Kinetic study of the epoxidation of alkenes by iodosylbenzene catalysed by iron(III) tetra(4-*N*-methylpyridyl)porphyrin in methanol

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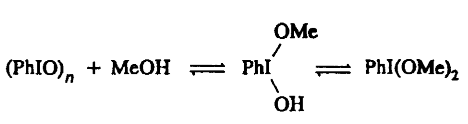
A kinetic analysis of the epoxidation of alkenes by iodosylbenzene catalysed by iron(III) tetra(4-*N*-methylpyridyl)porphyrin[†] ($\mathrm{Fe^{III}}$T4MPyP) in methanol solution is presented. Using the initial rate method, the rates of epoxidation are found to be first-order in $\mathrm{Fe^{III}}$T4MPyP and to show saturation kinetics in both the oxidant and the substrate. Interestingly, for the two most reactive styrenes, 4-methoxy- and 4-methylstyrene, the rate of epoxidation is first-order in the substrate: saturation kinetics in substrate are not observed. A Michaelis–Menten-like rate equation is derived for the system, under conditions where the catalyst is saturated in oxidant, and is used to compare the rates of epoxidation of a selection of aliphatic alkenes and styrenes.

The reactivity of an alkene is found to be determined by the influence of the substituent on the formation of a complex with the active oxidant and on the subsequent breakdown of this intermediate to give products. The results from the less reactive styrenes are analysed using the Hammett equation and the mechanism of the epoxidation is discussed.

Since Groves, Nemo and Myers[1] first reported the iron(III) tetraphenylporphyrin-catalysed epoxidation of alkenes by iodosylbenzene the mechanism of this and related iron(III) and manganese(III) porphyrin-catalysed systems has been the subject of intense investigations.[2] These have involved kinetic[3] and product studies, the latter have been used to examine the stereochemistry of the epoxidation[1,4] and to identify the reactions of the active oxidant that compete with epoxidation, for example allylic oxidation,[5] catalyst destruction[5] and catalyst *N*-alkylation.[7]

The active oxidant in these iron(III) porphyrin systems is generally accepted to be the high valent oxoiron(IV) porphyrin π radical cation which, being electrophilic, reacts most readily with electron rich alkenes.[3e,4a] Selected alkenes have been used as sensitive mechanistic probes to distinguish between alternative epoxidation mechanisms.[4c,d,f,8] The influence of substituents and of structure on the reactivity of the alkene has revealed important electronic and stereochemical features of the oxygenation step.[1,3c,e,4a,8c,d,9] Theoretical calculations have also been employed to model the active oxidants and their reaction with alkenes.[10]

In an earlier study, we reported the epoxidation of alkenes by iodosylbenzene in methanol catalysed by iron(III) tetra(4-*N*-methylpyridyl)porphyrin ($\mathrm{Fe^{III}}$T4MPyP).[‡][11] This is a homogeneous system since the alkene catalyst and iodosylbenzene all readily dissolve in methanol. Iodosylbenzene is insoluble in most organic solvents but in methanol it forms soluble hydroxymethoxy- and dimethoxy-derivatives (**1** and **2**, Scheme 1).[12] In this paper we describe our kinetic studies of alkene epoxidation by this system. This has clear advantages over the heterogeneous systems studied by Collman and his co-workers using $\mathrm{Mn^{III}}$TPP, $\mathrm{Mn^{III}}$TMP and iron(III) tetra(substituted phenyl)porphyrins.[3a,f,13] Analysis of the kinetic data provides further insight into the mechanism of epoxidation by oxoiron(III) tetraarylporphyrin π radical cations.[3a–f,12]



$$(\mathrm{PhIO})_n + \mathrm{MeOH} \rightleftharpoons \mathrm{PhI}\begin{smallmatrix}\mathrm{OMe}\\ \mathrm{OH}\end{smallmatrix} \rightleftharpoons \mathrm{PhI(OMe)_2}$$

1 **2**

Scheme 1

Results

The initial studies used cyclohexene as the substrate to develop the system for following the kinetics of epoxidation. Trial experiments showed that in homogeneous solution in methanol the cyclohexene was converted into epoxycyclohexane, cyclohex-2-en-1-ol and cyclohex-2-en-1-one in the molar proportions 85 : 5 : 10. This product distribution remained constant throughout all subsequent changes in reagent concentrations.

