

## Model Systems for Cytochrome P450 Dependent Monooxygenases. Part 8.<sup>1</sup> A study of the Epoxidation of (*Z*)-Cyclooctene by Iodosylbenzene Catalysed by Cationic Iron(III) Tetra(*N*-methylpyridyl)porphyrins Adsorbed on Dowex MSC1

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Tetra(*N*-methyl-4-pyridyl)porphyrinatoiron(III) pentachloride and its *N*-methyl-2-pyridyl isomer have been adsorbed onto the highly crosslinked cation ion-exchange resin Dowex MSC1 and have been used to catalyse the reaction of *Z*-cyclooctene with iodosylbenzene in methanol. Two oxidation products have been detected, epoxycyclooctane and formaldehyde. The dependence of the initial rate of epoxidation and the yields of the oxidation products on the concentrations of oxidant, alkene and catalyst and on the solvent composition and catalyst loading have been investigated. The results are interpreted in terms of the following competitive reactions of the active oxidant; alkene epoxidation, solvent oxidation and oxidative degradation of catalyst and support. Adsorption of the metalloporphyrins on the polymeric resin surprisingly leads to a decrease in the catalyst efficiency when compared with the same metalloporphyrin in free solution. The cause of this effect is discussed and it is proposed that it arises through the aggregation of the metalloporphyrins on the resin favouring the intermolecular self-oxidation of the catalyst.

The development of new oxidation catalysts is an important challenge<sup>2</sup> and is one of the reasons for the recent surge of interest in metalloporphyrin chemistry.<sup>3</sup> The potential of these compounds as catalysts depends on producing porphyrin ring systems that are stable towards oxidation and which introduce selectivity into the reactions. Stability<sup>4</sup> and selectivity<sup>4b,5</sup> can be increased by attaching large substituents to the porphyrin that prevent intermolecular self-oxidation and restrict access to the active oxidant. The utility of these catalysts, however, would be increased significantly if they could be readily attached to solid supports, since this should stabilise the catalysts further<sup>6</sup> and aid their recovery and re-use.<sup>7</sup> Furthermore, based on other work with supported reagents<sup>7</sup> and a very recent report by Mansuy and his co-workers<sup>8</sup> the support should also influence the selectivity of the oxidations.

In our previous paper,<sup>1</sup> we described studies using ionic iron(III) porphyrins, supported on ion-exchange resins, as catalysts for alkene epoxidation by iodosylbenzene in methanol. Two of the cationic iron(III) porphyrins, tetra(4-*N*-methylpyridyl)porphyrinatoiron(III) pentachloride, [Fe<sup>III</sup>T4MPyP], and its 2-*N*-methylpyridyl isomer, [Fe<sup>III</sup>T2MPyP], supported on the most promising of the cation exchange resins, Dowex MSC1, have been studied in more detail and these investigations are the subject of this paper.

### Results and Discussion

The metalloporphyrins were adsorbed onto Dowex MSC1 from 50% v/v aqueous acetone as described in the previous paper.<sup>1</sup> *Z*-Cyclooctene was used as the substrate in this study since it gives a clean conversion into *cis*-epoxycyclooctane without contamination from other alkene oxidation products. The reactions were carried out in methanol and the yield of formaldehyde from solvent oxidation was also routinely measured using Nash's method.<sup>9</sup>

*Dependence of Epoxidation on Z-Cyclooctene Concentration.*—Increasing the concentration of *Z*-cyclooctene leads to an increase in the yield of epoxide, up to a maximum of 55–60%, and to a less marked but significant decrease in the yield of formaldehyde (Table 1). A similar result was observed when

**Table 1** The dependence of the yields of oxidation products on initial alkene concentration in the reaction of *Z*-cyclooctene with iodosylbenzene in methanol catalysed by cationic iron(III)porphyrins on Dowex MSC1: PhIO,  $4.13 \times 10^{-2}$  mol dm<sup>-3</sup>; iron(III)porphyrins, ( $1.8 \times 10^{-6}$  mol g<sup>-1</sup>)  $5.4 \times 10^{-4}$  mol dm<sup>-3</sup>; methanol, 3 cm<sup>3</sup>; 20 °C in air

Fe <sup>III</sup> porphyrin	[Cyclooctene]/ 10 <sup>-1</sup> mol dm <sup>-3</sup>	Yield (%) <sup>a</sup>		
		Epoxide	Formaldehyde	Total
Fe <sup>III</sup> T4MPyP	1.17	19	33	52
	2.33	32	31	63
	3.50	39	41	80
	4.66	46	27	73
	6.99	53	22	75
	9.32	55	21	76
Fe <sup>III</sup> T2MPyP	1.17	33	44	77
	2.33	39	37	76
	3.50	51	36	87
	4.66	48	31	79
	6.99	58	26	84
	9.32	59	26	85

<sup>a</sup> ± 2% based on oxidant.

