Model Systems for Cytochrome P450 Dependent Mono-oxygenases. Part 7.[1] Alkene Epoxidation by Iodosylbenzene Catalysed by Ionic Iron(III) Tetraarylporphyrins Supported on Ion-exchange Resins

Donald R. Leanord and John R. Lindsay Smith *
Department of Chemistry, University of York, York YO1 5DD, UK

Ionic iron(III) tetraarylporphyrins are readily adsorbed onto cross-linked polystyrene ion-exchange resins. These supported metalloporphyrins can act as heterogeneous catalysts for the oxidation of organic compounds by iodosylbenzene in methanolic solution. Their catalytic activity for the epoxidation and allylic oxidation of cyclohexene and the epoxidation of (*Z*)-cyclooctene has been studied. With cyclohexene, epoxidation is favoured by increased cross-linking of the resin support, and allylic oxidation is shown to arise largely from an autoxidation which can be minimised by carrying out the reactions under nitrogen. (*Z*)-Cyclooctene gives only epoxidation which is also favoured by increased cross-linking and is unaffected by changes in the surface area of the support. The influence of the support cross-linking on catalyst performance is discussed. Supported anionic iron(III) porphyrins are poor catalysts unless they are sterically hindered with *ortho*-groups on the aromatic substituents. The fate of the oxidant in the heterogeneous oxidations is examined and comparison with the analogous homogeneous reactions suggests that some of the oxidant is consumed in oxidising the polymer support. A brief study of the oxidation of cyclohexene by iodosylbenzene catalysed by a cation exchange resin in its acidic form, in the absence of metalloporphyrins, is reported.

Tetraarylmetalloporphyrins can catalyse very similar oxidations to those brought about by cytochrome P450 and for this reason they have received much attention in recent years.[2] The majority of this work has been concerned with the mechanisms of these oxidations,[3] the nature of the active oxidant,[4] and with determining the factors that control the selectivity of the reactions.[5] This research has invariably been carried out on a very small scale. Another aspect of the chemistry of these metalloporphyrin enzyme models is the development of their potential as catalysts for larger scale oxidations.

Two major drawbacks have prevented progress with the practical application of metalloporphyrin catalysts in synthesis. First, during the course of reaction the catalyst also acts as a substrate for the active oxidant and is itself destroyed in an intermolecular process, and secondly, the catalyst that survives the reaction is hard to recover and reuse. The first problem has been extensively examined and can be reduced by the use of sterically hindered tetraarylmetalloporphyrins (aryl = di-*ortho*-substituted phenyl) which prevents the close approach of catalyst molecules.[5d,6] However, recovery of the expensive catalyst remains a problem.

An alternative approach which should overcome both problems is to support the metalloporphyrin on a solid surface. Thus site-isolation of the catalyst on the support should prevent intermolecular self-oxidation and simple filtration should allow the recovery of the catalyst for reuse.

Supported metalloporphyrins have been developed mainly to investigate the reversible binding of dioxygen.[7] Other uses have been in the surface modification of electrodes,[8] and in photo-induced electron-transfer[9] and as models for peroxidase,[10] catalase[11] and cytochrome P450.[12] These studies have commonly involved non-trivial chemistry to synthesise the porphyrin covalently bonded to a solid support. However, there are two very recent reports of the simple preparation of oxidation catalysts by adsorption of ionic manganese(III) tetraarylporphyrins onto inorganic oxides,[13] and iron(III) and manganese(III) tetra(4-sulphonatophenyl)porphyrin onto an anion exchange resin.[14]

In this paper we describe our work on the preparation of catalysts by adsorption of ionic iron(III) tetraarylporphyrins onto ion-exchange resins and their use in the epoxidation of alkenes by iodosylbenzene.

Results and Discussion

The Preparation and Properties of Iron(III) *Porphyrins Supported on Ion-exchange Resins.*—The ion-exchange resins were first washed sequentially with water, methanol and acetone to remove traces of impurities before being shaken with a solution of metalloporphyrin in 50% aqueous acetone or aqueous methanol. The lightly cross-linked resin Duolite 225 was also modified with Fe^{III}T4MPyP† in methanol containing the crown ether, 18-crown-6. The loading times were dependent on the resin, typically the uptake of 2 μmol of metalloporphyrin on 1 g of resin took 30 min for Dowex MSCl and 6 h for Duolite 225. The modified resin was ready for use after washing with water and drying. The range of materials obtained in this way is shown in Tables 1 and 2.

The physical strength of the modified resins was good and improved by increased cross-linking. However, even the most robust materials were slowly abraded when suspensions were stirred for prolonged times. The ionic bonding to the polymers was extremely strong for the tetra(*N*-methylpyridyl)- and tetra-(sulphonatophenyl)-porphyrins. For example, neither water, methanol, acetone, concentrated hydrochloric acid nor aqueous solutions of sodium, magnesium or barium ions elute the

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† *Abbreviations:* tetra(4-*N*-methylpyridyl)porphyrinatoiron(III), Fe^{III}-T4MPyP; tetra(2-*N*-methylpyridyl)porphyrinatoiron(III), Fe^{III}T2M-PyP; tetra(4-sulphonatophenyl)porphyrinatoiron(III), Fe^{III}TSPP; and tetra(2,6-dichloro-3-sulphonatophenyl)porphyrinatoiron(III), Fe^{III}-TDCSPP.