The reagent concentrations and reaction temperature were adjusted so that the rate of epoxidation was such that it could be followed by removing aliquots for GC analysis. This enabled the reactions to be monitored by following the change of the product yields with time. The most suitable reaction conditions were $\mathrm{Fe^{III}}$T4MPyP (1.56×10^{-4} mol dm^{-3}), iodosylbenzene (1.7–16.7×10^{-2} mol dm^{-3}) and cyclohexene (1–10×10^{-1} mol dm^{-3}) in a total methanolic solution of 3 cm^3 at 4.5 ± 0.5 °C. The reaction took several hours to go to completion and the final yield of epoxycyclohexane (based on PhIO) was approximately 30%. Replacing the solvent with methanol–acetonitrile (1:1) or with acetonitrile led to higher epoxide yields, 40% and 60%, respectively. However, the solubility of iodosylbenzene in the latter solvents is poor. To maximise the quantity of oxidant in solution while maintaining a single phase system methanol was chosen as the solvent for further studies.

The order of reaction in each of the three reagents (cyclohexene, iodosylbenzene and $\mathrm{Fe^{III}}$T4MPyP), was obtained by measuring the initial rate of epoxidation (V) as the concentration of one reagent was varied while the concentrations of the others were held constant. Studying the kinetics by the initial rate method minimised problems such as catalyst oxidative destruction and further reaction of the products that

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[†] 5,10,15,20-Tetra(*N*-methyl-4-pyridyl)porphyrinatoiron(III) pentachloride.

[‡] Abbreviations: 5,10,15,20-tetraarylporphyrin ligands; TDBPP, tetra-(2,6-dibromophenyl)porphyrin, TDCPP, tetra(2,6-dichlorophenyl)-porphyrin; TMP, tetramesitylporphyrin; T4MPyP, tetra(4-*N*-methylpyridyl)porphyrin; TPFPP, tetrapentafluorophenylporphyrin; TPP, tetraphenylporphyrin.

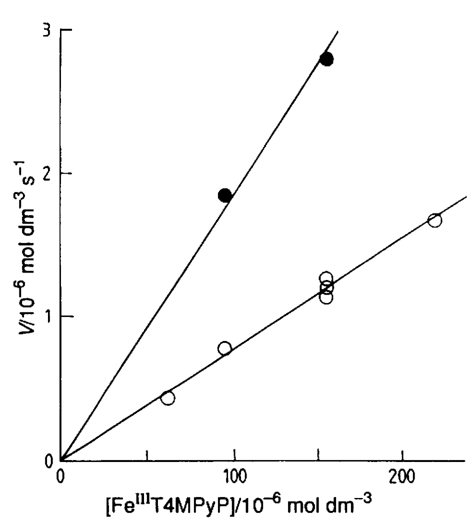


Fig. 1 Dependence of the initial rate of epoxidation of cyclohexene on Fe^{III}T4MPyP concentration: cyclohexene, 0.25 mol dm^{-3} in methanol total volume 3 cm^3, 4.5 °C; PhIO, (○) 16.7; (●) 50 mmol dm^{-3}