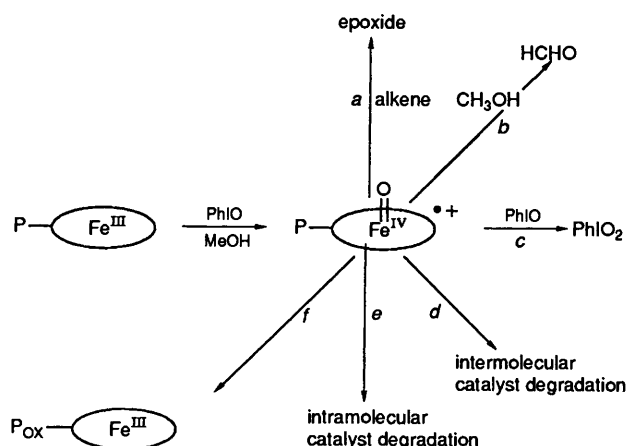
part of the methanol solvent was replaced with acetonitrile (the latter is more resistant to oxidation than methanol) (Table 2). These changes in product yields are readily understood in terms of a competition, between the alkene and the solvent, for the active oxidant (Scheme 1, paths *a* and *b*). The total yield of measured oxidation products was always significantly less than 100%. The fate of the missing oxidant was discussed in our previous paper where we concluded that the active oxidant is also consumed in oxidising the polymer support (Scheme 1, path *f*).

The build-up of epoxycyclooctane with time was monitored in reactions using different concentrations of *Z*-cyclooctene and the data were used to obtain initial rates of epoxidation. Although the systems are not homogeneous and kinetic studies should therefore be used with caution, Fig. 1 shows that the initial rate of epoxidation with both catalysts is linearly dependent on the initial alkene concentration, except at the

**Table 2** The dependence of the yields of oxidation products on the solvent composition in the reaction of *Z*-cyclooctene with iodosylbenzene catalysed by  $\text{Fe}^{\text{III}}\text{T4MPyP}$  on Dowex MSC1: PhIO,  $8.26 \times 10^{-2} \text{ mol dm}^{-3}$ ; *Z*-cyclooctene,  $0.7 \text{ mol dm}^{-3}$ ;  $\text{Fe}^{\text{III}}\text{T4MPyP}$ , ( $2.2 \times 10^{-6} \text{ mol g}^{-1}$ )  $6.6 \times 10^{-4} \text{ mol dm}^{-3}$ , solvent,  $3 \text{ cm}^3$ ;  $20^\circ\text{C}$  in air

Solvent Composition	Yield (%) <sup>a</sup>		
	Epoxide	Formaldehyde	Total
Methanol	40	25	65
80:20 v/v Methanol: acetonitrile	47	18	65
70:30 v/v Methanol: acetonitrile	48	16	64
30:70 v/v Methanol: acetonitrile	54	10	64
99:1 v/v Methanol: water	42	26	68
95:5 v/v Methanol: water	39	26	65

<sup>a</sup>  $\pm 2\%$  based on oxidant.

