield data were compatible, several reactions were run where the kinetics of catalyst decomposition and the product analysis were determined in the same run. A low catalyst concentration was used to give cleaner first-order kinetics and the results are gathered in Table 2.

The data of Table 2 help to illustrate more succinctly the key general finding of this work, i.e. *that the amount (and nature) of the alkene influences epoxide yield, but not catalyst decomposition.*

2.3. Test for $F_{20}TPPFe^{IV}{=}O$

Given that the UV–Vis changes accompanying the oxidation of catalyst *in the presence of alkene* are so different to those seen when the catalyst is oxidised to $F_{20}TPPFe^{IV}{=}O$ (i.e. in the absence of alkene),[15] we devised a test for the presence of $F_{20}TPPFe^{IV}{=}O$ *on the decomposition route* during the alkene oxidation reaction. Generation of the $F_{20}TPPFe^{IV}{=}O$ species (408 and ca. 550 nm) in 3:1 MeOH–CH_2Cl_2 containing 0.1 mM H_2O_2, followed by addition of 2,4-dimethoxyphenol gave *regeneration* of the UV–Vis spectrum of the original $F_{20}TPPFe^{III}$ catalyst with a second-order rate constant of the order of 100 $M^{-1}\ s^{-1}$. We reasoned that, since reaction of $F_{20}TPPFe^{IV}{=}O$ with H_2O_2 has a second-order rate constant of ca. 0.074 $M^{-1}\ s^{-1}$,[15] addition of 0.74 mM 2,4-dimethoxyphenol to any reaction in which decomposition via $F_{20}TPPFe^{IV}{=}O$ is significant would allow regeneration of the $F_{20}TPPFe^{III}$, in preference to destruction by H_2O_2 (see calculated pseudo first-order constants in Scheme 2).



Scheme 2. Kinetics of reaction of 2,4-dimethoxyphenol with $F_{20}TPPFe^{IV}{=}O$.

In effect, the 2,4-dimethoxyphenol would 'rescue' the catalyst at this point and allow the catalyst a 'second chance'. The net effect would be to *increase* significantly the yield of epoxide since, as shown earlier, oxidation of alkene terminates 'early' due to catalyst decomposition. It should be noted that, at sub-millimolar levels, the effect of the 2,4-dimethoxyphenol on consumption of H_2O_2 or epoxide product yield (typically at least 12 mM) in any *stoichiometric* reaction (as opposed to its effect on the catalyst decomposition) would be negligible. Reaction at $[H_2O_2]_0=173$ mM, $[F_{20}TPPFeCl]_0=4$ μM, $[\text{cyclooctene}]_0=1.5$ M and $[\text{2,4-dimethoxyphenol}]_0=0.74$ mM gave an epoxide yield of 12 mM somewhat lower than that in the absence of the phenol (see Table 2, entry 21 and footnote). The UV–Vis spectrum after 30 min showed some absorbance (ca. 0.5) in the 350 nm region characteristic of the oxidised phenol raising the possibility of stoichiometric oxidation.[9b] While this would not significantly affect the yield directly, it might indicate oxidation of *all* of the phenol, perhaps by the $(F_{20}TPP^{\cdot+})Fe^{IV}{=}O$ intermediate, before the phenol could react with any $F_{20}TPPFe^{IV}{=}O$ present. However, the absorbance in this region continued to climb over several hours (to ca. 2.0), probably due to oxidation of the phenol by H_2O_2 in the absence of catalyst (bleached after 30 min), suggesting that much of the 2,4-dimethoxyphenol had remained unoxidised during the period of the epoxidation. A similar result was found at higher catalyst concentration (Table 1, entry 15 and footnote).

