PERKIN 2

The oxidation of ethylbenzene and other alkylaromatics by dioxygen catalysed by iron(III) tetrakis(pentafluorophenyl)porphyrin and related iron porphyrins

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The oxidation of ethylbenzene with dioxygen catalysed by iron(III) porphyrins in a solvent free system has been studied over the temperature range 30–110 °C. The time dependence of the formation of the three main products, 1-phenylethanol, acetophenone and 1-phenylethyl hydroperoxide, and the fate of the iron porphyrin are interpreted in terms of a free radical autoxidation mechanism. The yields of the oxidation products are determined by the rate of reaction and by the lifetime of the catalyst. Catalyst degradation is shown to involve reaction of the porphyrin ligand with 1-phenylethoxyl and 1-phenylethylperoxyl radicals. The disadvantages of increased induction periods and longer reaction times of the oxidations observed at lower reaction temperatures are counter balanced by increased catalyst turnovers. Less extensive studies on the oxidations of toluene, cumene, (2-methylpropyl)-benzene and *tert*-butylbenzene support the overall mechanism proposed for ethylbenzene.

A comparative study using the catalysts iron(III) 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin and iron(III) tetrakis(pentafluorophenyl)porphyrin and five of its derivatives reveals that halogenation of the β-pyrrole positions markedly increases the activity of the catalysts but not the stability of the porphyrin towards degradation. The highest yields were obtained with the μ-oxodimer of iron(III) tetrakis(pentafluorophenyl)porphyrin and iron(III) tetrakis(4-dimethylamino-2,3,5,6-tetrafluorophenyl)-porphyrin.

Introduction

Environmental and economic pressures, in the field of organic oxidation, are forcing Industry to develop new catalytic routes to the desired products (alcohols, aldehydes, ketones and acids). Ideally these should employ the cheap, clean and atom efficient[1] oxidants, dioxygen or hydrogen peroxide, and a solid or supported catalyst to reduce the environmental impact (E factor)[2] of the process. Nature, which has evolved ways to bring about and control oxidations with these oxidants using enzymes, such as mono- and di-oxygenases, peroxidases and catalases, provides a fertile source of biomimetic ideas for catalyst design. Two of the most thoroughly studied of these are the haem and non-haem monooxygenases[3] and the synthetic complexes that model their catalytic behaviour.

Iron(III) porphyrins can catalyse two distinctly different oxidations of organic compounds by dioxygen. In the first, the reactions require an external reductant to provide two reducing equivalents and in this respect they can be considered as legitimate models for cytochrome P450 monooxygenases[4] [Reaction (1)]. The second class of reactions, investigated originally

$$R{-}H + O_2 + 2e^- + 2H^+ \longrightarrow ROH + H_2O \qquad (1)$$

by Ellis and Lyons[5] and more recently by Gray and Labinger and their co-workers,[6] involve oxidations which function without the need for an external reductant. The mechanisms of the latter are generally now considered to be metalloporphyrin-catalysed free radical oxidations and bear a stronger resemblance to autoxidations rather than to monooxygenase-catalysed oxidations.

The precise role of the iron porphyrin in the latter oxidations remains unclear although halogenation and perhalogenation of the porphyrin ligand have been shown to increase the catalytic activity of the iron complexes. Originally this was interpreted as increasing the oxygen-transfer reactivity of an oxoiron(IV) porphyrin intermediate which was considered an active species in alkane hydroxylation.[5b–d,6d] However, if the reactions are effectively autoxidations, the role of the iron porphyrin may be to maintain the oxy-radicals necessary for the chain reaction and, in support of this conclusion, perhalogenated iron porphyrins are known to be very effective at decomposing alkyl hydroperoxides.[4a,5b,e,6d]

This study was initiated with two aims in mind; first, to find out more about the mechanism of the homogeneous oxidation of saturated C–H bonds with dioxygen catalysed by iron porphyrins and, secondly, to try to develop new supported iron porphyrin systems to bring about the same oxidations. With these aims in mind, we selected alkylaromatics as substrates and iron(III) tetrakis(pentafluorophenyl)porphyrin as the principal catalyst. This iron porphyrin was chosen because it is reported to be a good catalyst for alkane oxidation by dioxygen,[5f,6c] it is easily prepared (the ligand is commercially available) and it can readily be modified by halogenation of the β-pyrrole positions and by nucleophilic substitution of the *para*-fluorines on the pentafluorophenyl groups. The last reaction provides a route to linking the catalyst covalently to the support.[7] This paper reports the results from our studies with homogeneous systems and a subsequent paper will describe our work with supported catalysts.

Results and discussion

Method

This study is concerned with the oxidation of alkylbenzenes, in particular ethylbenzene, by dioxygen catalysed by (FeTPFPP)-

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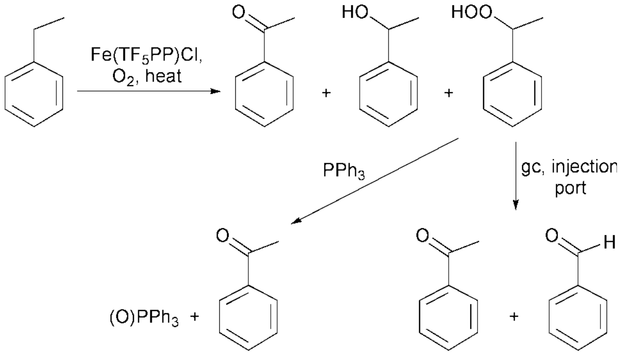
Cl† and some related iron porphyrins. The oxidations were carried out with the alkylbenzene acting as both the substrate and the solvent for the iron porphyrin under one atmosphere of dioxygen, in the temperature range 30–110 °C. The product formation and the catalyst destruction were followed by GC analysis and UV–VIS spectroscopy, respectively.

Oxidation of ethylbenzene

Products. The metalloporphyrin-catalysed oxidation of ethylbenzene with dioxygen gives three major products (1-phenylethyl hydroperoxide, 1-phenylethanol and acetophenone) (Scheme 1) and trace amounts of three other products [benzaldehyde, benzoic acid and bis(1-phenylethyl) ether]. All the products, except the hydroperoxide, were stable to the GC conditions. The latter, however, with the analytical conditions used in this study, was thermolysed in the gas chromatograph and an alternative method of analysis had to be devised to obtain the yields of this compound.



Scheme 1

The analysis of the hydroperoxide made use of the clean and quantitative room temperature reduction of hydroperoxides to alcohols by triphenylphosphine.[8] When the PPh_3 reduction was applied to the PhEt oxidation mixture, GC analysis showed that, compared to the measured yields before PPh_3 treatment, the amount of acetophenone detected decreased and the amount of 1-phenylethanol increased by an equal quantity. Interestingly the majority of the minor product benzaldehyde was also removed by the reduction. These results suggest that, apart from the small amount of benzaldehyde formed, effectively all of the hydroperoxide is thermolysed in the GC to acetophenone (Scheme 1). Consequently GC analysis of the reaction mixture before and after PPh_3 treatment allowed the hydroperoxide yield to be quantified. The direct analysis of the oxidation mixture gave the 1-phenylethanol and bis(1-phenylethyl) ether yields, repeat analysis after PPh_3 treatment gave the acetophenone and benzaldehyde yields and, by difference between the two analyses, the yield of the hydroperoxide was obtained. The excess of PPh_3 employed was optimised to ensure complete reduction of the hydroperoxide without reduction of the GC internal standard, 1,3-dichlorobenzene.[9] The benzoic acid yields were measured by GC analysis after conversion to the methyl ester using diazomethane.

$$\mathrm{PhCH_2CH_3 + O_2 \longrightarrow Ph\dot{C}HCH_3 + HO_2^{\bullet}} \tag{2}$$

$$\mathrm{Ph\dot{C}HCH_3 + O_2 \longrightarrow PhCH(CH_3)O_2^{\bullet}} \tag{3}$$

$$\mathrm{PhCH(CH_3)O_2^{\bullet} + PhCH_2CH_3 \longrightarrow PhCH(CH_3)O_2H + Ph\dot{C}HCH_3} \tag{4}$$

$$\mathrm{2PhCH(CH_3)O_2^{\bullet} \longrightarrow 2PhCH(CH_3)O^{\bullet} + O_2} \tag{5}$$

$$\mathrm{PhCH(CH_3)O^{\bullet} + PhCH_2CH_3 \longrightarrow PhCH(CH_3)OH + Ph\dot{C}HCH_3} \tag{6}$$

$$\mathrm{PhCH(CH_3)O^{\bullet} + PhCH(CH_3)O_2H \longrightarrow PhCH(CH_3)OH + PhCH(CH_3)O_2^{\bullet}} \tag{7}$$

$$\mathrm{2PhCH(CH_3)O_2^{\bullet} \longrightarrow PhCH(CH_3)OH + PhC(CH_3){=}O + O_2} \tag{8}$$

$$\mathrm{PhCH(CH_3)O_2^{\bullet} + Ph\dot{C}HCH_3 \longrightarrow PhCH(CH_3)OOCH(CH_3)Ph} \tag{9}$$

$$\mathrm{2PhCH(CH_3)O^{\bullet} \longrightarrow PhCH(CH_3)OH + PhC(CH_3){=}O} \tag{10}$$

$$\mathrm{PhCH(CH_3)O_2H \longrightarrow PhC(CH_3){=}O + H_2O} \tag{11}$$

$$\mathrm{PhCH(CH_3)O_2H \longrightarrow PhCH(CH_3)O^{\bullet} + HO^{\bullet}} \tag{12}$$