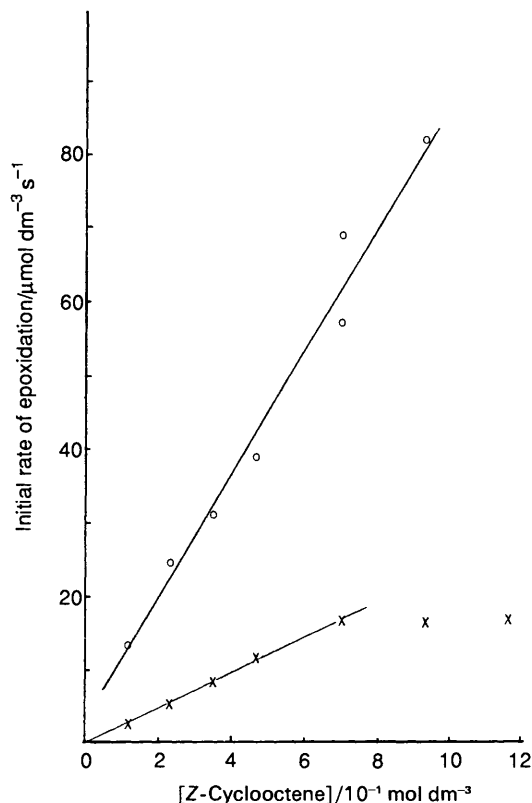


**Scheme 1** Oxidation pathways of supported oxoiron(IV) porphyrin  $\pi$ -radical cation

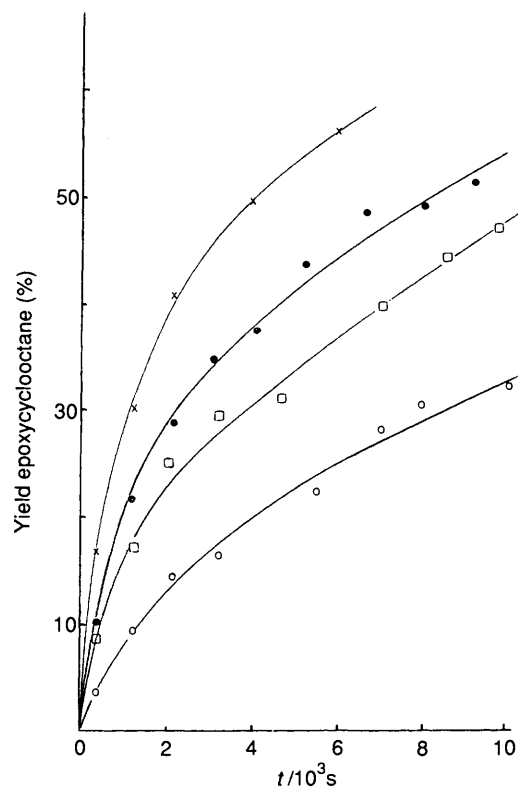
highest concentrations with  $\text{Fe}^{\text{III}}\text{T4MPyP}$ . The initial rate of epoxidation also increases when the concentration of methanol is decreased by the use of methanol–acetonitrile mixtures as solvent (Fig. 2).

Whether  $\text{Fe}^{\text{III}}\text{T2MPyP}$  exhibits saturation kinetics at higher concentrations of alkene, like  $\text{Fe}^{\text{III}}\text{T4MPyP}$ , could not be determined as the system would not dissolve more *Z*-cyclooctene. The origin of the saturation effect with  $\text{Fe}^{\text{III}}\text{T4MPyP}$  is unclear and since the systems are heterogeneous a thorough kinetic treatment is not possible. It could arise from the rate of epoxidation becoming limited by the diffusion of the substrate onto the supported catalyst. However, it is noteworthy that we have seen the same effect in homogeneous oxidations of cyclohexene with iodosylbenzene and  $\text{Fe}^{\text{III}}\text{T4MPyP}$ .<sup>10</sup> This suggests the effect is intrinsic to the oxidation mechanism and is not dependent on the support. A reaction scheme which would account for these results has been proposed by Collman and co-workers<sup>11</sup> and involves the reversible formation of an alkene–active oxidant complex (Scheme 2). The precise nature of this complex is still unclear, although recent work suggests it is more likely to be an electron-transfer complex<sup>12</sup> than the metallaoxetane proposed by Collman and his co-workers.<sup>11</sup>

*Dependence of the Epoxidation of Z-Cyclooctene on Iodosylbenzene Concentration.*—With both catalysts, the total yields of epoxide and formaldehyde reach a maximum with between 200 and 300 equiv. of iodosylbenzene. Further increases in the



**Fig. 1** The dependence on alkene concentration of the initial rate of the catalysed epoxidation of *Z*-cyclooctene by iodosylbenzene. PhIO,  $41.3 \text{ mmol dm}^{-3}$ ; methanol,  $3 \text{ cm}^3$ ; supported catalyst ( $1.8 \text{ μmol g}^{-1}$ )  $1.65 \text{ μmol}$ . ○,  $\text{Fe}^{\text{III}}\text{T2MPyP}$ ; ×,  $\text{Fe}^{\text{III}}\text{T4MPyP}$ .

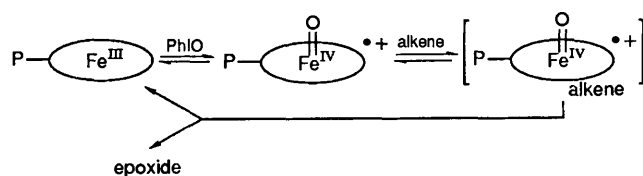


**Fig. 2** The build-up of epoxycyclooctane with time in the reaction of *Z*-cyclooctene with iodosylbenzene and Dowex MSC1/ $\text{Fe}^{\text{III}}\text{T4MPyP}$  in methanol–acetonitrile mixtures. PhIO,  $41.3 \text{ mmol dm}^{-3}$ ; *Z*-cyclooctene,  $0.7 \text{ mol dm}^{-3}$ ;  $\text{Fe}^{\text{III}}\text{T4MPyP}$  ( $1.8 \text{ μmol g}^{-1}$ )  $1.2 \text{ μmol}$  in solvent,  $3 \text{ cm}^3$ . ○, Methanol:acetonitrile, 10:0; □, 8:2; ●, 7:3; ×, 3:7.