Table 1. Yields of oxidation products from reaction of (*Z*)-cyclooctene with iodosylbenzene in methanol catalysed by cationic iron(III) tetraarylporphyrins adsorbed on cation-exchange resins: PhIO, 8.35 × 10^{-2} mol dm^{-3}; (*Z*)-cyclooctene, 0.7 mol dm^{-3}; iron(III)porphyrin, (2.2 × 10^{-6} mol g^{-1}) 6.7 × 10^{-4} mol dm^{-3}; methanol 3 cm^3; 20 °C in air.

Resin	Functional group	Cross-linking (%)	Iron(III)porphyrin	Yield (%)[a] Epoxide	Formaldehyde
Duolite 225	$-SO_3^-$	4	Fe^{III}T4MPyP	2.3	nm[b]
Dowex 50X8	$-SO_3^-$	8	Fe^{III}T4MPyP	1.5	nm[b]
Amberlite CG120 (100–200 mesh)	$-SO_3^-$	8	Fe^{III}T4MPyP	34	nm[b]
Amberlite CG120 (400–600 mesh)	$-SO_3^-$	8	Fe^{III}T4MPyP	7–23[c]	nm[b]
Dowex MSC1	$-SO_3^-$	20	Fe^{III}T4MPyP[d]	54	18
			Fe^{III}T2MPyP[d]	56	30
None	—	—	Fe^{III}T4MPyP[e]	50	nm[b]

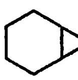
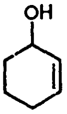
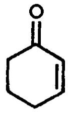
[a] ±2% based on oxidant after 2 h. [b] Not measured. [c] Wide range of yields. [d] Iron(III)porphyrin (1.8 × 10^{-6} mol g^{-1}), 5.5 × 10^{-3} mol dm^{-3} and PhIO, 4.13 × 10^{-2} mol dm^{-3}. [e] Homogeneous solution, yield after 20 min reaction.

Table 2. Yields of oxidation products from the reaction of (*Z*)-cyclooctene with iodosylbenzene in methanol catalysed by anionic iron(III) tetraarylporphyrins adsorbed on anion-exchange resins: PhIO, 2.75 × 10^{-2} mol dm^{-3}; (*Z*)-cyclooctene 0.7 mol dm^{-3}; Fe^{III}TSPP (2.35 × 10^{-6} mol g^{-1}), 7.1 × 10^{-4} mol dm^{-3} and Fe^{III}TDCSPP (1.7 × 10^{-6} mol g^{-1}), 5.2 × 10^{-4} mol dm^{-3}; methanol 3 cm^3; 20 °C in air.

Resin	Functional group	Cross-linking (%)	Iron(III)porphyrin	Yield of epoxide (%)[a]
Amberlite CG 400	$-\overset{+}{N}Me_3$	8	Fe^{III}TSPP	1.4
Amberlite IRA 45	$-NMe_2$	—	Fe^{III}TSPP	0.1
Amberlyst A-21	$-NMe_2$	20	Fe^{III}TSPP	2.6
Amberlyst A-27	$-\overset{+}{N}Me_3$	20	Fe^{III}TSPP	6.4
			Fe^{III}TDCSPP[b]	46.4
Dowex MSA1	$-\overset{+}{N}Me_3$	20	Fe^{III}TSPP	3.2

[a] ±2% based on oxidant after 24 h. [b] 4.13 × 10^{-2} mol dm^{-3} oxidant.

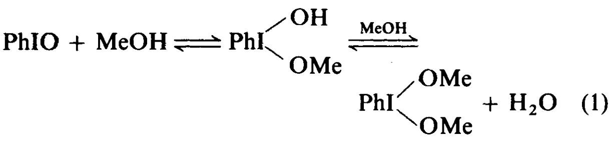
Table 3. Yields of oxidation products from the reaction of cyclohexene with iodosylbenzene in methanol catalysed by Fe^{III}T4MPyP adsorbed on cation exchange resins: PhIO, 8.36 × 10^{-2} mol dm^{-3}; cyclohexene, 0.78 mol dm^{-3}; Fe^{III}T4MPyP, (2.2 × 10^{-6} mol g^{-1}) 6.7 × 10^{-4} mol dm^{-3}; methanol, 3 cm^3; 20 °C in air.

Resin	Yield of product (%)[a] 			Total
Duolite 225	5	8	41	54
Dowex 50X8	2	11	38	51
Amberlite CG120	10	10	51	71
Dowex MSC1	42	7	22	71
Dowex MSC1[b]	55	1	1	57
—[c]	30	2	3	35

[a] ±2% based on oxidant after 6 h. [b] Under nitrogen. [c] Homogeneous solution, yield after 20 min.

Fe^{III}T4MPyP or Fe^{III}T2MPyP from columns prepared from modified Dowex MSC1. Similarly Fe^{III}TSPP cannot be eluted from Amberlyst A27 with organic solvents, water or aqueous sodium chloride or sodium hydroxide. By comparison Fe^{III}-T4MPyP adsorbed on Amberlite CT50 (a weak cation exchange resin) can be removed by elution with dilute hydrochloric acid.