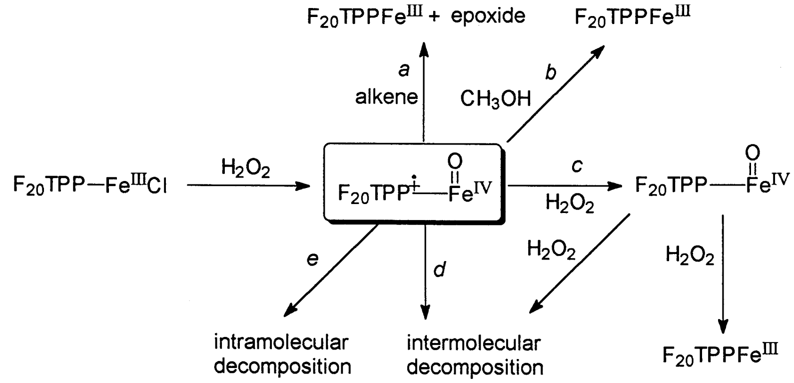
2.4. Fate of H_2O_2

It is clear from the results of Tables 1 and 2 that the yield of epoxide was less than quantitative based on H_2O_2. Certainly, some H_2O_2 remained unused and this was shown by the complete bleaching of the catalyst at the end of the reaction. The question arises as to the fate of the H_2O_2 that was *not* converted to epoxide; did it *all* remain unreacted or was some lost in side reactions such as 'catalase' activity (dismutation of H_2O_2 to H_2O and O_2)? Runs were carried out at much higher catalyst concentration so that the appearance of unbleached catalyst at the end of the reaction could be taken to indicate that no unreacted H_2O_2 remained. The

Table 3. Yield of epoxide for the $F_{20}TPPFeCl$-catalysed H_2O_2-epoxidation of cyclooctene in 3:1 MeOH–CH_2Cl_2 at high catalyst concentration at 25°C

Entry	[Cyclooctene]$_0$ (M)	[$F_{20}TPPFeCl$]$_0$[a] (μM)	[H_2O_2]$_0$ (mM)	[Cyclooctene oxide][b] (mM)	% yield[c]
22	1.5	250	86	68	79
23	0.25	250	86	48	56

The solvent contained 59 mM dodecane as GC standard.
[a] Calculated from stock concentration.
[b] Determined by GC.
[c] Based on H_2O_2.



Scheme 3. Potential reaction pathways for $(F_{20}TPP^{+\cdot})Fe^{IV}{=}O$.

results in Table 3 show that a proportion of the H_2O_2 was 'lost' in non-epoxide producing side reactions.

2.5. Summary

It is worthwhile summarizing the mechanistic evidence from this work [points (iii)–(ix)] and the literature. (i) Epoxide formation is evidence for reaction of alkene with the oxo*per*ferryl species, $(F_{20}TPP^{+\cdot})Fe^{IV}{=}O$.[1,2a,4,12,16] (ii) Reaction of $F_{20}TPPFeCl$ with H_2O_2 in the absence of alkene leads to the oxoferryl species $F_{20}TPPFe^{IV}{=}O$ via the oxoperferryl species (followed by slower bleaching).[15] (iii) Reaction of $F_{20}TPPFeCl$ with H_2O_2 in the presence of alkene results in decomposition of the catalyst without significant build up of $F_{20}TPPFe^{IV}{=}O$. (iv) Trapping evidence suggests that $F_{20}TPPFe^{IV}{=}O$ is *not* a significant 'decomposition' intermediate. (v) The rate of decomposition of $F_{20}TPPFeCl$ in the presence of alkene is independent of the amount and nature of the alkene. (vi) The rate of decomposition of $F_{20}TPPFeCl$ in the presence of alkene *is* dependent on the amount of H_2O_2 added. (vii) The yield of epoxide is, with H_2O_2 as limiting reagent, dependent on the amount and the nature of the alkene present. (viii) A significant proportion of the H_2O_2 consumed does not yield epoxide. (ix) The yield of epoxide appears to be inversely dependent on the amount of H_2O_2 present.