**Table 3** The dependence of the yields of oxidation products on the initial oxidant concentration in the reaction of *Z*-cyclooctene with iodosylbenzene catalysed by cationic iron(III)porphyrins on Dowex MSC1: *Z*-cyclooctene, 0.7 mol dm<sup>-3</sup>; iron(III)porphyrin, (1.8 × 10<sup>-6</sup> mol g<sup>-1</sup>) 5.4 × 10<sup>-4</sup> mol dm<sup>-3</sup>; methanol, 3 cm<sup>3</sup>; 20 °C in air

Fe <sup>III</sup> porphyrin	[PhIO]/ 10 <sup>-2</sup> mol dm <sup>-3</sup>	Yield (%) <sup>a</sup>			Total yield <sup>b</sup> / 10 <sup>-2</sup> mol dm <sup>-3</sup>
		Epoxide	Formaldehyde	Total	
Fe <sup>III</sup> T4MPyP	2.48	54	33	87	2.16
	4.13	47	34	81	3.34
	6.19	40	28	68	4.21
	8.26	35	26	61	5.04
	10.3	28	23	51	5.25
	12.4	27	20	47	5.83
	24.8	18	16	34	5.61
Fe <sup>III</sup> T2MPyP	2.48	51	24	75	1.84
	4.13	59	18	77	3.18
	6.20	58	18	76	4.71
	8.26	50	18	68	5.62
	12.4	31	14	55	6.82
	16.5	22	16	38	6.27

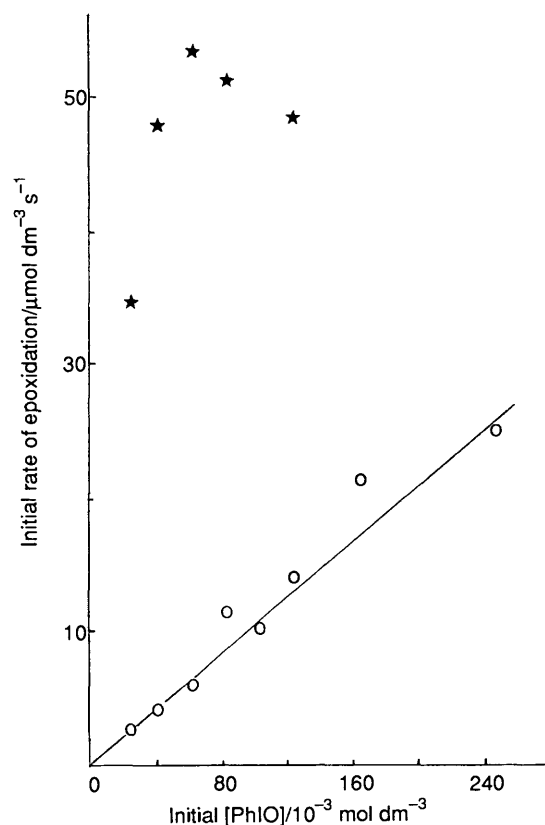
<sup>a</sup> ± 2% based on oxidants. <sup>b</sup> Yield of epoxide plus formaldehyde.



amount of oxidant used do not lead to more of these oxidation products (Table 3). This effect could arise from iodosylbenzene acting as a competitive substrate for the active oxidant (Scheme 1, path *c*). The latter reaction, which would become more favourable at the higher concentrations of iodosylbenzene, has been reported previously in iron(III)porphyrin-catalysed reactions with this oxidant.<sup>4b</sup> However, it is more likely that with a large excess of iodosylbenzene, catalyst destruction occurs and the reactions do not go to completion. This explanation for the limiting yield of epoxide is supported by the visible bleaching of the supported catalysts in reactions with >200-fold excess of oxidant and from studies using varying amounts of catalyst (see below).

The dependence of the initial rates of epoxidation on oxidant concentration differs with the two catalysts (Fig. 3). With iodosylbenzene concentrations between 2.5 × 10<sup>-2</sup> and 2.5 × 10<sup>-1</sup> mol dm<sup>-3</sup>, the supported Fe<sup>III</sup>T4MPyP shows a linear dependence of initial rate on initial oxidant concentration whilst the corresponding reaction with Fe<sup>III</sup>T2MPyP is almost independent of oxidant concentration except at the lowest value. Both these types of kinetic behaviour can be interpreted in terms of a mechanism involving the reversible formation of an active oxidant complex (Scheme 2). If the rate of epoxidation depends on the concentration of an active oxidant, then at low oxidant concentrations where the catalyst is not saturated in oxidant the rate of oxidation would be first-order in oxidant. However, at high oxidant concentrations, where all the catalyst is in effect present as the active oxidant, the rate would become independent of oxidant. If this argument is applied to the supported catalysts, the Fe<sup>III</sup>T4MPyP reactions were studied under non-saturating conditions, whereas with the 2-isomer, with all but the most dilute oxidant concentrations, the catalyst was saturated with oxidant. Alternative explanations involving different rate-controlling steps for the two catalysts are also possible.