Catalytic Activity of Ion-exchange Resins Modified with Ionic Iron(III) *Tetraarylprophyrins.—Tetra*(4-N-*methylpyridyl*)*porphinatoiron*(III) *pentachloride and tetra*(2-N-*methylpyridyl*)*porphinatoiron*(III) *pentachloride.* The potential of these supported iron(III) porphyrins as catalysts for epoxidation was initially investigated with cyclohexene using Fe^{III}T4MPyP and sulphonated crosslinked polystyrenes. The reactions were carried out in methanol since iodosylbenzene, which is almost insoluble in most organic solvents, readily dissolves in methanol [eqn. (1)][5] and this provides a convenient way for handling the oxidant. Epoxidation and allylic oxidation were observed (Table 3).



$$PhIO + MeOH \rightleftharpoons PhI\begin{matrix}OH\\OMe\end{matrix} \overset{MeOH}{\rightleftharpoons} PhI\begin{matrix}OMe\\OMe\end{matrix} + H_2O \quad (1)$$

During the course of the oxidations the solutions remained colourless and there was no evidence of leaching of the catalyst from the support into the methanol. The containment of the metalloporphyrin on the resin made it possible to remove the catalyst at the end of the reaction to measure the yield of formaldehyde, from the oxidation of the solvent methanol, by Nash's method.[16] In the homogeneous reactions the presence of catalyst in the solutions complicates the spectroscopic determination of the coloured complex of formaldehyde and pentane-2,4-dione.

Control experiments using modified resins in the absence of the oxidant gave no oxidation products and with the unmodified resins (Na$^+$ form) iodosylbenzene gave only traces of allylic oxidation. Interestingly, however, iodosylbenzene with the acid form of Dowex 50X8 leads to a variety of oxidation products (see below).

There are two marked differences in cyclohexene oxidations catalysed by supported and unsupported Fe^{III}T4MPyP. First, the homogeneous oxidations are faster; typically they are complete within 20 min[17] compared with the heterogeneous

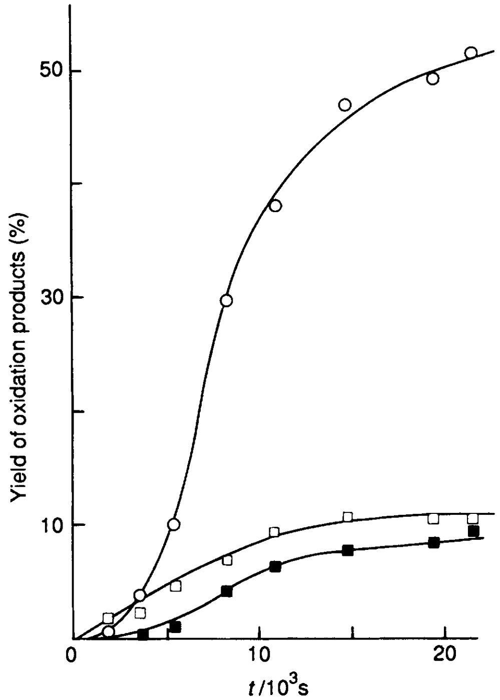
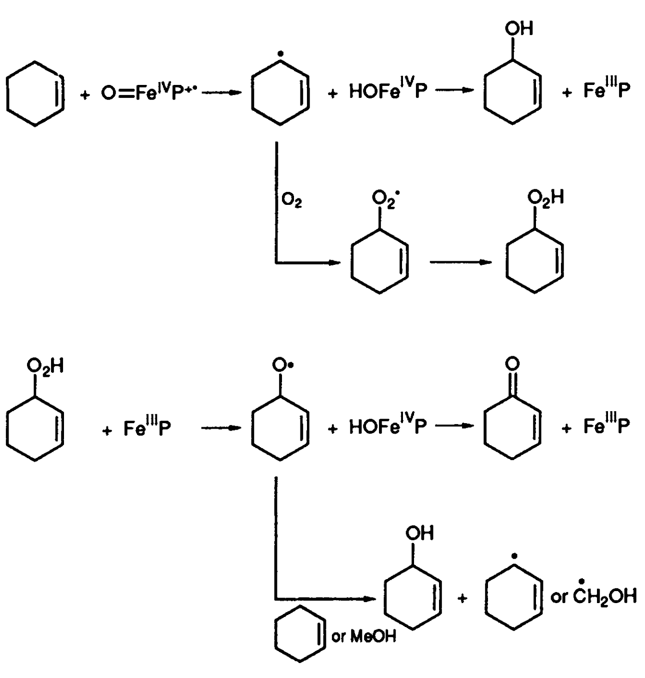


Fig. 1. The build-up of products from the oxidation of cyclohexene by iodosylbenzene catalysed by Fe^{III}T4MPyP on Amberlite CG120 Type 1. PhIO, 83.6 mmol dm^{-3}; cyclohexene, 0.78 mol dm^{-3}; methanol, 3 cm^3; supported Fe^{III}T4MPyP (2.2 μmol g^{-1}) 2 μmol. cyclohexen-2-ol (■), epoxycyclohexane (□) and cyclohexen-2-one (○).