Scheme 3, based on a general one for iron porphyrins outlined by Lindsay Smith in 1991[17] and incorporating additional routes proposed since, shows the various *possible* pathways centred on the formation and subsequent reaction of the proposed $(F_{20}TPP^{+\cdot})Fe^{IV}{=}O$ intermediate (at this point nothing is implied about the *detail* of how this is formed). Pathway *a* is the accepted electrophilic oxygenation of an alkene that regenerates the catalyst in the Fe^{III} state, while pathway *b* represents reaction with solvent (most likely MeOH in this case) to return to Fe^{III}. Pathway *c* involves reaction with H_2O_2 to give the oxoferryl $F_{20}TPPFe^{IV}{=}O$ species (a non-H_2O_2 pathway *c* to $F_{20}TPPFe^{IV}{=}O$ is also possible), which in turn is reduced by further H_2O_2 back to Fe^{III},[1,2a,11,12,18,19] or bleached by H_2O_2.[15,20] Pathways *d* and *e* involve oxidation of the porphyrin part of the catalyst, but mechanistic detail is often unclear. Suggestions include 'self oxidation' (intramolecular), and bleaching of unoxidised catalyst $F_{20}TPPFe^{III}$ by the oxoperferryl intermediate (intermolecular).[1,21]

2.6. The catalytic cycle

There are several immediate inferences considering Scheme 3 in light of the summarised findings above. Firstly, the epoxidation is relatively efficient, most of the H_2O_2 can be converted to epoxide given sufficient catalyst and turnover can be as high as 6410 (see entry 17, Table 2).[‡] Clearly most of the reaction 'flux' is via path *a*. Secondly, analysis of the reaction in the early stages (see Table 1, entry 2 and footnote) gave a yield of cyclooctene oxide of ca. 63 mM after 2 min. A rough calculation, assuming that the initial oxidation of $F_{20}TPPFeCl$ is rate-limiting and therefore that $d[\text{cyclooctene oxide}]/dt=k[H_2O_2]\cdot[F_{20}TPPFeCl]$, gives a lower limit to *k*, the second order rate constant for oxidation of the catalyst to $(F_{20}TPP^{+\cdot})Fe^{IV}{=}O$, of $>149\ M^{-1}\,s^{-1}$. This value is much higher than the $26\ M^{-1}\,s^{-1}$ obtained by us for the same system, but using a 2-hydroxynaphthoquinone as substrate,[15] and closer to the value quoted by Traylor using β-carotene as substrate.[2a] In our earlier paper we were surprised by this discrepancy and postulated (admittedly with little conviction) that the hydroxy substrate

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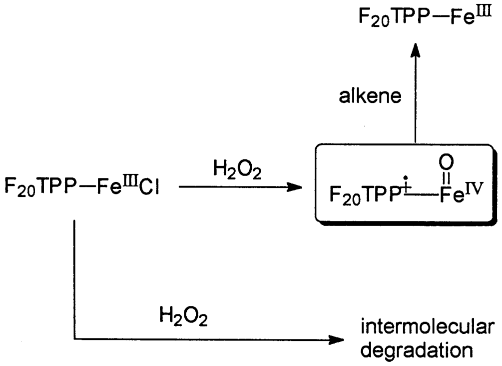
[‡] Turnover is defined as [oxide]/[catalyst]$_0$, and, in effect, the number of epoxide molecules produced during the life of one catalyst molecule.



Scheme 4. Regeneration vs. degradation of $F_{20}TPPFeCl$.

used in that work might have inhibited the catalyst, perhaps by complexation. The present result suggests that there *is* an inhibiting effect when using such hydroxy substrates.