*The Influence of Water on the Epoxidation of Z-Cyclooctene.*—The rates of some homogeneous metalloporphyrin-



**Fig. 3** The dependence of the initial rate of the catalysed epoxidation of *Z*-cyclooctene on the initial concentration of iodosylbenzene. *Z*-Cyclooctene, 0.7 mol dm<sup>-3</sup>; methanol, 3 cm<sup>3</sup>; supported catalyst (1.8 μmol g<sup>-1</sup>) 1.62 μmol; ★, Fe<sup>III</sup>T2MPyP; ○, Fe<sup>III</sup>T4MPyP.

catalysed oxidations by methanolic solutions of iodosylbenzene have been found to increase with the addition of small quantities of water to the reaction mixture.<sup>10,13</sup> This has been attributed to the shift in the equilibrium in Scheme 3 from 2 in dry methanol in favour of the more reactive species 1. However, with the supported Fe<sup>III</sup>T4MPyP the presence of small quantities of water (0–5% v/v) in the methanol had no significant influence on the initial rates of epoxidation or on the final yields of products (Table 2). It is possible that the absence of an effect from added water comes from the resins ability to retain a

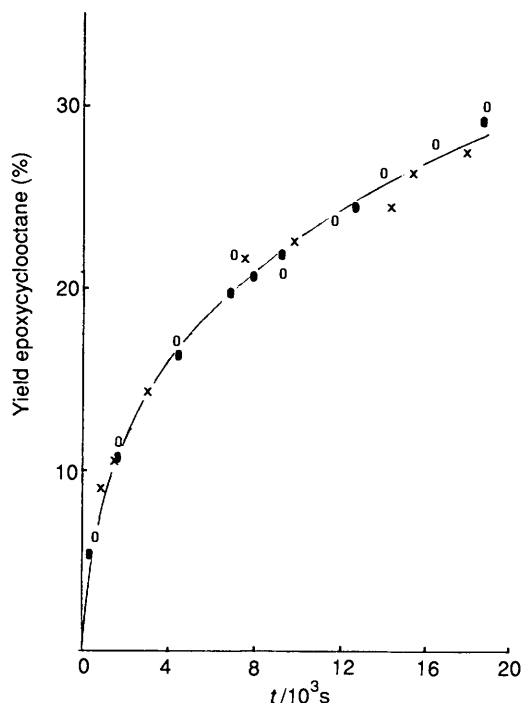
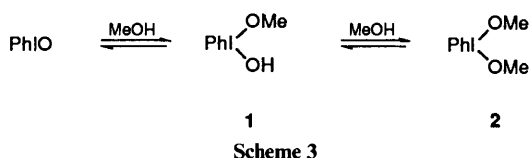


Fig. 4 The build-up of epoxy cyclooctane with time in the reaction of *Z*-cyclooctene with iodosylbenzene using different loadings of Fe<sup>III</sup>T4MPyP on MSC1 as catalysts. PhIO, 82.6 mmol dm<sup>-3</sup>; *Z*-cyclooctene, 0.7 mol dm<sup>-3</sup>; methanol 3 cm<sup>3</sup>, Fe<sup>III</sup>T4MPyP 1.62 μmol; ●, loading 1.35; ○, 2.71; ×, 4.52 μmol g<sup>-1</sup>.

considerable amount of water, even after drying. The presence of resin bound water could ensure that species 1 is favoured even in dry methanol.



*Dependence of Z-Cyclooctene Epoxidation on the Loading of Catalyst on Dowex MSC1.*—Changing the loading of Fe<sup>III</sup>T4MPyP on Dowex MSC1 from 1.35 to 4.5 μmol g<sup>-1</sup>, while maintaining a constant catalyst concentration in each reaction, had no effect on the initial rate of formation, build-up and final yield of epoxy cyclooctane (Fig. 4). Likewise, loading the porphyrin onto the resin from aqueous solutions at pH 1.0, 7.0 and 13.0 did not change the activity of the catalyst.

There have been numerous studies on the pH dependent equilibria in aqueous solutions of Fe<sup>III</sup>T4MPyP<sup>14</sup> and it is generally accepted that in acidic solution the metalloporphyrin exists as a monomeric species. However, in aqueous base the system is less well-defined although it seems likely that the solutions contain a concentration dependent equilibrium of monomer and μ-oxo-dimer.<sup>14d</sup> However, since catalytic activity is not dependent on the pH of, or on the presence of acetone in, the aqueous solutions used for loading the polymers, it is not clear whether the adsorbed metalloporphyrins are present as monomers or as aggregates (possibly dimers). We suspect that, because the rates of the catalysed oxidations are significantly faster in homogeneous solution than with the supported catalyst, the metalloporphyrin is aggregated on the surface of the ion exchange resin. Recent experiments with anionic iron(III) tetraarylporphyrins reveal that the μ-oxo-dimers are less reactive catalysts than the monomeric species.<sup>15</sup> Although the metalloporphyrin may be present as a monomer in homo-