analogues which require 6 h or more. We infer that the slower reactions with the solid catalyst reflect a more restricted access to the metalloporphyrin or a less active species formed on the polymer surface. Secondly, the supported catalysts lead to significantly more allylic oxidation. Interestingly the relative proportion of epoxidation to allylic oxidation increases with the extent of crosslinking in the ion-exchange resin. Furthermore, carrying out the reactions under nitrogen reduces the allylic oxidation dramatically showing that with the heterogeneous catalysts the majority of the allylic oxidation involves dioxygen as the oxidant. When a mercury manometer was attached to a sealed aerated reaction mixture, a pressure drop occurred after a 45–50 min induction period. Monitoring the formation of the oxidation products with time shows that the end of the induction period coincides with an increase in the rate of formation of allylic products (Fig. 1) but not with a change in the rate of formation of epoxide. These results suggest that allylic oxidation in these heterogeneous systems occurs by a metalloporphyrin-catalysed autoxidation.[18]

Based on the allylic oxidation mechanism proposed by Groves and Subramanian,[3d] autoxidation could be initiated by dioxygen trapping the cyclohexenyl radicals leading to cyclohexenyl peroxyl radicals. Further, reactions of the peroxyl radicals would lead to the cyclohexenoxyl radical and subsequently cyclohexenol and cyclohexenone by the metalloporphyrin-catalysed decomposition of the hydroperoxide (Scheme 1). Interestingly, in the homogeneous iron(III) porphyrin-catalysed hydroxylation of aliphatic C–H bonds by iodosylbenzene autoxidation is normally unimportant,[1] although dioxygen does influence analogous manganese(III) porphyrin systems.[19] In the former system, the carbon radicals are formed and very rapidly oxidised (oxygen rebound mechanism)[20] before they can diffuse from the cage to react with dioxygen. However, with the manganese catalysts the oxidation of carbon radicals by the equivalent hydroxymanganese(IV) species is less efficient and cage escape and the subsequent reaction with dioxygen becomes an important reaction.[3c] These results suggest that the hydroxyiron(IV) porphyrin is a less effective oxidant for carbon radicals when supported on an ion-exchange resin, possibly through steric hindrance from the polymer, and thus allows dioxygen to compete more effectively in the heterogeneous systems.



Scheme 1.

Because of the complication of allylic oxidation with cyclohexene we examined the reactions of (Z)-cyclooctene, a substrate that is less prone to autoxidation. As expected, oxidation of this substrate using the supported catalysts simplified the study by giving epoxide with negligible amounts (< 1%) of other oxidation products apart from formaldehyde from solvent oxidation. Furthermore, the product yields were insensitive to the presence of dioxygen.

The results in Table 1 allow comparison of the ion-exchange resins, modified with cationic iron(III) porphyrins, as catalysts for the epoxidation of (Z)-cyclooctene. Data from analogous homogeneous oxidations are also included. Fig. 2 shows a typical graph recording the growth of epoxide with time.

The yield of epoxidation improves with increased crosslinking in the ion exchange support but is unaffected by increased surface area (compare Fe^{III}T4MPyP on Amberlite C120, 400–600 and 100–200 mesh). On the best resin, Dowex MSCl, both cationic porphyrins give yields of epoxide that are very comparable with those of the homogeneous catalysts although the reactions of the former are significantly slower.

It was argued that the lower yields of epoxide from the catalysts on the less cross-linked resins could arise from the swelling of these resins in polar solvents. (Table 4 shows that in water and 50% v/v water–acetone the less cross-linked resins show larger increases in volume than the highly cross-linked Dowex MSCl). This was tested by loading the catalyst in the presence of 18-crown-6 ether, onto Duolite 225 (K^+ form) in methanol rather than in aqueous acetone. The crown ether was needed in the less polar solvent to aid the cationic porphyrin's displacement of the potassium ions from the resin into the solution. Use of this modified loading procedure gave a catalyst with a twenty-fold increase in activity (Fig. 3). The low activity of catalysts prepared using aqueous acetone arises from the swelling of the resin which allows the metalloporphyrin to be

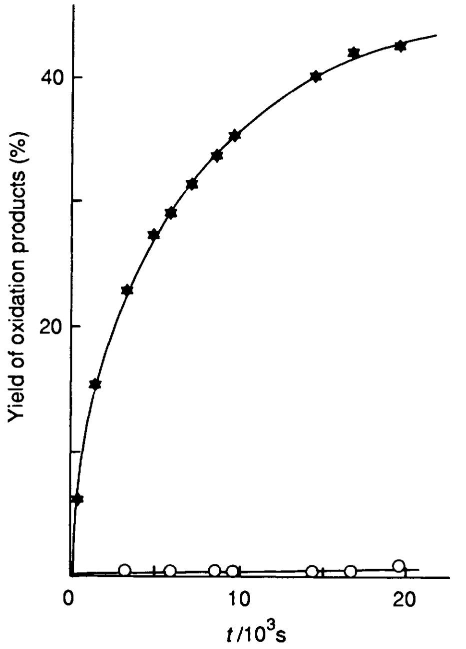


Fig. 2. The build-up of products from the oxidation of (*Z*)-cyclooctene by iodosylbenzene catalysed by $\mathrm{Fe^{III}}$T4MPyP on Dowex MSC1.