The results obtained are wholly consistent with a typical autoxidation process [Reactions (2)–(12)] in which the redox reactions of the iron porphyrin catalyse the formation and maintain the flux of oxygen centred radical chain carriers [Reactions (13)–(19)]. Two key characteristic features of these reactions, namely the induction period which increases with a decrease in reaction temperature and the formation of 1-phenylethyl hydroperoxide as a major reaction product, support this conclusion. The radicals also lead to the oxidation of the iron porphyrin and the reaction effectively stops when all the catalyst is destroyed (Figs. 1 and 2), thus the overall yield is determined by the rate of reaction and the lifetime of the catalyst.

$$\mathrm{PhCH(CH_3)O_2^{\bullet} + Fe^{II}P \longrightarrow PhCH(CH_3)OOFe^{III}P} \tag{13}$$

$$\mathrm{PhCH(CH_3)OOFe^{III}P \longrightarrow PhC(CH_3){=}O + HOFe^{III}P} \tag{14}$$

$$\mathrm{PhCH(CH_3)O_2H + Fe^{II}P \longrightarrow PhCH(CH_3)O^{\bullet} + HOFe^{III}P} \tag{15}$$

$$\mathrm{PhCH(CH_3)O_2H + Fe^{II}P \longrightarrow PhCH(CH_3)OH + OFe^{IV}P} \tag{16}$$

$$\mathrm{PhCH(CH_3)O_2H + Fe^{III}P \longrightarrow PhCH(CH_3)O_2^{\bullet} + Fe^{II}P + H^+} \tag{17}$$

$$\mathrm{PhCH(CH_3)O_2H + Fe^{III}P \longrightarrow PhCH(CH_3)O^{\bullet} + OFe^{IV}P} \tag{18}$$

$$\mathrm{PhCH(CH_3)O_2H + OFe^{IV}P \longrightarrow PhCH(CH_3)O_2^{\bullet} + HOFe^{III}P} \tag{19}$$

$$\mathrm{PhCH(CH_3)O^{\bullet} + Ph\dot{C}HCH_3 \longrightarrow PhCH(CH_3)OCH(CH_3)Ph} \tag{20}$$

$$\mathrm{Ph\dot{C}HCH_3 + PhCH(CH_3)OOFe^{III}P \longrightarrow PhCH(CH_3)OCH(CH_3)Ph + OFe^{IV}P} \tag{21}$$

Bis(1-phenylethyl) ether has been reported previously as a product from the autoxidation of ethylbenzene[10] and it is likely that it arises from the 1-phenylethyl radical either by combination with the 1-phenylethoxyl radical [Reaction (20)] or by an S_H2 reaction such as Reaction (21). The 1-phenylethyl radical

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† The following abbreviations are used for porphyrin ligands: TPFPP, 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin; $TTFNMe_2$-PP, 5,10,15,20-tetrakis(4-dimethylamino-2,3,5,6-tetrafluorophenyl)-porphyrin; TTFOPhPP, 5,10,15,20-tetrakis(4-phenoxy-2,3,5,6-tetrafluorophenyl)porphyrin; TPFPP-Cl_8, 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin; TPFPP-Br_8, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin; TDCPP-Cl_8, 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra-2,6-dichlorophenyl)porphyrin and $[Fe(TPFPP)]_2O$ is the μ-oxo dimer of Fe(TPFPP). Porphyrin ligands in reactions are denoted by P.

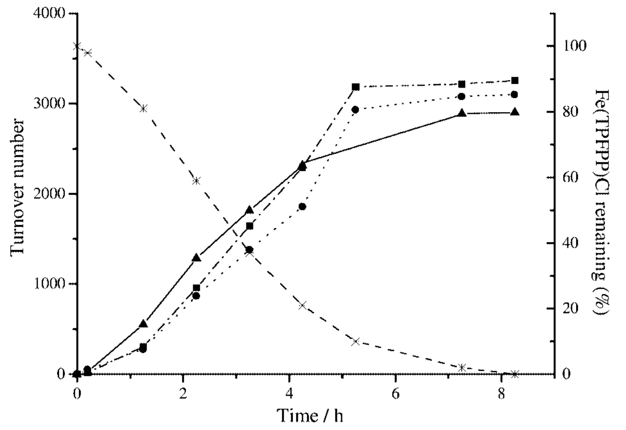


Fig. 1 Product turnover *versus* time (left axis) and catalyst destruction *versus* time (right axis) in the Fe(TPFPP)Cl-catalysed oxidation of ethylbenzene by dioxygen at 70 °C; ···●··· 1-phenylethyl alcohol, —▲— 1-phenylethyl hydroperoxide, —·■·— acetophenone, —*— Fe(TPFPP)Cl.

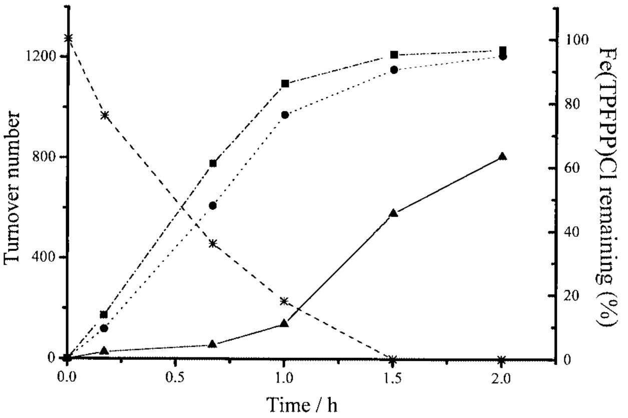


Fig. 2 Product turnover *versus* time (left axis) and catalyst destruction *versus* time (right axis) in the Fe(TPFPP)Cl-catalysed oxidation of ethylbenzene by dioxygen at 100 °C; ···●··· 1-phenylethyl alcohol, —▲— 1-phenylethyl hydroperoxide, —·■·— acetophenone, —*— Fe(TPFPP)Cl.

will only be present in very low concentrations as it is efficiently scavenged by dioxygen [Reaction (3)]. However, Caldwell and Porter[11] recently showed that the cumylperoxyl radical at 80 °C in one atmosphere of dioxygen is in equilibrium with the cumyl radical and dioxygen. Assuming the same equilibrium occurs with 1-phenylethylperoxyl radicals, this would provide the low steady-state concentration of 1-phenylethyl radicals necessary for the formation of the ether.

The traces of benzaldehyde detected by GC analysis of the oxidation mixtures arise from the thermolysis of 1-phenylethyl hydroperoxide and are almost entirely removed by pretreatment of the oxidation mixture with triphenylphosphine. The small amount that is present even after the reduction of the hydroperoxide most probably arises from thermal degradation in the reaction mixture or from loss of a methyl radical in the β-scission of the 1-phenylethoxyl radical [Reaction (22)]. An

$$PhCH(CH_3)O^{\bullet} \longrightarrow PhCHO + CH_3^{\bullet} \qquad (22)$$

alternative source of the benzaldehyde, the thermal degradation of benzyl hydroperoxide from the autoxidation of traces of toluene in the ethylbenzene, was eliminated since triphenylphosphine treatment would have given benzyl alcohol and this was not detected in the pretreated reaction mixtures.

Temperature dependence of the reaction. The oxidation of PhEt was investigated between 30 and 110 °C. Under all the conditions, the reactions showed an induction period, oxidative destruction of the catalyst and the same three major products. Figs. 1 and 2, which show typical reaction profiles for oxidations at 70 and 100 °C, illustrate how the reaction is much faster at higher temperatures. A further change that occurs at ~80 °C involves the build-up of the hydroperoxide which below this temperature occurs from the start of the oxidation (Fig. 1) whereas at higher temperatures it is only significant towards the end of the reaction, when most of the catalyst has been destroyed (Fig. 2). Other changes that occur as the temperature of the oxidation is lowered include increases in the induction period, the catalyst's life-time (Fig. 3) and the final yields (measured as catalyst turnovers, Fig. 4); the total numbers of catalyst turnovers were 2500 and 10 000 at 100 and 40 °C, respectively.

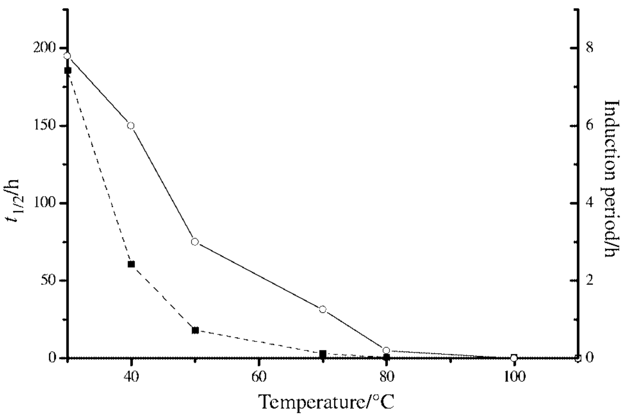


Fig. 3 The effect of temperature on the catalyst activity/stability in the Fe(TPFPP)Cl-catalysed oxidation of ethylbenzene; —■— $t_{1/2}$ (left axis), —○— induction period (right axis).