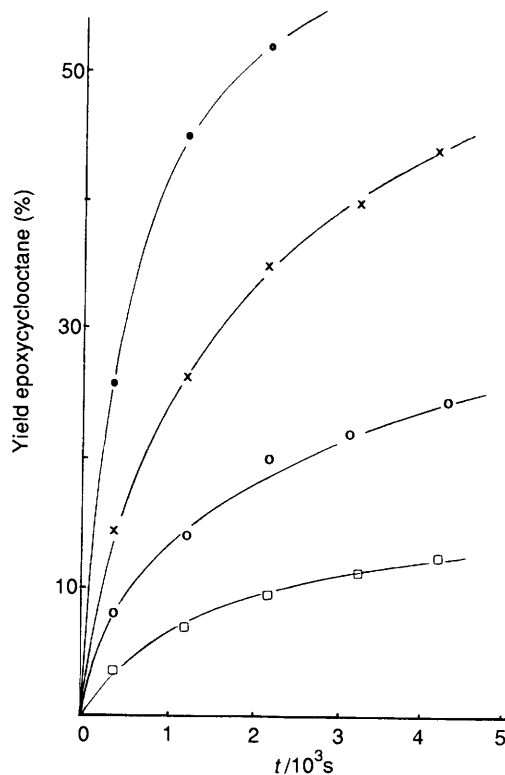
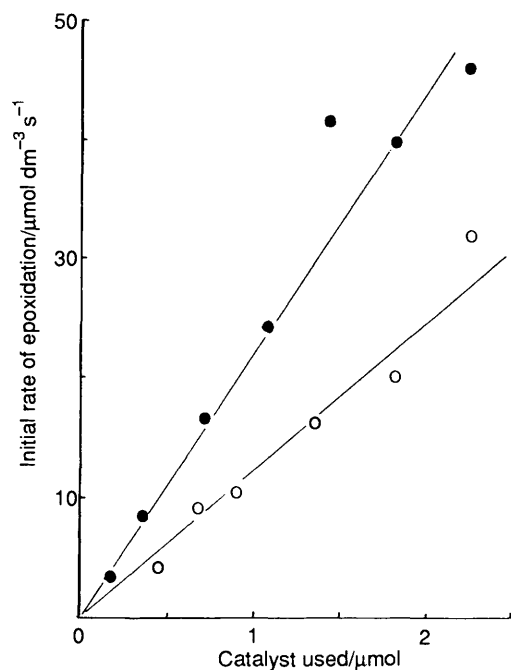


Fig. 5 The dependence of the build-up of epoxy cyclooctane with time on catalyst concentration in the reaction of *Z*-cyclooctene with iodosylbenzene. PhIO, 41.3 mmol dm<sup>-3</sup>; *Z*-cyclooctene, 0.7 mol dm<sup>-3</sup>; methanol, 3 cm<sup>3</sup>; Dowex MSC1/Fe<sup>III</sup>T4MPyP (1.8 μmol g<sup>-1</sup>): □, 0.45; ○, 0.68; ×, 1.35; ●, 2.26 μmol.

geneous solution, it is quite possible that because its effective concentration on the surface of the polymer is much higher than in free solution it is loaded as aggregates under all the conditions employed here. Support for this suggestion comes from recent spectroscopic studies on the binding of Fe<sup>III</sup>T4MPyP<sup>16</sup> and zinc tetra(*N*-methyl-4-pyridyl)porphyrin<sup>17</sup> to water soluble un-crosslinked polystyrene sulphonate.

*Dependence of the Rate and Yield of Epoxidation on Catalyst Concentration.*—The build-up of epoxy cyclooctane was monitored in reactions using different amounts of supported Fe<sup>III</sup>T4MPyP and Fe<sup>III</sup>T2MPyP (Fig. 5) and data such as these were used to obtain initial rates of epoxidation. Fig. 6 shows that there is a linear relationship between the initial rate and the catalyst concentration. The final yields of epoxide and formaldehyde are recorded in Table 4. These results reveal that with sufficient catalyst (oxidant:catalyst ratio < 150–200) the reactions reach a maximum yield of oxidation products [72% for supported Fe<sup>III</sup>T4MPyP and 85% for Fe<sup>III</sup>T2MPyP]. However, with low catalyst concentrations the product yields are less than this maximum, even after prolonged reaction times. This suggests that under the latter conditions the activity of the catalyst is lost before the oxidations are complete.

*Catalyst Re-use.*—The stability of the supported Fe<sup>III</sup>T4MPyP and Fe<sup>III</sup>T2MPyP catalysts was studied in repeat epoxidations of *Z*-cyclooctene by iodosylbenzene. The build-up of the epoxy cyclooctane was monitored following the addition of an aliquot of the oxidant (61 equiv. with respect to the metalloporphyrin) and the formaldehyde yield was measured at the end of the reaction. The catalyst was then removed, washed and re-used in a repeat oxidation. For both catalysts, the first two aliquots of oxidant gave little change in the catalyst's performance. However, subsequent additions



**Fig. 6** The dependence of the initial rate of epoxidation of *Z*-cyclooctene by iodosylbenzene on the concentration of supported catalyst. PhIO,  $41.3 \text{ mol dm}^{-3}$ ; *Z*-cyclooctene,  $0.7 \text{ mol dm}^{-3}$ ; methanol,  $3 \text{ cm}^3$ ; Dowex MSC1-supported catalyst ( $1.8 \text{ } \mu\text{mol g}^{-1}$ ): ●,  $\text{Fe}^{\text{III}}\text{T2MPyP}$ ; ○,  $\text{Fe}^{\text{III}}\text{T4MPyP}$ .