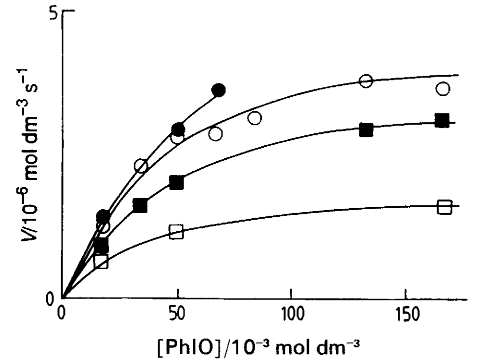


Fig. 2 Dependence of the initial rate of epoxidation of cyclohexene on oxidant concentration: Fe^{III}T4MPyP, 1.56 × 10^{-4} mol dm^{-3} in methanol total volume 3 cm^3, 4.5 °C; cyclohexene, (□) 8.2 × 10^{-2}; (■) 16.5 × 10^{-2}; (○) 24.7 × 10^{-2}; (●) 33.0 × 10^{-2} mol dm^{-3}

might occur in the later stages of these oxidations. The results obtained with catalyst : oxidant : substrate molar ratios of 1 : 100–500 : 500–2000 are given in Figs. 1–3. From Fig. 1 it can be seen that the reaction is first-order in the catalyst concentration. However, the order of the reaction in the oxidant and in cyclohexene is not constant. The epoxidation shows saturation kinetics and changes from being first-order to zero-order as the concentration of oxidant or alkene is increased. The oxidant concentrations at which first, intermediate and zero-order behaviour in oxidant occurred were found not to vary with substrate concentration. In contrast, varying the substrate concentration, using a range of oxidant concentrations, shows that the reaction order in the substrate at a particular substrate concentration is also dependent on the oxidant concentration.

The influence of steric and electronic effects on epoxidation by the homogeneous Fe^{III}T4MPyP–PhIO system was examined using a selection of alkene substrates. With all these alkenes the epoxide was either the sole or the major oxidation product (> 85%) and where a choice of diastereoisomeric products was possible the reactions were *syn*-stereospecific. Small or very small amounts of allylic oxidation products were obtained in the oxidations of cyclohexene, as noted above, and cyclopentene and the two *trans*-disubstituted alkenes, (*E*)-oct-2-ene and (*E*)-4-methylpent-2-ene. The epoxidations of styrene and of 4-methyl- and 4-methoxy-styrene gave the corresponding phenylacetaldehyde as a minor by-product.

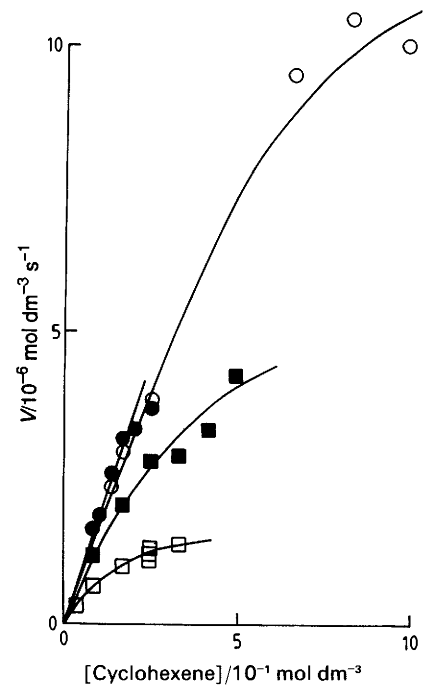


Fig. 3 Dependence of the initial rate of epoxidation of cyclohexene on substrate concentration: Fe^{III}T4MPyP, 1.56 × 10^{-4} mol dm^{-3} in methanol total volume 3 cm^3, 4.5 °C; PhIO, (□) 1.7 × 10^{-2}; (■) 5.0 × 10^{-2}; (○) 13.3 × 10^{-2}; (●) 16.7 × 10^{-2} mol dm^{-3}