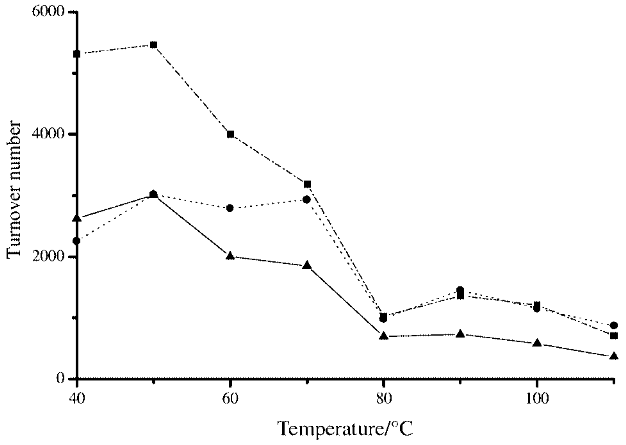


Fig. 4 The effect of temperature on the total turnovers obtained in the Fe(TPFPP)Cl-catalysed oxidation of ethylbenzene; ···●··· 1-phenylethyl alcohol, —▲— 1-phenylethyl hydroperoxide, —·■·— acetophenone.

Control reactions were carried out at all the temperatures studied. These involved oxidations in the absence of the Fe(TPFPP)Cl catalyst and oxidations with the iron porphyrin replaced by an equivalent amount of iron(III) chloride. In neither case were products formed in yields greater than 1.5% of those found in the analogous Fe(TPFPP)Cl-catalysed oxidation.

The reactions of ethylbenzene are most simply discussed under two temperature regimes, above and below 80 °C.

High temperature (80–110 °C) oxidations of ethylbenzene. Increasing the oxidation temperature from 80 to 110 °C reduces the reaction time from 1.5 h to 30 min. Unfortunately this increase in the rate of oxidation is matched by an equivalent increase in the rate of destruction of the catalyst and the overall

Table 1 Low resolution FAB$^+$-MS data from analysis of partially degraded Fe(TPFPP)Cl removed from an ethylbenzene oxidation at 100 °C

Mass (m/z)	Intensity (%)	Mass gain over parent ion	Product inference
1028	100	0	Fe(TPFPP)
1148	11	120	$PhCH(CH_3)O^•$, substitution
1150	4	122	$PhCH(CH_3)OH$, addition
1164	3	136	$PhCH(CH_3)O_2^•$, substitution
1166	5	138	$PhCH(CH_3)O_2H$, addition
1268	2	240	$PhCH(CH_3)O^•$, substitution × 2
1286	2	258	$PhCH(CH_3)O^•$, substitution and $PhCH(CH_3)O_2H$ addition or *vice versa*
1304	1	276	$PhCH(CH_3)O_2H$, addition × 2

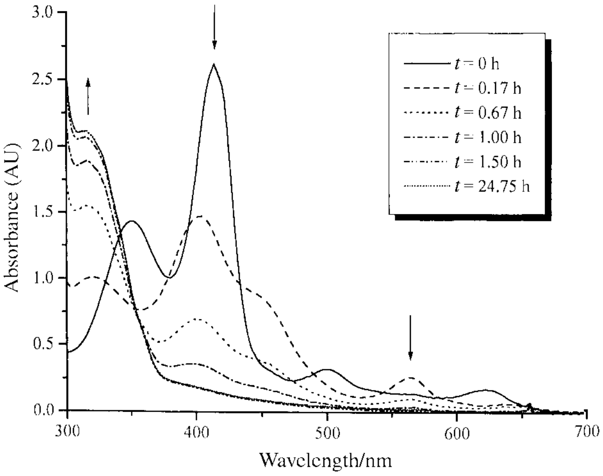


Fig. 5 UV–VIS spectra showing the decay of Fe(TPFPP)Cl with time, over 25 h, in the oxidation of ethylbenzene by dioxygen at 100 °C.

yield of products (measured as catalyst turnovers) remains relatively unchanged, 2300 ± 500 turnovers. The fate of the catalyst in the reactions was investigated by UV–VIS and mass spectroscopy.

In the first few minutes of all the reactions carried out at ≥80 °C, the colour of the solution changed from green–black to vivid orange. UV–VIS spectra of the latter reaction mixtures revealed that the initial Fe(TPFPP)Cl species (Soret λ_{max} 414 nm) was converted to a new iron porphyrin (Soret λ_{max} 404 nm with a shoulder at 448 nm) and this species subsequently decayed as the catalyst was consumed during the oxidation (Fig. 5). We attribute these changes to the exchange of the axial chloride ligand. The alternative explanation that the iron porphyrin has been either oxidised to the oxoiron(IV) species or reduced to iron(II) tetrakis(pentafluorophenyl)porphyrin can be eliminated. Neither species would be expected to be stable under the reaction conditions, furthermore the absorption maxima of their Soret bands would be ~420 nm,[12,13] which is not consistent with the spectrum of the reaction mixture. Two possible species, Fe(TPFPP)OH and $[Fe(TPFPP)_2O]$, that have blue-shifted Soret bands relative to that of Fe(TPFPP)Cl were shown not to be the orange species formed in the reaction by comparison of UV–VIS spectra using authentic samples. A third porphyrin complex, $Fe(TPFPP)O_2CH(Me)Ph$, was rejected because, although, based on the work of Balch and co-workers with the analogous ethylperoxy species of iron(III) tetrakis(4-methylphenyl)porphyrin,[14] it might be stable at low temperatures it will only be a reactive intermediate at the temperatures used in this study. The possibility that the axial chloride was replaced by the product 1-phenylethanol seems unlikely since reacting Fe(TPFPP)Cl with 100 equivalents of the alcohol did not result in a change in the UV–VIS spectrum of the iron porphyrin. We conclude that the vivid orange species in the oxidation mixture is the 1-phenylethoxide complex, Fe(TPFPP)-OCH(Me)Ph, which arises from the reaction of the iron(II) porphyrin with the 1-phenylethoxyl radical [Reaction (23)].

$$PhCH(CH_3)O^• + Fe^{II}P \longrightarrow PhCH(CH_3)OFe^{III}P \quad (23)$$

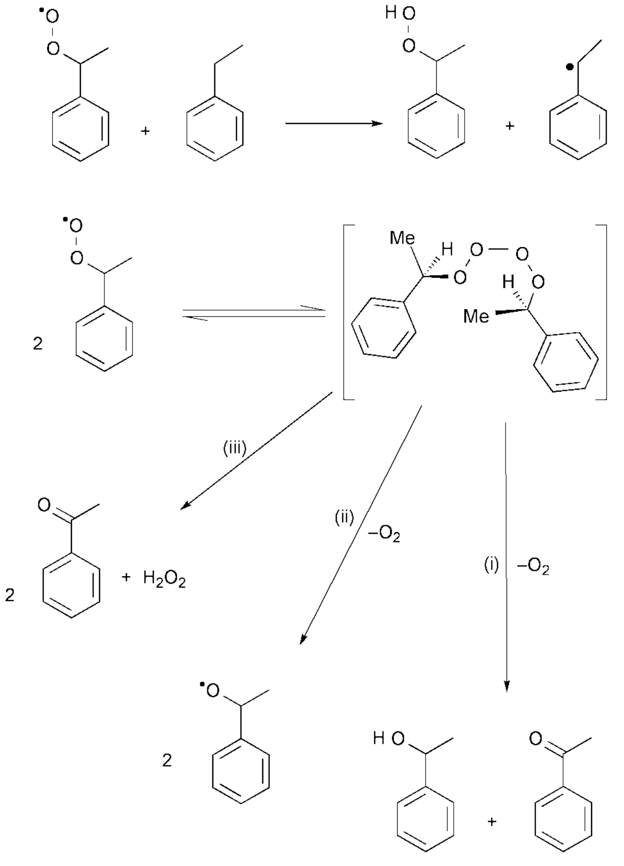
Confirmation of the identity of the porphyrin species comes from the reaction of Fe(TPFPP)Cl with potassium 1-phenylethoxide which resulted in identical colour and UV–VIS spectral changes to those observed in the oxidation of 1-phenylethanol.

Catalyst degradation. The cause of the catalyst destruction was examined by recovering the catalyst and partially oxidised catalyst from an oxidation of ethylbenzene at 100 °C after 30 min reaction and subjecting this to FAB$^+$-MS. From the intensities of the peaks relative to that from the parent porphyrin molecular ion, two types of reaction on the macrocycle are readily identified, namely addition of PhCH(OH)Me and $PhCH(O_2H)Me$ (increase in m/z of 122 and 138 mass units) and substitution of H by 1-phenylethoxyl and 1-phenylethylperoxyl (increase in m/z of 120 and 136 mass units) (Table 1).