**Table 4** The dependence of the yields of oxidation products on catalyst concentration in the reaction of *Z*-cyclooctene with iodosylbenzene in methanol: PhIO,  $4.13 \times 10^{-2} \text{ mol dm}^{-3}$ ; *Z*-cyclooctene,  $0.7 \text{ mol dm}^{-3}$ ; methanol,  $3 \text{ cm}^3$ ;  $20^\circ\text{C}$  in air

Catalyst on Dowex MSC1	[Catalyst] <sup>b</sup> $10^{-3} \text{ mol dm}^{-3}$	Yield (%) <sup>a</sup>		
		Epoxide	Formaldehyde	Total
$\text{Fe}^{\text{III}}\text{T4MPyP}$	0.15	20	12	32
	0.23	39	17	56
	0.30	50	18	68
	0.45	55	19	74
	0.60	54	18	72
	0.75	54	18	72
$\text{Fe}^{\text{III}}\text{T2MPyP}$	0.06	13	12	25
	0.12	27	16	43
	0.24	51	20	71
	0.36	60	26	86
	0.48	56	27	83
	0.60	56	30	86
	0.75	47	32	79

<sup>a</sup>  $\pm 2\%$  based on oxidant. <sup>b</sup> Loading of catalyst  $1.8 \times 10^{-6} \text{ mol g}^{-1}$  of Dowex MSC1.

revealed a bleaching of the catalyst and a significant reduction in the rate and yield of epoxidation and to a lesser extent the yield of formaldehyde (Table 5). Based on the total yield of products, the supported catalyst was bleached and deactivated with approximately 300 equiv. of oxidant. This value agrees well with the value suggested above from the data in Table 3. By comparison the values for the analogous homogeneous reactions of unsupported  $\text{Fe}^{\text{III}}\text{T4MPyP}$  and  $\text{Fe}^{\text{III}}\text{T2MPyP}$  in methanol are 500 and 4000, respectively. The supported catalysts, far from being more stable, are more readily deactivated than their homogeneous analogues.

There are two possible causes for the loss of catalytic activity, (i) catalyst destruction and (ii) catalyst masking, both could lead to a bleaching of supported metalloporphyrin. In the latter the

**Table 5** Yields of oxidation products on repeated use of catalyst in the reaction of *Z*-cyclooctene with iodosylbenzene in methanol: PhIO,  $4.13 \times 10^{-2} \text{ mol dm}^{-3}$  per reaction; *Z*-cyclooctene,  $0.7 \text{ mol dm}^{-3}$  per reaction; iron(III)porphyrin, ( $2.2 \times 10^{-6} \text{ mol g}^{-1}$ )  $6.6 \times 10^{-4} \text{ mol dm}^{-3}$ ; methanol,  $3 \text{ cm}^3$ ;  $20^\circ\text{C}$  in air

$\text{Fe}^{\text{III}}$ porphyrin	Experiment number	Yield (%) <sup>a</sup>		
		Epoxide	Formaldehyde	Total
$\text{Fe}^{\text{III}}\text{T4MPyP}$	1	53	18	71
	2	53	18	71
	3	56	16	72
	4	21	18	39
	5	6	14	20
$\text{Fe}^{\text{III}}\text{T2MPyP}$	1	54	17	71
	2	53	18	71
	3	55	18	73
	4	21	18	39
	5	6	11	17

<sup>a</sup>  $\pm 2\%$  based on oxidant added in each experiment.

catalyst becomes buried under a layer of insoluble material, for example iodosylbenzene.

Scanning electron microscopy was used to examine the supported  $\text{Fe}^{\text{III}}\text{T4MPyP}$  before and after reaction with iodosylbenzene (230 equiv. with respect to  $\text{Fe}^{\text{III}}\text{T4MPyP}$ ) and *Z*-cyclooctene. Although the catalyst had been visibly bleached by the reaction, the electron micrographs showed that no major structural changes had occurred and there was no evidence for solid deposits on the surface. The iodosylbenzene content of the used catalyst was also studied by iodimetric titration and found to account for less than 5% of the iodosylbenzene. From these results we conclude that catalyst deactivation and bleaching arises from the destruction of the porphyrin and is not caused by a layer of insoluble solid masking the surface of the resins.