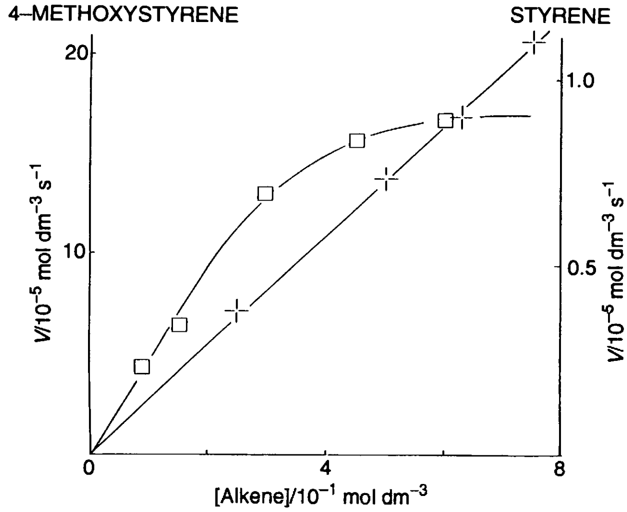


Fig. 4 Dependence of the initial rate of epoxidation of styrene (□) and 4-methoxystyrene (+) on substrate concentration: Fe^{III}T4MPyP, 1.56 × 10^{-4} mol dm^{-3}; PhIO, 1.0 × 10^{-1} mol dm^{-3} (styrene) and 2.0 × 10^{-1} mol dm^{-3} (4-methoxystyrene) in methanol total volume 3 cm^3; 4.5 °C

The rates of epoxidation of the alkenes were compared using the kinetic method described above. For each substrate the concentration of oxidant required to obtain zero-order kinetics in the oxidant, while keeping the concentration of substrate and catalyst constant, was determined. The oxidant concentration required to obtain saturation kinetics was dependent on the nature of the substrate but, as found for cyclohexene, was not found to vary with substrate concentration. The oxidant concentration was then held at this level while the substrate concentration was varied to find the dependence of the reaction rate on the substrate concentration. For each substrate, except 4-methyl- and 4-methoxy-styrene, the plot of initial epoxidation

Table 1 Dependence on substrate concentration of initial rates of epoxidation of aliphatic alkenes by PhIO catalysed by Fe^{III}T4MPyP in methanol: Fe^{III}T4MPyP, 1.56 × 10^{-4} mol dm^{-3}, MeOH 3 cm^3 at 4.5 °C

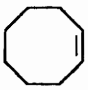
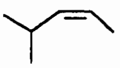
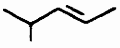
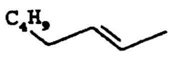
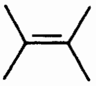
Substrate	[PhIO]/ mol dm^{-3}	[Alkene]/ mol dm^{-3}	Initial rate (V)/ 10^{-6} mol dm^{-3} s^{-1}
	0.13	0.38	7.28
	0.13	0.46	8.31
	0.13	0.57	10.31
	0.13	0.76	13.1
	0.13	1.14	16.9
	0.13	0.10	1.77
	0.13	0.13	2.31
	0.13	0.17	2.92
	0.13	0.20	3.31
	0.13	0.25	3.82
	0.13	0.66	9.52
	0.13	0.82	10.5
	0.13	0.99	10.1
	0.083	0.13	2.30
	0.083	0.19	2.76
	0.083	0.26	3.81
	0.083	0.38	5.40
	0.083	0.51	6.09
	0.083	0.77	7.96
	0.10	0.27	4.70
	0.10	0.40	6.59
	0.10	0.53	8.86
	0.10	0.66	10.2
	0.10	0.27	0.98
	0.10	0.40	1.48
	0.10	0.53	1.95
	0.10	0.78	2.56
	0.13	0.43	2.52
	0.13	0.85	4.89
	0.13	1.28	6.23
	0.13	1.71	7.42
	0.13	2.13	8.06
	0.20	0.14	10.3
	0.20	0.28	19.7
	0.20	0.35	22.0
	0.20	0.42	30.0
	0.20	0.49	32.5
	0.20	0.56	32.2
	0.033	0.11	1.48
	0.033	0.18	1.88
	0.033	0.27	1.76
	0.033	0.35	2.31
	0.033	0.53	2.17
	0.033	1.04	2.43