Based on the peak intensities in the mass spectrum, the main attacking species is the alkoxyl radical and the major reaction is substitution, presumably of the β-pyrrole hydrogens. In support for this conclusion, Gonsalves and co-workers reported that catalyst destruction in the reaction of iron(III) 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin with H_2O_2 occurs by substitution of the chlorines at the β-pyrrole positions.[15] However, whether the reaction proceeds *via* radical addition, to give the observed product with m/z 1150, followed by oxidation or directly by oxidation of the radical adduct is unclear. The resulting chemically modified iron porphyrin species are likely to act as catalysts for the oxidation of ethylbenzene, however, their further reaction will inevitably lead to the destruction of the macrocycle and loss of catalytic activity.

Low Temperature (30–70 °C) oxidations of ethylbenzene. Lowering the temperature of the oxidations from 70 to 30 °C slows down the reactions dramatically and leads to very long induction periods; at 70 °C the reaction is complete in 8 h (including the induction period) (Fig. 1), whereas at 30 °C the induction period is 8 h and the reaction is only half complete in 174 h (Fig. 3). However, there are yield benefits from carrying out the reactions at low temperatures; the oxidation at 40 °C gave 10 000 turnovers overall whilst only 2800 were obtained at 80 °C. There are three other key differences between the high and low temperature oxidation regimes. In the low temperature oxidations, 1-phenylethyl hydroperoxide is detected as a major product from the start of the reaction (*e.g.* Fig. 1), the yield of acetophenone is higher than that of 1-phenylethanol (alcohol : ketone ratio < 1.0) (Fig. 4) and there is no change in colour of the reaction or UV–VIS spectrum of the iron porphyrin. The last observation suggests that at the lower temperatures no exchange of the chloride ligand occurs.

Mechanistic conclusions based on the oxidation of ethylbenzene. In the autoxidation of ethylbenzene, the two key chain carriers are the 1-phenylethyl and 1-phenylethylperoxyl radicals [Reactions (3) and (4)] and since Reaction (3) is diffusion controlled, essentially all the former radicals are trapped by dioxygen, except under low dioxygen concentration (not those used in this study), to give 1-phenylethylperoxyl radicals.[6a,16] Consequently the oxidation products depend on the fate of the peroxyl radicals: these undergo competing reactions, the relative importance of which depends on the reaction temperature and on the concentration of the radicals (Scheme 2). At low temperatures, 1-phenylethyl hydroperoxide, the product of the propagation reactions (3) and (4), is thermally stable and termination is by the combination of 1-phenylethylperoxyl radicals to give tetroxides. The latter decompose predominantly by the Russell mechanism[17] [Reaction (8), Scheme 2, pathway (i)] giving equal yields of alcohol and ketone. At high temperatures the Russell mechanism is disfavoured relative to fragmentation to give two phenylethoxyl radicals [Reaction (5), Scheme 2, pathway (ii)].[18] Gal and co-workers,[18b] studying the autoxidation of ethylbenzene, estimated that, at 90 °C, 55% of the tetroxide decomposes *via* the alkoxyl pathway.

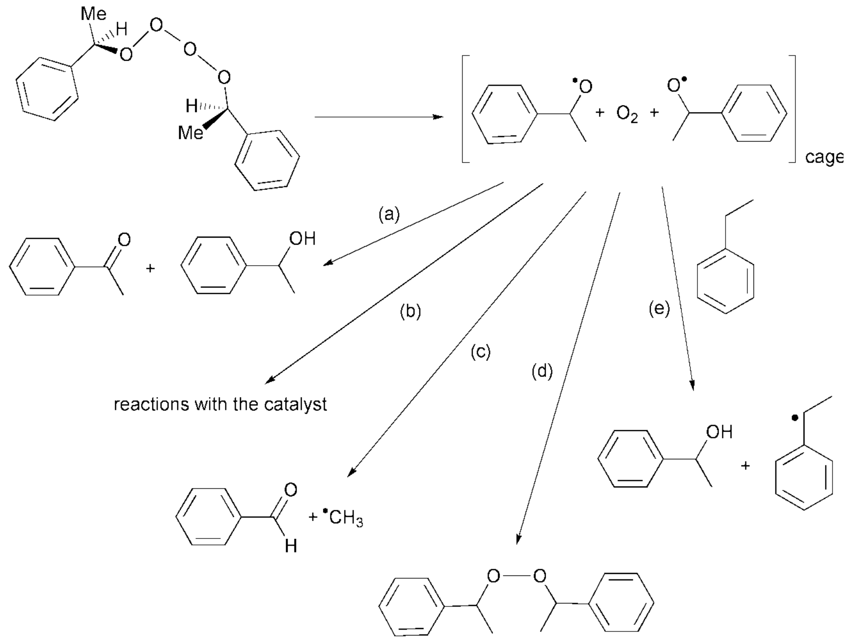


Scheme 2

From the above discussion it is clear that the low temperature autoxidation of ethylbenzene would be expected to give mainly 1-phenylethyl hydroperoxide with 1-phenylethanol and acetophenone formed in smaller but approximately equal amounts. Although the Fe(TPFPP)Cl-catalysed oxidation gives the expected three products, the ketone and not the hydroperoxide predominates (Fig. 4). We interpret this difference in product distribution to two types of reaction involving the catalyst which consume 1-phenylethylperoxyl radicals and 1-phenylethyl hydroperoxide, namely Reaction (13) followed by Reaction (14), and the redox reactions of the iron porphyrin species with the hydroperoxide [Reactions (15)–(19)]. The former, which were first proposed by Balch and co-workers[14,19] for the reaction of alkylperoxyiron(III) tetraarylporphyrins, are effectively a chain terminating step leading to acetophenone. On the other hand, the redox reactions, all of which result in the consumption of 1-phenylethyl hydroperoxide, with the exception of Reaction (16), initiate new radical chain reactions with either peroxyl or alkoxyl radicals.

A further reaction that could contribute to the greater yield of acetophenone over 1-phenylethanol is path (iii) in Scheme 2. Bennett and Summers[20] proposed this reaction to account for the preference for ketone formation in the reactions of secondary alkylperoxyl radicals at low temperatures and it was used by Waddington and co-workers[21] to account for the excess of acetone over propan-2-ol formed in the photolysis of 2,2′-azopropane in oxygenated decane.

Increasing the temperature of the autoxidation leads to increased production of 1-phenylethoxyl radicals by decomposition of the tetroxide, however, since the alkoxyl radicals are formed as a geminate pair in a solvent cage,[18b,c,22] they are well set up to self-react: this, like the Russell mechanism above, gives equivalent yields of alcohol and ketone [Reaction (10), Scheme 3, path (a)].[18b,23] A further minor pathway, not detected in this study, forms the peroxide [Scheme 3, path (d)][6a,18c] which at



Scheme 3

high temperatures is known to decompose to regenerate the solvent caged geminate pair of alkoxyl radicals.[24] Alternatively, the alkoxyl radicals can diffuse from the solvent cage to react with the catalyst or ethylbenzene or undergo β-scission [Scheme 3, paths (b), (e) and (c), respectively]. The first of these leads to the observed exchange of the axial ligand and to catalyst degradation [Reactions (23) and (24)]. The second leads to

$$\mathrm{PhCH(CH_3)O^{\bullet} + Fe^{III}P \longrightarrow Catalyst\ destruction} \quad (24)$$

1-phenylethanol and initiation of a new chain reaction. The last gives benzaldehyde and its further oxidation product, benzoic acid; the low yields of these, however, suggest that, under the reaction conditions studied, loss of a methyl radical by β-scission [Scheme 3, path (c)] is a minor pathway for the 1-phenylethoxyl radicals.

Increasing the temperature of the autoxidation leads to an increase in 1-phenylethanol relative to acetophenone and at the highest temperature studied the alcohol becomes the major product (alcohol : ketone = 1.23 at 110 °C). We attribute this change in the product distribution to the increasing importance of the 1-phenylethoxyl radical in the reaction mixture with increasing temperature arising from the preferred radical fragmentation of the tetroxide [Reaction (5), Scheme 2, path (ii)] and possibly from the thermolysis of the hydroperoxide [Reaction (12)]. The geminate radical pair from the former reaction can, as discussed above, disproportionate, however, cage escape leading to alternative reactions of the alkoxyl radical will become more important at higher temperatures due to the reduced viscosity of the reaction solution.[25]

The oxidation temperature of 80 °C appears to be a mechanistic turning point for the oxidation. Below this temperature, no axial ligand exchange occurs, no benzaldehyde is detected and catalyst destruction becomes very slow. These three observations can be accounted for by assuming that the 1-phenylethoxyl radical is involved in all these reactions. Reactions at $\leqslant 70$ °C generate peroxyl radicals and relatively few of the more aggressive alkoxyl radicals whereas increasing the temperature above 70 °C leads to more alkoxyl radicals and their reaction products.