PhIO, 83.6 mmol $\mathrm{dm^{-3}}$; (*Z*)-cyclooctene, 0.7 mol $\mathrm{dm^{-3}}$; methanol 3 $\mathrm{cm^3}$, supported $\mathrm{Fe^{III}}$T4MPyP (2.2 μmol $\mathrm{g^{-1}}$) 2 μmol cyclooctanone (○), epoxycyclooctane (✱).

Table 4. Increase in volume of cation exchange resins when suspended in water, methanol and acetone.

	Increase in resin volume (%)[a]			
Resin	Water	Acetone	50% v/v aq. acetone	Methanol
Duolite 225	160	2.5	—	15
Dowex 50X8	90	0	—	30
Amberlite CG120	85	2.5	85	20
Dowex MSC1	40	5	40	30

[a] ± 10% based on dry volume.

Table 5. Yields of oxidation products on repeated use of Amberlyst A27-$\mathrm{Fe^{III}}$TDCSPP catalyst in the reaction of (*Z*)-cyclooctene with iodosylbenzene in methanol: (*Z*)-cyclooctene, 0.7 mol $\mathrm{dm^{-3}}$ per aliquot of PhIO; $\mathrm{Fe^{III}}$TDCSPP (1.7×10^{-6} mol $\mathrm{g^{-1}}$) 5.2×10^{-4} mol $\mathrm{dm^{-3}}$; methanol, 3 $\mathrm{cm^3}$; 20 °C in air.

		Yield (%)[a]		
Experiment	[Oxidant added]/ 10^{-2} mol $\mathrm{dm^{-3}}$	Epoxide	Formaldehyde	Total
1	4.13	46	15	61
2	4.13	64	21	85
3	8.26	61	21	82
4	8.26	68	17	85
5	16.5	60	22	82
6	24.7	61	20	81
7	41.3	52	24	76
8	4.13	53	22	75
9	90.9	38	24	62
10	4.13	29	23	52

[a] ± 2% based on oxidant added in each experiment.

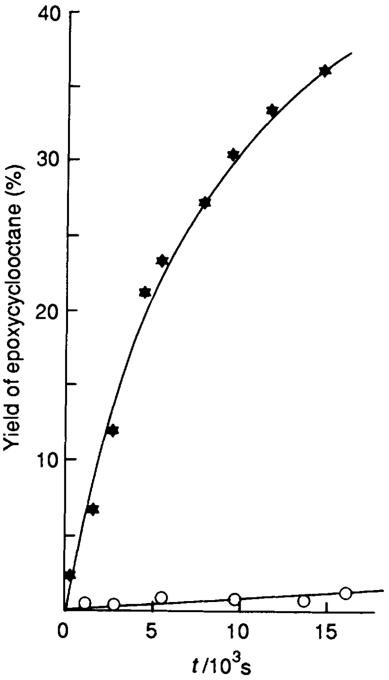


Fig. 3. The build-up of epoxycyclooctane in the reaction of (*Z*)-cyclooctene with iodosylbenzene catalysed by $\mathrm{Fe^{III}}$T4MPyP on Duolite 225.

PhIO, 41.3 mmol $\mathrm{dm^{-3}}$; (*Z*)-cyclooctene, 0.7 mol $\mathrm{dm^{-3}}$; methanol, 3 $\mathrm{cm^3}$; catalyst loading 2.2 μmol $\mathrm{g^{-1}}$. $\mathrm{Fe^{III}}$T4MPyP loaded in aqueous acetone (50% v/v) (○) and methanol containing 18-crown-6 (✱).

adsorbed on the internal and external surfaces of the polymer. Subsequent use of this supported catalyst in a less polar solvent, such as methanol, leads to a shrinking of the resin which effectively traps a large proportion of the catalyst in inaccessible sites within the resin core and reduces the catalyst's activity. When the catalyst is loaded and used in methanol the adsorption is on the external surface and catalyst activity is retained.

Tetrasodium tetra(4-*sulphonatophenyl*)*porphyrinatoiron*(III), *$\mathrm{Fe^{III}}$TSPP and Tetrasodium tetra*-(2,6-*dichloro*-3-*sulphonatophenyl*)*porphyinatoiron*(III), *$\mathrm{Fe^{III}}$TDCSPP*. None of the materials prepared from $\mathrm{Fe^{III}}$TSPP adsorbed onto anion exchange resins were efficient catalysts for the epoxidation of (*Z*)-cyclooctene by iodosylbenzene. The best, Amberlyst A27–$\mathrm{Fe^{III}}$TSPP, gave only 2.5 catalytic turnovers before the catalyst was destroyed (Table 2). However, the sterically hindered porphyrin $\mathrm{Fe^{III}}$TDCSPP on Amberlyst A27 was dramatically better. Repeat oxidations showed that after 4000 turnovers it still retained *ca.* 50% of its activity (Table 5). This effect of the *ortho*-chloro substituents on the catalyst efficiency has been observed previously with homogeneous non-ionic iron(III) porphyrins[6a,c] and suggests that the poor catalyst performance of $\mathrm{Fe^{III}}$TSPP arises from catalyst self-oxidation. The steric and electronic effects of the *ortho*-chloro groups block this oxidation of the porphyrin ring.