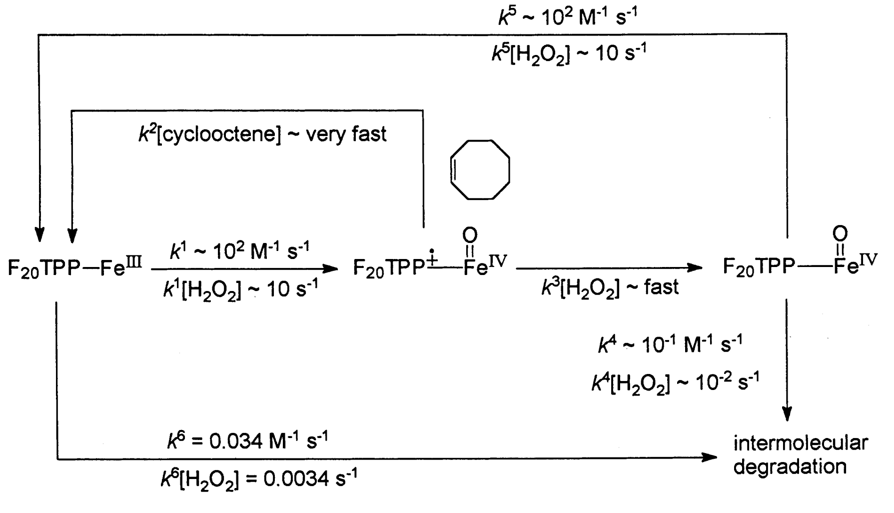
2.7. Catalyst decomposition

The most striking finding in this work is that an increase in concentration of substrate alkene, despite increasing the yield of epoxide, *does not have any effect on the rate of catalyst decomposition* (see Table 2). Clearly, none of the decomposition routes *d*, *e* or the combined *c*$\rightarrow F_{20}TPPFe^{IV}{=}O\rightarrow$ 'decomposition' of Scheme 3 is the *dominant* decomposition route. More generally the result rules out any decomposition route in direct competition with the $(F_{20}TPP^{+\cdot})Fe^{IV}{=}O$+alkene reaction and, in particular, any significant decomposition via the $(F_{20}TPP^{+\cdot})Fe^{IV}{=}O\rightarrow F_{20}TPPFe^{IV}{=}O$ route seen in the absence of alkene. We propose, therefore, a 'new' decomposition pathway in *parallel* with the 'epoxidation cycle' as shown in Scheme 4.

Evidence has recently been reported for parallel heterolytic and homolytic pathways in metalloporphyrin-catalysed epoxidation,[22] and this led us to consider whether our parallel decomposition route is via $F_{20}TPPFe^{IV}{=}O$ or its protonated analogue $F_{20}TPPFe^{IV}{-}OH$ (as distinct from via $F_{20}TPPFe^{IV}{=}O$ formed through $(F_{20}TPP^{+\cdot})Fe^{IV}{=}O$), i.e. a competing *homolytic* route. However, we believe it is not, since addition of 2,4-dimethoxyphenol, known to regenerate $F_{20}TPPFe^{III}$ from $F_{20}TPPFe^{IV}{=}O$ or $F_{20}TPPFe^{IV}{-}OH$, does *not* increase epoxide yield as might be expected if decaying catalyst was regenerated. We believe, therefore, that decomposition results from direct oxidation due to attack by hydroxyl radicals on the porphyrin ring of the 'resting' catalyst, $F_{20}TPPFe^{III}$, while epoxidation activity results from oxidation at the metal. It is, of course, possible that a homolytic cleavage yields $[F_{20}TPPFe^{IV}{-}OH\cdots HO^{\cdot}]$ within a solvent cage; in this case the added phenol would be unable to compete with the caged $HO^{\cdot}$.