Further support for this conclusion is evident from the build-up of 1-phenylethyl hydroperoxide in the reactions. At low temperatures it is a major product from the start of the reaction but at high temperatures it only builds up towards the end of the reaction. This can be accounted for by considering the main competing reactions of the peroxyl radical, [Reactions (4) and (8)], the rates of which are given by eqns. (25) and (26), respectively.

$$\mathrm{d[RO_2H]/d}t = k_4\mathrm{[RO_2^{\bullet}][PhEt]} \quad (25)$$

$$-\,\mathrm{d[RO_2^{\bullet}]/d}t = k_8\mathrm{[RO_2^{\bullet}]^2} \quad (26)$$

Based on literature values for k_4 and k_8, 1.2 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ and 3.03×10^7 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$, respectively at 30 °C,[26] a steady state concentration of 1-phenylethylperoxyl radicals of 10^{-6} mol $\mathrm{dm^{-3}}$ favours the self-reaction of the peroxyl radicals, however, at 10^{-8} mol $\mathrm{dm^{-3}}$ there is a 30-fold preference for 1-phenylethyl hydroperoxide formation. From these data, in the slow, low temperature oxidations or in the high temperature reactions when most of the catalyst has been destroyed $\mathrm{[RO_2^{\bullet}]}$ will be very small and hydroperoxide formation, Reaction (4), will be the favoured route. At high temperatures, before the catalyst has been degraded, $\mathrm{[RO_2^{\bullet}]}$ will be relatively high and the self-reaction of $\mathrm{RO_2^{\bullet}}$ will be favoured. Furthermore, the latter reaction will result predominantly in 1-phenylethoxyl radicals [Scheme 2, path (ii)] with significant cage escape leading to the observed products.

Oxidations in the presence of a hydroperoxide initiator. The oxidations of ethylbenzene at $\leqslant 80$ °C have significant induction periods and show that 1-phenylethyl hydroperoxide builds up from the beginning of the reaction suggesting that, somewhat surprisingly, the catalyst does not decompose the hydroperoxide very efficiently at the lower temperatures. Two commercially available hydroperoxides, $\mathrm{{}^tBuO_2H}$ and $\mathrm{PhCMe_2O_2H}$ [65–260 equivalents relative to Fe(TPFPP)Cl], were investigated as potential initiators for the oxidation at 40 °C and also to examine the ability of Fe(TPFPP)Cl to decompose hydroperoxides at these lower reaction temperatures. The two hydroperoxides showed marked differences in reactivity, the former removes the induction period and clearly reacts very rapidly with the iron porphyrin (Fig. 6) although the increase in $\mathrm{[RO^{\bullet}]}$ leads to more rapid catalyst destruction and lower yields overall. In contrast, the latter hydroperoxide reduces but does not eliminate the induction period (50 min compared with 6 h) and is decomposed slowly during the course of the reaction and the catalyst is destroyed more slowly than with *tert*-butyl hydroperoxide (Fig. 7). These results suggest that both arylalkyl hydroperoxides and *tert*-butyl hydroperoxide react with Fe(TPFPP)Cl but that reactions of the former are much slower.

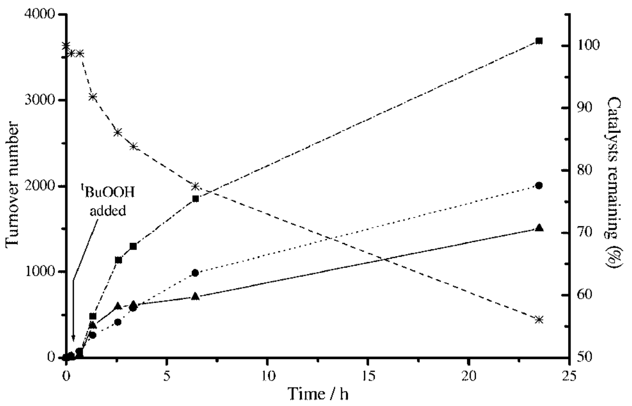


Fig. 6 Product turnover *versus* time (left axis) and catalyst destruction *versus* time (right axis) in the Fe(TPFPP)Cl-catalysed oxidation of ethylbenzene by dioxygen in the presence of $\mathrm{{}^tBuO_2H}$ [260-fold excess over Fe(TPFPP)Cl] at 40 °C; ···●··· 1-phenylethyl alcohol, —▲— 1-phenylethyl hydroperoxide, –·–■–·–– acetophenone, --*-- Fe(TPFPP)Cl.

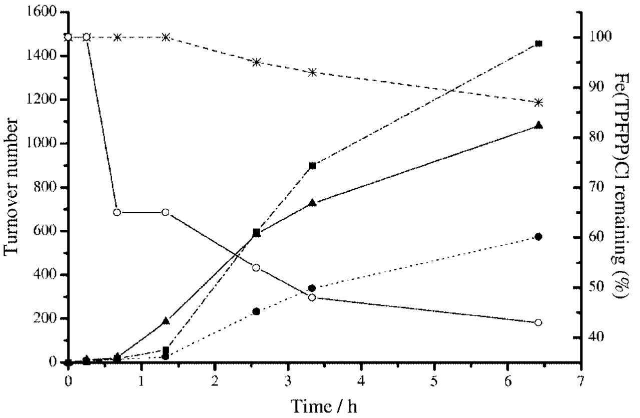


Fig. 7 Product turnover *versus* time (left axis) and catalyst destruction and hydroperoxide consumption *versus* time (right axis) in the Fe(TPFPP)Cl-catalysed oxidation of ethylbenzene by dioxygen in the presence of cumene hydroperoxide [260-fold excess over Fe(TPFPP)Cl] at 40 °C; ···●··· 1-phenylethyl alcohol, —▲— 1-phenylethyl hydroperoxide, –·–■–·– acetophenone, ––*–– Fe(TPFPP)Cl, —○— $\mathrm{PhMe_2O_2H}$.

The initiation of the low temperature ethylbenzene oxidations is likely to involve redox reactions between the catalyst and traces of 1-phenylethyl hydroperoxide in the substrate. Interestingly these do not involve removal of the axial chloride ligand. Although, in contrast, at temperatures $\geqslant 80$ °C the axial ligand is replaced by 1-phenylethoxide. Although the latter

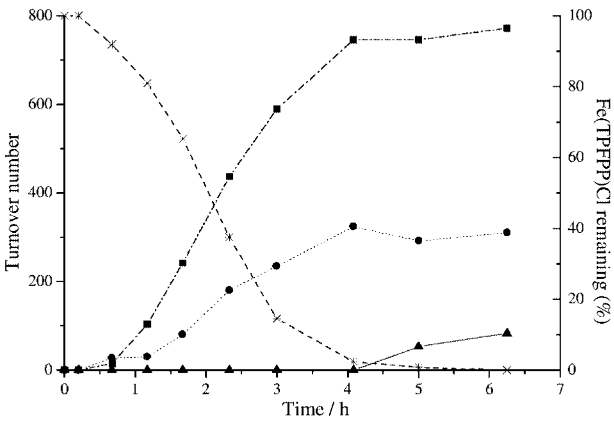


Fig. 8 Product turnover *versus* time and catalyst destruction *versus* time in the Fe(TPFPP)Cl-catalysed oxidation of toluene by dioxygen at 120 °C; ···●··· benzyl alcohol (left axis), —▲— 1-benzyl hydroperoxide (right axis), –·–■–·– benzaldehyde (left axis), —*— Fe(TPFPP)Cl (right axis).

could arise by thermolysis of the Fe–Cl bond [Reaction (27)] as

$$\mathrm{ClFe^{III}P} \longrightarrow \mathrm{Cl^{\bullet}} + \mathrm{Fe^{II}P} \tag{27}$$

suggested by Lyons and Ellis[5] and their co-workers this seems unlikely since this process does not occur in the reaction of toluene at 120 °C (see below).

It is noteworthy that the mechanisms of the low temperature reactions require the retention of the axial chloride in all the iron porphyrin species including the iron(II) compound. That this is likely in the non-polar reaction solution is supported by research by the groups of Birnbaum[27] and Dolphin[28] and their co-workers who show that, with electron withdrawing groups on the porphyrin ligands, chloride remains ligated to the iron(II) porphyrin in organic solution. The former used ^{19}F NMR spectroscopy to study $\mathrm{Fe^{II}(TPFPP\text{-}Br_8)Cl}$ and the latter measured the dissociation constants for the axial chloride in a series of iron(II) porphyrins.

Oxidation of toluene

The oxidation of toluene, carried out as described above, gave mainly benzaldehyde with smaller yields of benzyl alcohol, and trace quantities of benzyl hydroperoxide and benzoic acid. Benzyl hydroperoxide was thermolysed to benzaldehyde under the GC conditions employed in this study and was quantified as benzyl alcohol, as described above for 1-phenylethyl hydroperoxide, using triphenylphosphine as the reducing agent.

The oxidation of toluene was significantly slower than that of ethylbenzene (at 120 °C the reaction times were 5 and 1.5 h, respectively), had longer induction periods and gave lower yields (Fig. 8). These results show that, as expected, the larger bond dissociation energy of the C–H bond in toluene (BDE 368.2 kJ mol^{-1}, *cf.* BDE of ethylbenzene 357.3 kJ mol^{-1})[29] makes toluene a less reactive substrate than ethylbenzene by slowing down both the initiation and the propagation steps of the radical autoxidation. As a consequence, the competitive reactions of alkoxyl radicals leading to catalyst destruction become more important. Interestingly, unlike the ethylbenzene oxidation, no iron porphyrin axial ligand exchange occurs which seems to rule out direct homolysis of the Fe–Cl bond [Reaction (27)] as an initiation process in the Fe(TPFPP)Cl-catalysed oxidations.