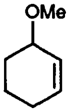
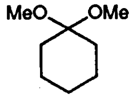
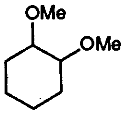
The Fate of the Oxidant in the Supported Metalloporphyrin-catalysed Oxidations.—In the homogeneous oxidation of methanol by iodosylbenzene catalysed by $\mathrm{Fe^{III}}$T4MPyP, $\mathrm{Fe^{III}}$T2MPyP and $\mathrm{Fe^{III}}$TSPP virtually all of the oxidant ($<96\%$) can be accounted for as formaldehyde (Table 6). When *cis*-cyclooctene is added, the active oxidant is competitively diverted to epoxycyclooctane and accountability remains excellent (Table 6). By contrast, in none of the oxidations catalysed by supported metalloporphyrins can all the oxidant

Table 6. Oxidant balance in homogeneous reactions of iodosylbenzene in methanol catalysed by iron(III) metalloporphyrins.

			Yield (%)[a]			
[Fe^{III}porphyrin]/ mol dm^{-3}	[Oxidant]/ 10^{-3} mol dm^{-3}	[Cyclooctene]/ mol dm^{-3}	Formaldehyde	Epoxide	PhIO unreacted	Oxidant accountability
Fe^{III}T4MPyP	2.14	—	100	—	—	100
(2.14 × 10^{-5})	5.36	—	98	—	—	98
	31.1	—	52		45	97
Fe^{III}T2MPyP	53.5	—	49	—	52	101
(8.91 × 10^{-6})	89.1	—	40	—	56	96
Fe^{III}TSPP	0.6	—	100	—	—	100
(1.22 × 10^{-5})	2.0	—	98	—	—	98
	3.1	0.51	31	70	—	101
	3.1	0.77	24	82	—	106

[a] Based on initial concentration of oxidant added.

Table 7. Yields of oxidation products from the reaction of cyclohexene with iodosylbenzene catalysed by acidic Dowex 50X8 in methanol: PhIO, 8.3 × 10^{-2} mol dm^{-3}, cyclohexene 0.78 mol dm^{-3}; Dowex 50X8, 1 g; methanol 3 cm^3; 20 °C in air.

	Yield (%)[a]		
Acid catalyst			
Dowex 50X8 (H$^+$) with Fe^{III}T4MPyP[b]	16	20	14
Dowex 50X8 (H$^+$)	15	10	13
4-Toluenesulphonic acid	2	0.5	1.3

[a] Yield after 6 min based on oxidant. [b] Fe^{III}T4MPyP (2.2 × 10^{-6} mol g^{-1}), 6.7 × 10^{-4} mol dm^{-3}. [c] 20 min reaction.

be accounted for (Tables 1 and 5). Even in the best systems 15–25% is missing and with other catalysts this figure is substantially higher. Iodometric titration shows that the missing oxidant cannot be accounted for as iodoxybenzene or as unreated iodosylbenzene and, since the further oxidation of formaldehyde is unimportant in homogeneous systems, it is unlikely that this is a significant reaction with the heterogeneous oxidations. By a process of elimination this suggests that the most likely fate of the missing oxidant is in the competitive oxidation of the polystyrene support. Thus the active oxidant is diverted from reactions with the solvent and substrate towards oxidation of the readily accessible benzyl C–H bonds and any unreated vinyl groups on the support. This conclusion can also account for the interesting increase in the catalyst efficiency of supported Fe^{III}TDCSPP following the addition of the first aliquot of oxidant. At the start of the reaction, easily oxidised groups on the support compete for the active oxidant. With subsequent additions of iodosylbenzene fewer such reactive groups on the support are available and the oxidation of methanol and (*Z*)-cyclooctene become more favourable.

Oxidations Catalysed by Dowex 50X8 (*Acid Form*).—The oxidation of cyclohexene by iodosylbenzene in the presence of Fe^{III}T4MPyP adsorbed onto acidic Dowex 50X8 rapidly gives products (Table 7) that are quite distinct from those using analogously modified resins in their sodium forms (Table 3). Interestingly, essentially the same oxidation occurs with acidic Dowex 50X8 in the absence of Fe^{III}T4MPyP indicating that the products arise from an acid-catalysed oxidation of cyclohexene by iodosylbenzene and does not involve the metalloporphyrin (Table 7). The results also show that toluene-4-sulphonic acid can also catalyse the reaction but not as effectively as the exchange resin.

The mechanism of the acid-catalysed oxidations of cyclohexene by iodosylbenzene was not investigated further, although the results do emphasise the influence the support can have on the course of the oxidation. It is likely that these reactions involve protonated iodosylbenzene or species such as $PhI(OH)O_3SR$ (where R is the polymer) as the active oxidant. There is substantial literature on the generation of electrophilic iodine(III) species, by reaction of iodosylbenzene and its diacetate with Lewis and protic acids, and their reactions with alkenes.[21]

In conclusion, ionic iron(III) porphyrins on ion exchange resins catalyse the epoxidation of alkenes by iodosylbenzene in an analogous manner to the prophyrins in free solution. However, with the heterogeneous catalysts the iron porphyrin remains strongly bonded to the support during the reaction and this simplifies the product analysis. From this study it is also clear that increased rigidity of the ion-exchange resin improves the catalyst's performance. Other aspects of oxidation catalysed by supported iron porphyrins, including the nature and the stability of the adsorbed catalyst and the mechanisms leading to catalyst destruction will be reported in the following paper in this series.