2.8. Competition for the oxoperferryl

Of course, if this were the complete reaction scheme, the epoxide yield would be constant across a wide alkene concentration range; examination of Tables 1–3 shows that this is not the case. There is a clear trend of increasing epoxide yield as the alkene concentration is increased. This observation, coupled with the finding that a significant amount of the H_2O_2 is consumed without yielding epoxide, indicates one (or more) additional pathways from $(F_{20}TPP^{+\cdot})Fe^{IV}{=}O$ back to $F_{20}TPPFe^{III}$. The 'yield' studies where H_2O_2 concentration was varied (Table 1, entries 14–16) suggest that the competing route involves H_2O_2, although oxidation of solvent MeOH by the oxoperferryl species (Scheme 3, route *b*) cannot be ruled out. The possibility of reaction of H_2O_2 with $(F_{20}TPP^{+\cdot})Fe^{IV}{=}O$ is surprising because reports have suggested that $(por^{+\cdot})Fe^{IV}{=}O$ species where the porphyrin ring is substituted by electron-withdrawing substituents do *not* react significantly with peroxides in competition with alkene.[2a,11] However, where reaction does occur, the concensus is that regeneration of por-Fe^{III} by H_2O_2 from $(por^{+\cdot})Fe^{IV}{=}O$ is via por-$Fe^{IV}{=}O$ or por-$Fe^{IV}{-}OH$.[1,2a,12,18,23] The reaction of por-$Fe^{IV}{=}O$ (or por-$Fe^{IV}{-}OH$) itself back to por-Fe^{III} does not appear to have been investigated in detail, although it is usually assumed again to involve H_2O_2.[18] Our earlier results show a *decomposition* pathway (*k* ca. $0.074\ M^{-1}\ s^{-1}$) involving $F_{20}TPPFe^{IV}{=}O$ and H_2O_2 so regeneration and destruction may be in competition at this stage. Whatever the $F_{20}TPPFe^{IV}{=}O$



Scheme 5. Pathways involved in $F_{20}TPPFeCl$-catalysed alkene epoxidation by H_2O_2.

reductant is, the rate of the $F_{20}TPPFe^{IV}{=}O \rightarrow F_{20}TPPFe^{III}$ 'regeneration' must, under our reaction conditions, be must faster than degradation of $F_{20}TPPFe^{IV}{=}O$ to be consistent with the kinetic findings above.

2.9. Overall scheme

The above findings are summarised in Scheme 5 where approximate values, from this and others works, are given for some second order rate constants, k^1 (ref.2a), k^4 (ref.15) and k^6 (this work); the accompanying pseudo first order rate constants are calculated for a typical $[H_2O_2]$ of 0.1 M. For step k^5 ($F_{20}TPPFe^{IV}{=}O \rightarrow F_{20}TPPFe^{III}$) it was argued above that this step must be faster than k^4; however, since in the absence of alkene substrate there appear to be both $F_{20}TPPFe^{IV}{=}O$ *and* $F_{20}TPPFe^{III}$ present we have assumed that k^5 is of the same order-of-magnitude as k^1.[§] Steps k^2 and k^3 are likely to be much faster than any of the others. Based on the result of entry 23, Table 3, we propose that $k^2 \sim k^3$.

Scheme 5 is consistent with the results of this and our earlier study.[15] Starting from the resting catalyst $F_{20}TPPFe^{III}$ the reaction flux is partitioned between 'decomposition' and oxidation in the ratio of ca. 0.00034:1 (k^6 vs. k^1). In the *absence* of alkene there is a second partitioning between decomposition and regeneration in the ratio of ca. 0.001:1 (k^4 vs. k^5), so that, overall, decomposition via $F_{20}TPPFe^{IV}{=}O$ and via k^6 are both significant (ca. 3:1). Furthermore, the rapid re-oxidation of regenerated $F_{20}TPPFe^{III}$ in steps k^1 and k^3 allows build-up of $F_{20}TPPFe^{IV}{=}O$ prior to decomposition.[15] However, in the *presence* of alkene the main oxidation flux (k^1) is diverted via k^2[alkene] *away from* the route to $F_{20}TPPFe^{IV}{=}O$ (k^2[cyclooctene] vs. $k^3[H_2O_2]$ ca. 20:1), hence decomposition via $F_{20}TPPFe^{IV}{=}O$ becomes *insignificant*. The partitioning of $(F_{20}TPP^{+\cdot})Fe^{IV}{=}O$ between reaction with alkene and H_2O_2 (k^2 vs. k^3) accounts for the 'non-epoxide' consumption of H_2O_2. Finally, the inclusion of the k^5 step explains why, with ca. 1:20 reaction flux leading to $F_{20}TPPFe^{IV}{=}O$, the overall epoxidation cycle does not 'sink' to non-epoxidising $F_{20}TPPFe^{IV}{=}O$ after ca. 20 cycles (turnover can be >6000).