Lowering the temperature of the reactions slows down the oxidations but, unlike those of ethylbenzene, it has no effect on the product distribution and the overall yield. Benzyl hydroperoxide was only a very minor product in all the oxidations and built up towards the end of the reaction when almost all the catalyst had been consumed.

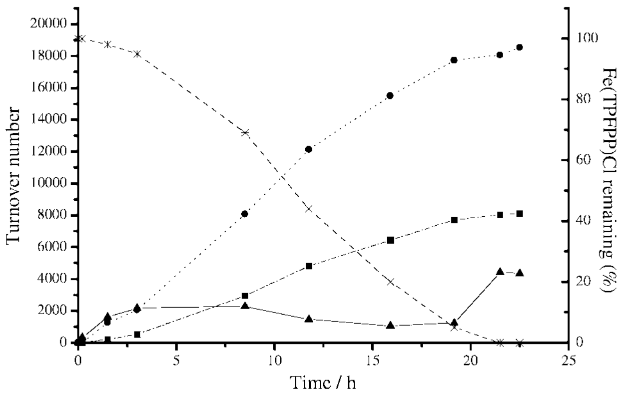


Fig. 9 Product turnover *versus* time (left axis) and catalyst destruction *versus* time (right axis) in the Fe(TPFPP)Cl-catalysed oxidation of cumene by dioxygen at 100 °C; –·–■–·– 2-phenylpropan-2-ol, —▲— cumyl hydroperoxide, ···●··· acetophenone, —*— Fe(TPFPP)Cl.

In all the reactions it is likely that the concentration of the benzylperoxyl radical is very low and, as discussed above, the main reactions of the radical are with the iron porphyrin to give benzaldehyde [*cf.* Reactions (13) and (14)] and hydrogen atom abstraction from the substrate to form benzyl hydroperoxide [*cf.* Reaction (4)]. The latter product is consumed in redox reactions *via* benzyloxyl and benzylperoxyl radicals giving benzyl alcohol, benzaldehyde and catalyst degradation.

Oxidation of cumene and *tert*-butylbenzene

Cumene gave three main products in the Fe(TPFPP)Cl-catalysed oxidation, namely, acetophenone, 2-phenylpropan-2-ol and cumene hydroperoxide and two very minor products, 2-phenylpropanal and α-methylstyrene. Cumene hydroperoxide was thermolysed to a mixture of acetophenone and 2-phenylpropan-2-ol during the GC analysis. The yields from the oxidations were obtained by quantifying the alcohol to ketone ratio (1 : 0.89) from thermolysis during GC analysis using commercial cumene hydroperoxide and by measuring the yields of these two products in reaction mixtures before and after treatment with $\mathrm{Ph_3P}$.

The cumene oxidation profile at 100 °C (Fig. 9) shows that the reaction gives very high turnovers and the catalyst stability is much greater than in the comparable reaction of ethylbenzene (Fig. 2). UV–VIS analysis reveals that after ~1 min the chloride axial ligand is replaced by an alkoxyl group to give an orange species analogous to that observed with ethylbenzene.

The most likely route to acetophenone is the rapid β-scission of the cumyloxyl radical.[30] This in turn is formed by the self-reaction of two cumylperoxyl radicals [*cf.* Reaction (5)] or by thermolysis or reduction of cumyl hydroperoxide [*cf.* Reaction (12) and Reactions (15) and (18)]. From the higher yield of acetophenone compared to cumyl alcohol, the cumyloxyl radicals formed in these oxidations preferentially fragment rather than abstract a hydrogen atom from the substrate.

The formation of trace amounts of 2-phenylpropanal suggested that a small amount of abstraction from the primary C–H bond of cumene (BDE 418 kJ mol^{-1}) might be occurring in competition with that from the more reactive tertiary position (BDE 353.1 kJ mol^{-1}).[29] However, attempts to oxidise the analogous C–H bonds in *tert*-butylbenzene at 100 °C in the presence or absence of cumene gave no products, showing that H-abstraction from the primary C–Hs is an unlikely route to 2-phenylpropanal. That the route to this aldehyde is by further oxidation of the primary product, α-methylstyrene, was confirmed since the latter when added to a standard ethylbenzene oxidation mixture at 100 °C gave 2-phenylpropanal.

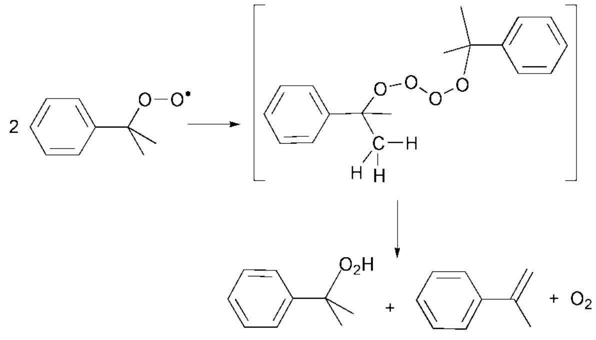
Russell,[17] Walling[16] and Boozer *et al.*[31] have reported the formation of α-methylstyrene in the autoxidation of cumene

Table 2 Catalyst activity and stability in the oxidation of ethylbenzene by dioxygen at 100 °C

Catalyst	Catalyst lifetime/h	Catalyst $t_{1/2}$/h	Catalyst turnovers[a]	Overall rate turnovers/h^{-1}
Fe(TPFPP)Cl	1.5	0.5	2900	2000
Fe(TTFNMe$_2$PP)Cl	20	—	14000	1000
Fe(TTFOPhPP)Cl	0.8	0.2	2000	3000
Fe(TPFPP-Br$_8$)Cl	0.75	0.2	4700	6500
Fe(TPFPP-Cl$_8$)Cl	0.75	—	5000	9200
Fe(TDCPP-Cl$_8$)Cl	1.5	0.3	5000	6500
[Fe(TPFPP)]$_2$O	—[b]	60	25000[c]	1300

[a] Total number of turnovers obtained before complete destruction of catalyst. [b] Reaction only run to $t_{1/2}$. [c] Turnovers at $t_{1/2}$.

and have suggested that it arises from cumylperoxyl radicals. Although no mechanisms were proposed, a plausible route is shown in Scheme 4. An alternative route to the alkene, the dehydration of 2-phenylpropan-2-ol, was eliminated since adding the latter to an oxidation mixture of ethylbenzene at 100 °C gave no α-methylstyrene.



Scheme 4

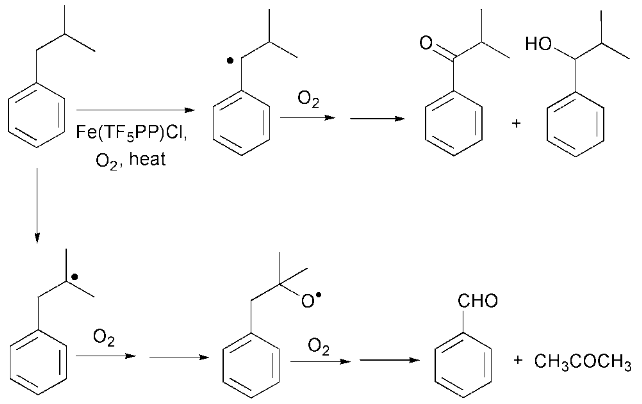
The greater reactivity of cumene over ethylbenzene is expected from C–H bond dissociation energies (BDE, PhCMe$_2$–H, 353.1 kJ mol^{-1}; PhCHMe–H, 357.3 kJ mol^{-1} [29]) as discussed above for toluene. This increased rate of reaction would be expected to result in a higher concentration of peroxyl and alkoxyl radicals. That this does not result in rapid catalyst destruction can be accounted for by both the rapid β-scission of the cumyloxyl radicals, which will compete effectively with attack on the porphyrin ligand, and by steric factors which will make these radicals less reactive than 2-phenylethoxyl radicals towards attacking the porphyrin ligand.

Oxidation of (2-methylpropyl)benzene

Further support for the radical nature of these oxidations and in particular for the involvement of alkoxyl radicals was obtained from the oxidation of (2-methylpropyl)benzene. The main products from a 3 h oxidation of this substrate at 100 °C were benzaldehyde (>1000 turnovers) and 2-methyl-1-phenylpropanone (1500) and the minor products (≤40 turnovers) detected were benzyl alcohol, 2-methyl-1-phenylpropan-1-ol, 2-methyl-1-phenylpropan-2-ol and 2-methyl-1-phenylpropene. These products arise from competitive oxidations of the benzylic and the tertiary C–H bonds (Scheme 5). The former gives 2-methyl-1-phenylpropanone and the corresponding alcohol and the latter, *via* the extremely rapid β-scission of the tertiary alkoxyl radical, gives benzyl radicals and subsequently benzaldehyde.[30]