Experimental

Materials.—All materials were commercial reagent grade unless otherwise stated and were obtained from Aldrich Chemical Co. Ltd., BDH Chemicals Ltd., Lancaster Chemicals Ltd., Sigma Chemicals Ltd. and Strem Chemicals Ltd. Methanol and acetonitrile were purified and dried following standard procedures.[22] Cyclohexene and (*Z*)-cyclooctene we purified by elution through a dry packed alumina column before use. Iodosylbenzene was prepared following the method of Sharefkin and Saltzmann[23] and its purity shown to be $>99\%$ by iodometric titration.[24]

The tetrapyridylporphryins were prepared using the method of Kim, Leonard and Longo[25] and had the following spectroscopic properties: 5,10,15,20-tetrakis(4-pyridyl)porphyrin, $\lambda_{max}(CHCl_3)$ 373, 417, 512, 546, 587 and 642 nm; $\delta_H(CDCl_3)$ 9.06 (8 H, d, *J* 4.34 Hz), 8.86 (8 H, s), 8.15 (8 H, d, *J* 4.34 Hz) and -2.92 (2 H, s); 5,10,15,20-tetrakis(2-pyridyl)porphyrin, λ_{max} 373, 419, 514, 546, 588 and 646 nm; $\delta_H(CDCl_3)$ (4 H, dd, *J* 4.94 and 1.83 Hz), 8.86 (8 H, s), 8.21 (4 H, dd, *J* 7.69 and 1.20 Hz), 8.09 (4 H, ddd, *J* 8.00, 7.69 and 1.83 Hz), 7.71 (4 H, ddd, *J* 8.00, 4.94 and 1.20 Hz) and $-$ 2.82 (2 H, s).

5,10,15,20-Tetrakis(2,6,dichlorophenyl)porphyrin was prepared by the method of Lindsey *et al.*[26]; $\lambda_{max}(CHCl_3)$ 372, 418, 513, 585 and 633 nm; $\delta_H(CDCl_3)$ 8.90 (8 H, s), 8.34–8.28 (12 H, m) and -2.88 (2 H, s).

5,10,15,20-Tetrakis(2,6-dichloro-3-sulphatophenyl)porphyrin was prepared as a mixture of atropisomers by sulphonation of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin following Dolphin *et al.*[27]; $\delta_H(D_2O)$ 8.77 (8 H, s), 8.62 (4 H, m) and 8.00 (4 H, m).

The pyridylporphyrins were metallated with iron(II) chloride using the method of Adler *et al.*[28] The *N*-methylated derivative was obtained using methyl toluene-4-sulphonate and precipitated as its perchlorate following the procedure of Hambright *et al.* for methylation of the unmetallated tetra(4-pyridyl)porphyrin.[29] The perchlorate salt was converted to the water-soluble chloride by slurrying with excess of Amberlite CG-400 (Cl^- form) in water and then passing the solution down a short Amberlite CG-400 (Cl^- form) column. The final stage of purification was by ion exchange chromatography on Amberlite CG-50 (H^+ form) with 1 mol dm^{-3} hydrochloric acid. The eluted solution of iron(III) porphyrin in aqueous acid was concentrated to dryness with a rotary evaporator and a cool water bath. The 5,10,15,20-tetra(4-*N*-methylpyridyl)porphyrinatoiron(III) pentachloride was dissolved in methanol and precipitated with chloroform; $\lambda_{max}(H_2O$, pH 7.02) 338, 424 (ε 1004 dm^3 mol^{-1} cm^{-1}) (lit.,[30] 899 dm^3 mol^{-1} cm^{-1}), 506, 596 and 635 nm; $\delta_H(CD_3OD)$ 80.50 (8 H, br s), 13.15 (8 H, s), 11.88 (8 H, s) and 6.73 (12 H, s) (Found: C, 50.9; H, 4.5; N, 10.55; Fe, 5.6. Calc. for $C_{44}H_{36}N_8FeCl_5\cdot7H_2O$: C, 51.00; H, 4.83; N, 10.82; Fe, 5.4%). Tetra(2-*N*-methylpyridyl)porphyrinatoiron(III) pentachloride; $\lambda_{max}(H_2O$, pH 7.02) 343, 411 (ε 1140 dm^3 mol^{-1} cm^{-1}) (lit.,[31] 1270 dm^3 mol^{-1} cm^{-1}) 472, 530 and 588 nm; $\delta_H(CD_3OD)$ 75.69 (8 H, br s), 12.01 (4 H, s), 10.45 (4 H, s), 10.36 (4 H, s) 9.29 (4 H, s) and 7.38–7.80 (12 H, m) (Found: C, 51.0; H, 4.7; N, 10.65; Fe, 5.5. Calc. for $C_{44}H_{36}N_8FeCl_5\cdot7H_2O$: C, 51.00; H, 4.83; N, 10.82; Fe, 5.41%).