*The Mechanism of Porphyrin Destruction with Supported Catalysts.*—The generally accepted mechanism for the destruction of metalloporphyrin catalysts in oxidation is an intermolecular process in which the metalloporphyrin acts as a substrate for the active oxidant (Scheme 1, path *d*).<sup>4b</sup> It was hoped that this reaction would be eliminated by site-isolating the metalloporphyrins on the surface of the ion exchange resins. Indeed it is well known that the use of bulky substituents which prevent the close approach of metalloporphyrins in homogeneous solution leads to catalysts that are more resistant to oxidation.<sup>4a</sup> However, even with rigid ion-exchange resins, where porphyrin–porphyrin interactions that arise through the flexibility of the support are minimised, the catalysts are inferior to the iron(III) porphyrins in homogeneous solution. Furthermore, they are dramatically less stable than  $\text{Mn}^{\text{III}}\text{T4MPyP}$  adsorbed onto rigid inorganic oxides (e.g. silica gel).<sup>8</sup>

There are three possible explanations for the oxidative destruction of metalloporphyrins on the ion-exchange resins. This could arise from an intramolecular self-oxidation, from a reaction between the activated catalyst and the polymer support or from an intermolecular process favoured by aggregation of the metalloporphyrins on the polymer surface. The first process would involve migration of oxygen in the active oxidant from the iron to the porphyrin ring. Such a process might be initiated by rearrangement of an oxoiron porphyrin-active oxidant to an iron porphyrin *N*-oxide<sup>18</sup> followed by a further rearrangement leading to oxidative destruction of the conjugated ring system. This intramolecular oxidation could become important with the supported catalyst if one assumes that the support slows down the diffusion of substrates to the active oxidant in competing oxidations (Scheme 1, path *e*). However, this explanation for

catalyst destruction seems unlikely since Mn<sup>III</sup>T4MPyP on silica gel is an effective and stable oxidation catalyst.<sup>8</sup>

In the second explanation the catalyst deactivation might arise from oxidation of the polymer support. The benzyl C–H bonds and residual vinyl groups of the polymer backbone are present in a locally high concentration near the adsorbed catalyst. Oxidation of these groups could generate intermediate radicals or radical ions which react with and deactivate the metalloporphyrins. The reaction of porphyrin rings with reactive intermediates from metalloporphyrin-catalysed reaction is well known. Typical examples include, the *N*-alkylation of iron porphyrins and of cytochrome P450 in the catalysed oxidation of terminal alkenes,<sup>19</sup> *N*- and *C*-alkylation of porphyrins in haem enzymes by carbon radicals derived from alkylhydrazines,<sup>20</sup> and the suicide inactivation of cytochrome P450 by intermediates in the metabolism of cyclopropylamines.<sup>21</sup> However, we eliminated this as the likely cause for catalyst instability by carrying out oxidations with Fe<sup>III</sup>T4MPyP adsorbed on the very inert perfluorinated cation exchange resin Nafion NR50. The modified Nafion NR50 ( $5.4 \times 10^{-6}$  mol Fe<sup>III</sup>T4MPyP g<sup>-1</sup> resin) catalyses the epoxidation of *Z*-cyclooctene by iodosylbenzene in methanol but the stability of the iron(III) porphyrin is remarkably poor. The catalyst is totally bleached and deactivated with <100 equivs. of oxidant.

We conclude, as described above, that the metalloporphyrins are aggregated and not site-isolated on the surface of Dowex MSC1 and as a consequence adsorption on the ion-exchange resin favours, rather than prevents, the intermolecular self-destruction of the catalysts. We are currently exploring alternative methods for preparing oxidatively stable supported metalloporphyrin catalysts.

## Experimental

**Materials.**—All materials were commercial reagent grade or were prepared and purified as described previously.<sup>1</sup>

**Methods.**—The chromatographic, spectroscopic and other analytical procedures used in this study were as reported previously.<sup>1</sup>

For scanning electron microscopy the sample was coated with gold in a Polaron spotter coater and viewed with an ISI 100A microscope.

The concentration of unchanged iodosylbenzene in reaction mixtures was determined by removing and washing the resin with methanol. The washings and reaction mixture were combined and acidified with glacial acetic acid (20 cm<sup>3</sup>). A few small chips of solid carbon dioxide followed by saturated aqueous potassium iodide were added and the liberated iodine was titrated with standardised 0.01 mol dm<sup>-3</sup> sodium thio-sulphate using a starch indicator. The iodylbenzene on the resin was determined by first removing the iodosylbenzene with methanol and then dissolving the iodylbenzene with portions of glacial acetic acid (2 × 10 cm<sup>3</sup>). This solution was treated as above and the iodine liberated was determined titrimetrically.

## Acknowledgements

One of us (D. R. L.) thanks the SERC for a research studentship. We also thank Mr. P. Crosby in the Department of Biology, University of York for running the scanning electron micrographs.

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Paper 0/02944K

Received 3rd July 1990

Accepted 20th August 1990