Oxidation of ethylbenzene using a selection of Fe(TPFPP)Cl derivatives

Iron(III) 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin Fe(TDCPP)Cl and five iron(III) porphyrin derivatives of Fe(TPFPP)Cl (**1**) were compared as catalysts for the oxidation of ethylbenzene by dioxygen at 100 °C. In two of the catalysts the *para*-fluorine atoms of the fluorophenyl rings were replaced by NMe$_2$ and by OPh to give Fe(TTFNMe$_2$PP)Cl and Fe(TTFOPhPP)Cl, respectively, to examine the electronic effects of the substituents on the oxidations. In two others the β-pyrrole positions were perhalogenated [Fe(TPFPP-Cl$_8$)Cl and Fe(TPFPP-Br$_8$)Cl] since this has been reported to improve catalytic activity. The fifth catalyst selected was the μ-oxodimer [Fe(TPFPP)]$_2$O because μ-oxodimers have been reported to be intermediates in these oxidations. The same products were obtained with all these catalysts and catalyst axial ligand exchange, noted above, occurred in the reactions of all the monomeric catalysts, but not with the μ-oxodimer. The reaction profiles of all, except those of Fe(TTFNMe$_2$PP)Cl and [Fe(TPFPP)]$_2$O, were very similar to that of Fe(TPFPP)Cl (Fig. 2); with the latter two catalysts the reaction profiles resemble those of Fe(TPFPP)Cl at 40 and 50 °C, not 100 °C, with the hydroperoxide yield building up from the start of the reaction rather than after the majority of the catalyst has been destroyed. This suggests that these two iron porphyrins are poor catalysts for the decomposition of 1-phenylethyl hydroperoxide. The stability and activity data of the catalysts, given in Table 2, show that the least active monomeric catalyst, Fe(TTFNMe$_2$PP)Cl, gives the highest turnovers and that perhalogenation of β-pyrrole positions leads to an increase in catalyst activity and in the number of turnovers obtained, however, it also leads to an increase in the rate of catalyst destruction. Interestingly the best of all the catalysts examined was the μ-oxodimer [Fe(TPFPP)]$_2$O which, after an induction period of 1.5 h, gave >25 000 turnovers in its first half-life (60 h).



Scheme 5

For Fe(TPFPP)Cl and its four monomeric derivatives used in this study, in agreement with earlier work by Lyons and Ellis[5] and their co-workers, there is a clear correlation between the overall rate of oxidation (turnovers h^{-1}) and the oxidation potential of the iron(II) porphyrin (Fig. 10).[5f] Thus the more readily the iron(III) porphyrin is reduced the more active the catalyst becomes.

Comparison of the behaviour of the catalysts Fe(TPFPP)Cl, Fe(TTFOPhPP)Cl and Fe(TTFNMe$_2$PP)Cl shows that the last

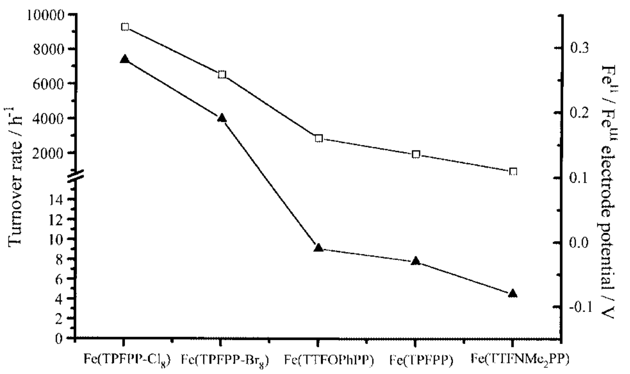


Fig. 10 A comparison of the Fe^{II}/Fe^{III} oxidation potentials of iron porphyrins (right axis) and overall turnover rate (left axis) for the oxidation of ethylbenzene by dioxygen at 100 °C; —□— overall turnover rate, —▲— redox potential of catalyst.

is slightly less active than the others but is an order of magnitude more stable under the reaction conditions (catalyst lifetimes increase from 0.8 to 20 h) (Table 2). Based on the reported behaviour of amino and phenoxy substituted iron fluorophenylporphyrins where the former was reported to be a poor catalyst for alkane hydroxylation by iodosylbenzene,[32] the superior performance of Fe(TTFNMe$_2$PP)Cl was unexpected and suggests that the radical and non-radical oxidation systems show a marked difference in behaviour. We believe that in the dioxygen based systems a combination of two factors increases the stability and lifetime of Fe(TTFNMe$_2$PP)Cl and makes it the best of these catalysts. First, the substituents which are prone to oxidation protect the porphyrin ring from destruction. Aromatic amines are commonly used as anti-oxidants and in this respect they act as built-in anti-oxidants which are able to absorb, through oxidations of the amino groups (demethylation and *N*-oxidation), radical oxidative damage which would otherwise destroy the porphyrin ring. This conclusion is supported by FAB$^+$MS analysis of the partially oxidised catalyst which reveals extensive demethylation and *N*-oxidation as well as the substitution and addition of oxyl radicals on the ligand noted above for Fe(TPFPP)Cl. Secondly, the slow reaction with Fe(TTFNMe$_2$PP)Cl, due in part to the low reactivity of this catalyst towards 1-phenylethyl hydroperoxide, ensures that the oxyl radical concentrations, and particularly that of the more aggressive 1-phenylethoxyl radical, are very low. This in turn increases the lifetime of the catalyst.

It has been reported that halogenation of the β-pyrrole positions of porphyrins improves their performance as catalysts for alkane oxidation by dioxygen.[5d,f] This has been attributed to the electronic effect of the halogen on the redox Fe^{II}/Fe^{III} potential and to the steric protection of the porphyrin to attack by electrophilic oxygen radicals.[5] However, perhalogenation also distorts the porphyrin from its preferred planar shape which disrupts the conjugated π-system. This reduces the stability of the porphyrin ring towards oxygen radical attack. The present study shows that the benefit of the increased activity, arising from perhalogenation of Fe(TPFPP)Cl, is not matched by a large increase in catalyst stability.

The μ-oxodimer, [Fe(TPFPP)]$_2$O, has been used previously by Ellis and Lyons[5d,f] as a catalyst for the oxidation of isobutane by dioxygen and μ-oxodimers have also been proposed as intermediates in the recycling of the iron catalysts in these systems.[5] Interestingly, in the present study the μ-oxodimer is dramatically more stable towards oxidative destruction than Fe(TPFPP)Cl (catalyst $t_{1/2}$ values at 100 °C, 60 and 0.5 h, respectively). Furthermore, the μ-oxodimer remains intact during the reactions and, contrary to some reported mechanisms, is not cleaved to give monomeric units. Like the monomeric Fe(TTFNMe$_2$PP)Cl discussed above the success of the μ-oxodimer catalyst appears to be due to its low activity which allows the build-up of 1-phenylethyl hydroperoxide and minimises the involvement of 1-phenylethoxyl radicals.

Conclusions

1. The products and reaction profiles from the Fe^{III}P-catalysed oxidation of ethylbenzene are typical of a free radical autoxidation process.

2. Iron porphyrin catalysts are destroyed by reaction with oxygen-centred radicals, in particular 1-phenylethoxyl radicals.

3. The greater the Fe(II)/Fe(III) redox potential of the iron porphyrin the greater its catalytic activity.

4. Oxidation yields are determined by the catalysts activity and stability. High yields are in general favoured by less active catalysts or conditions where 1-phenylethyl hydroperoxide is relatively stable and the 1-phenylethoxyl radical concentration is very low.

5. Halogenation of the β-pyrrole positions results in a more active catalyst but provides little protection from radical destruction.

Experimental

Instrumental methods

UV–VIS spectra were recorded on a Hewlett Packard 8452A diode array spectrometer using 1 cm quartz cuvettes. ^{1}H and ^{19}F NMR spectra were recorded on a JEOL JNM-EX270 spectrometer using TMS and CFCl$_3$ as the respective internal standards. Gas chromatography was carried out with a glass column (3 m × 2.5 mm) packed with 10% w/w carbowax 20M on GasChrom Q (80–120 mesh) in a Pye Unicam GCD chromatograph equipped with a flame ionisation detector. The results were analysed with a JCL6000 for windows programme (Jones Chromatography Ltd.) using 1,3-dichlorobenzene as the internal standard. Gas chromatography–mass spectrometry was carried out using a Hewlett Packard 5896 series II capillary chromatograph linked to a VG Analytical Autospec micromass mass spectrometer. TLC used aluminium plates coated with Kieselgel 60 F$_{254}$ (Merck). Column chromatography was carried out on Kieselgel 60 (230–400 mesh) (Macherey-Nagel) or on alumina (UGI) (Phase Sep).

Reagents

All the reagents were commercially available and used without purification unless otherwise stated. All the alkylaromatic substrates were passed through a short activated alumina column and screened by GC to ensure the absence of autoxidation products. Fe(TPFPP-Br$_8$) was kindly supplied by Professor Mansuy.

Diazomethane was prepared from Diazald using a standard procedure.[32] Potassium 1-phenylethoxide and 2-phenylprop-2-oxide were obtained by adding potassium hydride to the corresponding alcohol.[33]

Iron(III) tetrakis(pentafluorophenyl)porphyrin was prepared by refluxing tetrakis(pentafluorophenyl)porphyrin[34] (0.8 g) with FeCl$_2$·4H$_2$O (2.52 g) under nitrogen in acetonitrile (350 cm^3). After 24 h, when TLC analysis (MeOH–CH$_2$Cl$_2$, 5:95) showed the reaction was complete, the solution was cooled, concentrated under vacuum and Fe(TPFPP)OH was isolated by column chromatography (silica, benzene followed by CH$_2$Cl$_2$). Repeat chromatography using CH$_2$Cl$_2$, followed by washing with HCl and removal of solvent under vacuum and drying (100 °C, 1 mmHg, 2.5 h) gave Fe(TPFPP)Cl (0.623 g, 71%). TLC (MeOH–CH$_2$Cl$_2$, 1:99) single spot R_f 0.79; λ_{max} (CH$_2$Cl$_2$) nm 350, 410 (ε = 1.10 × 10^4 m^2 mol^{-1}, lit.[35] 1.15 × 10^4 m^2 mol^{-1}), 502, 628; FAB$^+$MS (NOBA) *m*/*z* 1028, Calc. C$_{44}$H$_8$F$_{20}$N$_4$Fe, 1028; ^{19}F NMR δ (CDCl$_3$) −153.54, −151.10 (*meta* F), −145.80 (*para* F), −104.00, −101.00 (*ortho* F).