Iron was inserted into commercial tetrasodium 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin using the method of Fleischer *et al.*[32] The iron(III) porphyrin had $\lambda_{max}(H_2O$, pH 4.01) 393 (ε 1514 dm^3 mol^{-1} cm^{-1}) (lit.,[32] 1520 dm^3 mol^{-1} cm^{-1}), 529 and 680 nm; δ_H(0.1 mol dm^{-3} DCl in D_2O) 51.66 (8 H, br s), 14.34 (8 H, s) and 10.20 (8 H, s) (Found: C, 41.3; H, 2.8; N, 4.7; Fe, 4.6. Calc. for $C_{44}H_{24}N_4S_4O_{12}(SO_4)_{0.5}Na_4\cdot8H_2O$: C, 41.65; H, 31.13; H, 4.42; Fe, 4.40%).

Tetrasodium 5,10,15,20-tetrakis(2,6-dichloro-3-sulphonatophenyl)porphyrinatoiron(III) chloride was prepared by heating to reflux the free base porphyrin (125 mg) with a 40-fold excess of iron(II) chloride in water (10 cm^3) containing sodium hydrogen carbonate (50 mg). When UV-VIS spectroscopy showed that the conversion was complete the solution was cooled and acidified to pH 3.0 and the excess iron was removed by elution with water through a short column of Dowex 50X8 (H^+). The eluent was immediately neutralised with sodium carbonate. Further repeated chromatography on Sephadex LH-20-100 using methanol gave, after removal of solvent, the metalloporphyrin (47 mg), $\lambda_{max}(H_2O$, pH 2.5) 327, 393 (ε 914 dm^3 mol^{-1} cm^{-1}) (lit.,[33] 920 dm^3 mol^{-1} cm^{-1}) 507 and 579 nm, $\delta_H(D_2O)$ (8 H, br s), 10.81 (4 H, s) and 9.82 (4 H, s) (Found: C, 33.1; H, 1.6; N, 3.0. Calc. for $C_{44}H_{16}Cl_8S_4O_{12}Na_4\cdot(SO_4)_{0.5}$-$Na_2SO_4\cdot6H_2O$: C, 33,14; H, 1.76; N, 3.51%).

Methods.—GC analysis used 10% w/w OV-17 on Gas Chrom Q (100–120 mesh) in Pye-Unicam 104, 204 and 4500 gas chromatographs equipped with flame ionisation detectors. The results were analysed using a Trivector Scientific Ltd. Trilab 2000 chromatography data system and integrator.

For GC–MS a Pye series 104 chromatograph was coupled to an AEI MS 30 mass spectrometer.

Neutral porphyrins and metalloporphyrins were analysed by TLC on alumina 60 F_{254} neutral (type E, Merck) on aluminium sheet. For charged metalloporphyrins reversed-phase TLC (Whatman KCl 18F ODS-2) was used with water–methanol saturated with KCl as eluant.

Fixed wavelength (412 nm) determinations of formaldehyde by the Nash method were determined with a Pye-Unicam SP1750 spectrometer.

The determination of the iron content of the metalloporphyrins used a Philips PU9200 atomic absorption spectrometer. The iron was removed from the porphyrin prior to analysis by heating with aqueous acid.

Preparation of Polymer Supported Catalysts.—The commercial cation-exchange resins were first washed with a fourfold (v/v) excess of 5% (w/v) aqueous sodium carbonate (tenfold excess if the resin was initially in its acid form) and then sequentially with water, methanol and acetone before drying to constant weight under reduced pressure. A typical loading procedure used the dry resin (4 g) in aqueous acetone (80 cm^3, 50:50, v/v) to which was added an aqueous solution of the cationic metalloporphyrin (10 mg). The mixture was stoppered and shaken until the supernatant liquid became colourless. The modified resin was collected by filtration and washed sequentially with water, methanol and acetone before being dried under reduced pressure.

The anion-exchange resins were washed with a fourfold (v/v) excess of 5% (w/v) aqueous sodium chloride followed by water, methanol and acetone. These materials were dried and loaded as described above.

Oxidation Procedures.—In a typical heterogeneous oxidation the metalloporphyrin modified resin (1.0 g; loading 2 μmol cm^{-3}) was mixed with alkene (0.7 mol dm^{-3}) and methanol (1 cm^3). The reaction was initiated by the addition of iodosylbenzene in methanol (2 cm^3; 41.3 mol dm^{-3}). The reaction was then sealed with a Subba-seal and monitored at regular intervals by GC analysis. At the end of the reaction the formaldehyde concentration was estimated by the Nash test,[16] or the iodosylbenzene or iodylbenzene content was determined by iodimetric titration.

When examining the repeated use of Fe^{III}TDCSPP on Amberlyst A27, each oxidation was carried out as in single use experiments. At the end of each reaction the formaldehyde yield was measured and the catalyst was recovered by filtration, washed with methanol and acetone and briefly dried under reduced pressure. The reaction was then repeated with fresh (*Z*)-cyclooctene and iodosylbenzene.

The products were identified by comparison of GC retention times and GC–mass spectra with those of authentic materials.

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