3. Conclusions

We have shown that the $F_{20}TPPFeCl$-catalysed H_2O_2-epoxidation of alkene, via an oxoperferryl species in a catalytic cycle, is *in parallel* with decomposition which probably involves direct oxidation of the porphyrin rather than the metal. There is no significant decomposition of catalyst via the oxoperferryl or oxoferryl species. The alkene reacts with the high-valent oxoperferryl species in competition, probably with further H_2O_2, both routes leading back (ultimately) to the Fe^{III} species.

4. Experimental

4.1. Materials

$F_{20}TPPFeCl$ was purchased from Aldrich Chemical Co. and was used as received. Aqueous H_2O_2 (ca. 30%) was purchased from Fisons and the concentration was determined by UV–Vis spectroscopy on diluted solutions (λ=242 nm, ϵ=39.4 $M^{-1}\,cm^{-1}$). Solvents were Analar or similar grade. The 2,4-dimethoxyphenol was prepared as described previously.[9b]

4.2. Equipment

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 Philips PU8700 or a Hewlett–Packard 8452A (diode array) spectrometer was used along with a thermostated circulating water bath.

4.3. Protocol

When reactions were carried out using an older batch of H_2O_2 there was some difficulty in reproducibility for decay rates and yield. Therefore, to ensure that results are comparable, the following 'protocol' was adopted. Firstly, stock solutions were prepared and/or tested on a weekly basis. A 'new' bottle of aqueous 30% H_2O_2 was used over ca. six weeks. Furthermore, where trends were to be determined, e.g. the variation in epoxide yield with [cyclooctene] (Table 1, entries 2–5) the same stocks were used and reactions were carried out within 1–2 days. However, duplicate runs were, as far as possible, carried out on different stocks and several days apart (e.g. the duplicated runs giving the data of Table 2, entries 17–21) to ensure that no deterioration had occurred. In general all runs were carried out in at least duplicate, and the uncertainties quoted in the tables refer to standard deviations.

4.4. Method

A typical procedure is as follows. To a silica cuvette were added in order by microsyringe, 1579 μl of 3:1 MeOH–CH_2Cl_2 (containing 59 mM dodecane as GC standard), 390 μl of neat cyclooctene and 8 μl of $F_{20}TPPFeCl$ in 3:1 MeOH–CH_2Cl_2 stock solution (ca. 1 mM). The exact concentration of the $F_{20}TPPFeCl$ was determined by UV–Vis spectroscopy assuming $\epsilon=1.2\times10^5\,M^{-1}\,cm^{-1}$ at 400 nm. After allowing the solution to equilibrate to 25°C for ca. 5 min in a thermostatted UV–Vis spectrometer, the reaction was initiated by the injection of 23 μl of 30% aqueous H_2O_2. (Under these conditions 'cell' concentrations are [dodecane]=47 mM. $[\text{cyclooctene}]_0$=1.5 M, $[F_{20}TPPFeCl]_0$=3.8 μM, $[H_2O_2]_0$=86 mM). For kinetic analysis the decay of the $F_{20}TPPFeCl$ peak at 400 nm was monitored every 10 s for ca. 20 min. For *all* runs, the UV–Vis spectrum after 20 min was checked for bleaching of the catalyst. After 20 min the reaction mixture was analysed by direct injection into the GC and the peaks were identified by comparison of retention times with those of authentic

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[§] In effect, in the absence of alkene, $F_{20}TPPFe^{IV}{=}O$ and $F_{20}TPPFe^{III}$ are in equilibrium with slow decomposition of the latter.

samples. The amount of cyclooctene oxide was quantified by comparison of peak area with that of the dodecane standard (the relative response factor having been established by calibration runs). The *Abs* vs. *t* data from the kinetics experiments was analysed using Excel© (© Microsoft) by Guggenheim's method[24] to give a pseudo-first order rate constant k_{obs}.

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