Iron(III) tetrakis(pentafluorophenyl)porphyrin μ-oxodimer was obtained in quantitative yield by leaving a solution of Fe(TPFPP)OH in CH_2Cl_2 to stand overnight following the method of Jayaraj *et al.*[36] λ_{max} (CH_2Cl_2) nm 324, 396 (Soret), 426, 558; ^1H NMR δ ($CDCl_3$) 13.89 (β-pyrrole, lit.[36] 13.9); ^{19}F NMR δ ($CDCl_3$) −163.29, −160.57 (*meta* F), −151.29 (*para* F), −134.76, −133.48 (*ortho* F).

Iron(III) tetrakis(4-phenoxy-2,3,5,6-tetrafluorophenyl)-porphyrin was prepared by adding a solution of Fe(TPFPP)Cl (50.3 mg) in dry THF (10 cm^3) to sodium phenoxide (sodium, 24.8 mg with phenol 0.225 g) in dry THF (10 cm^3) under nitrogen. After refluxing for 20 h the solution was cooled, concentrated under vacuum and purified by chromatography on alumina (cyclohexane–CH_2Cl_2, 40:60 followed by CH_3OH–CH_2Cl_2, 5:95). The product in CH_2Cl_2 was washed with HCl and water, and following solvent removal was dried (100 °C, <0.1 mmHg, 2.5 h) to give Fe(TTFOPhPP)Cl (56.3 mg, 85%). TLC (MeOH–CH_2Cl_2, 5:95) single spot R_f 0.97; λ_{max} (CH_2Cl_2) nm 352, 412 (Soret $\varepsilon = 1.15 \times 10^4$ m^2 mol^{-1}), 502, 632; FAB$^+$MS (NOBA) *m*/*z* 1325, Calc. $C_{68}H_{28}F_{16}N_4O_4Fe$, 1325; ^1H NMR δ ($^2H_6$ DMSO) 8.09–6.83 (m, 20H), 7.65 (s, 8H, β-pyrrole); ^{19}F NMR δ ($CDCl_3$) −147.00, −144.62 (*meta* F), −105.73, −101.99 (*ortho* F); no *para* fluorine resonances detected.

Iron(III) 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis-(pentafluorophenyl)porphyrin was prepared from ZnTPFPP (0.199 g) by dissolving the zinc porphyrin in dry methanol (700 cm^3) under nitrogen, heating to 65 °C and adding *N*-chlorosuccinimide (8.5 g). The chlorination was monitored by UV–VIS spectroscopy (Soret λ_{max} changes from 396 to 446 nm) and at the end of the reaction (~100 min) the solution was cooled and diluted with water to give ZnTPFPP-Cl_8 which was purified by chromatography on silica (hexane–CH_2Cl_2, 1:1) (0.18 g, 71%). TLC (CH_2Cl_2) single spot R_f 0.58; λ_{max} (CH_2Cl_2) nm 362, 446 (Soret), 582, 630; FAB$^+$MS (NOBA) *m*/*z* 1312, Calc. $C_{44}Cl_8F_{20}N_4Zn$, 1312. The zinc porphyrin was then dissolved in CH_2Cl_2 (50 cm^3) and, after the addition of trifluoroacetic acid (1 cm^3), stirred for 20 h to give the porphyrin free base. The latter was washed with water and, following solvent removal, was dried (100 °C, <0.1 mmHg, 2.5 h) H_2TPFPP-Cl_8 (0.130 g, 98%). The free base porphyrin (0.109 g) was metallated with $FeCl_2 \cdot 4H_2O$ (0.263 g) by refluxing for 24 h in acetonitrile (150 cm^3). The solvent was removed and the residue was dissolved in CH_2Cl_2 and washed sequentially with water, HCl and water. After solvent removal the product was dried (100 °C, <0.1 mmHg, 2.5 h) to give Fe(TPFPP-Cl_8)Cl (18.8 mg, 16%). λ_{max} (CH_2Cl_2) nm 394, 430 ($\varepsilon = 3.8 \times 10^3$ m^2 mol^{-1}, lit.[37] 3.9×10^3 m^2 mol^{-1}), 630, 657; FAB$^+$MS (NOBA) *m*/*z* 1304, Calc. $C_{44}Cl_8F_{20}N_4Fe$, 1304.

Iron(III) 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin was obtained from H_2TDCPP[38] by metallation with $FeCl_2 \cdot 4H_2O$ in refluxing DMF for 5 h, followed by chromatography on silica (hexane–CH_2Cl_2, 1:1 with 1% MeOH), 93% yield. TLC (hexane–CH_2Cl_2, 1:1 with 1% MeOH) single spot; λ_{max} (CH_2Cl_2) nm 364, 414 ($\varepsilon = 9.6 \times 10^3$ m^2 mol^{-1}, lit.[39] 9.8×10^3 m^2 mol^{-1}), 510, 580, 642; ^1H NMR δ ($CDCl_3$) 81.23 (8H, β-pyrrole), 14.09 (aryl), 12.78 (aryl), 8.21 (aryl). Chlorination was achieved following Wijesekera *et al.*[28] to give the required Fe(TDCPP-Cl_8)Cl in 83% yield. TLC (hexane–CH_2Cl_2, 1:1 with 1% MeOH) single spot; λ_{max} (CH_2Cl_2) nm 394, 444 ($\varepsilon = 4.5 \times 10^3$ m^2 mol^{-1}, lit.[35] 4.8×10^3 m^2 mol^{-1}), 580; FAB$^+$MS (NOBA) *m*/*z* 1219.6, Calc. $C_{44}H_{12}Cl_8N_4Fe$, 1219.5.

Iron(III) 5,10,15,20-tetrakis(4-dimethylamino-2,3,5,6-tetrafluorophenyl)porphyrin was prepared by heating a solution of H_2TPFPP (0.127 g), $FeCl_2 \cdot 4H_2O$ (0.258 g) and $Me_2NH \cdot HCl$ in DMF (40 cm^3) to reflux for 16 h. After solvent removal under vacuum the residue was dissolved in CH_2Cl_2 (50 cm^3), washed with water and evaporated to dryness. TLC analysis (hexane–CH_2Cl_2, 1:1 with 1% MeOH) showed this to contain a mixture of H_2TTFNMe_2PP and Fe(TTFNMe_2PP)Cl with R_f 0.9 and 0.3, respectively, which were separated by column chromatography on silica (CH_2Cl_2 with 0–0.5% MeOH) to give, after solvent removal, 54% H_2TTFNMe_2PP and 25% Fe(TTFNMe_2PP)Cl. The former was metallated with $FeCl_2 \cdot 4H_2O$ in DMF to give Fe(TTFNMe_2PP)Cl in 96% yield. H_2TTFNMe_2PP had a single spot (R_f 0.9) by TLC (hexane–CH_2Cl_2, 1:1 with 1% MeOH); λ_{max} (CH_2Cl_2) nm 420 (Soret $\varepsilon = 2.8 \times 10^4$ m^2 mol^{-1}, lit.[40] 2.82×10^4 m^2 mol^{-1}), 510, 546, 584; FAB$^+$MS (NOBA) *m*/*z* 1075, Calc. $C_{52}H_{34}F_{16}N_8$, 1075. Fe(TTFNMe_2PP)Cl had a single spot (R_f 0.3) by TLC (hexane–CH_2Cl_2, 1:1 with 1% MeOH); λ_{max} (CH_2Cl_2) nm 350, 418 (Soret $\varepsilon = 1.1 \times 10^4$ m^2 mol^{-1}), 506, 642; FAB$^+$MS (NOBA) *m*/*z* 1128, Calc. $C_{52}H_{32}F_{16}N_8Fe$, 1128.

Oxidation methods

In a typical oxidation, a solution of iron porphyrin (6.6×10^{-7} mol) in 1,3-dichlorobenzene (0.25 cm^3) was mixed with the alkylaromatic (25 cm^3) and analysed by GC and UV–VIS spectroscopy prior to being heated in a slow stream of dioxygen at the required temperature. The course of the reaction was followed by removing small samples for UV–VIS spectroscopy (2 cm^3) and for GC analysis (0.4 cm^3). The latter sample was used to analyse the oxidation mixture both before and after treatment with PPh_3. The UV–VIS sample was subsequently returned to the reaction mixture.

For reactions carried out in the presence of added *tert*-butyl or cumyl hydroperoxide, the initial procedures and analyses were as described above. The hydroperoxide (10 or 40 μl) was added after the reaction had been running for 15–30 min.

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