Table 2 Dependence on substrate ($XC_6H_4CH{=}CH_2$) concentration of initial rates of epoxidation of substituted styrenes by PhIO catalysed by Fe^{III}T4MPyP in methanol: Fe^{III}T4MPyP, 1.56 × 10^{-4} mol dm^{-3}, MeOH 3 cm^3 at 4.5 °C

X	[PhIO]/ mol dm^{-3}	[Alkene]/ mol dm^{-3}	Initial rate (V)/ 10^{-6} mol dm^{-3} s^{-1}
4-OMe	0.20	0.24	71.1
	0.20	0.49	137
	0.20	0.61	169
	0.20	0.73	207
4-Me	0.17	0.25	19.3
	0.17	0.37	35.3
	0.17	0.50	40.6
	0.17	0.62	46.4
	0.17	0.74	70.3
H	0.10	0.24	6.99
	0.10	0.44	8.38
	0.10	0.58	8.96
4-Cl	0.13	0.28	7.33
	0.13	0.41	9.46
	0.13	0.55	10.4
	0.13	0.83	11.4
3-Cl	0.13	0.50	10.3
	0.13	0.75	14.0
	0.13	1.25	19.1
	0.13	2.49	28.6
	0.13	2.99	29.6
4-CF_3	0.10	0.62	6.24
	0.10	1.77	13.0
	0.10	2.22	15.7
4-NO_2	0.10	0.26	3.21
	0.10	0.52	6.17
	0.10	1.95	17.1

rate against substrate concentration showed saturation kinetics similar to cyclohexene. For example Fig. 4 shows the results for styrene. The data for all the alkenes studies are recorded in Tables 1 and 2. 4-Methyl- and 4-methoxy-styrene epoxidations were first-order in the substrate under all the conditions studied (*e.g.* Fig. 4).

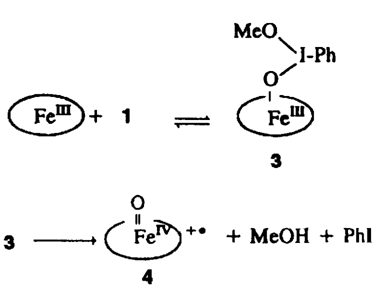
One competitive epoxidation was studied using equimolar quantities of styrene and 3-chlorostyrene in sufficient concentration to saturate the system in each substrate. Furthermore, as with the single substrate kinetic studies, the iodosylbenzene concentration was high enough so that the system was also saturated in the oxidant.

Discussion

This and a previous study[11] show that Fe^{III}T4MPyP successfully catalyses the homogeneous epoxidation of a wide range of alkenes by PhIO in methanol. In all the reactions the epoxide was the principal or only product detected from the alkene.

Competitive epoxidations of aliphatic alkenes have shown the Fe^{III}T4MPyP–PhIO system in methanol has very similar stereoelectronic characteristics to the heterogeneous Fe^{III}TPP–PhIO system in dichloromethane and we have concluded that the mechanism of epoxidation in the two systems is essentially the same.[11] However, since the solvent methanol can be oxidised in the former system,[12b,c] it competes with the alkene for the active oxidant. This leads to lower epoxide yields, particularly with less reactive alkenes, than have been reported with more oxidatively stable solvents, such as dichloromethane. Furthermore it accounts for the increase in the yield of epoxycyclohexane from cyclohexene when the methanol was partially or totally replaced by acetonitrile. In previous studies we have quantified the yield of formaldehyde from the methanol,[12b,c] in the present investigation the kinetics were monitored by following the growth of epoxide, however, the formaldehyde yields were not measured. For the kinetic analyses the methanol concentration was assumed to be constant since the methanol was always in a very large excess and its concentration was not varied by more than 10%.

The general mechanism for oxygen transfer from iodosylbenzene to the iron(III) porphyrin involves a reversible axial ligation of the oxidant to the metal centre followed by the elimination of iodobenzene. With iodosylbenzene in methanol it is probable that the methanol adduct (**1**, Scheme 1), which Traylor *et al.*[7a] liken to a peroxyacid, ligates to the iron(III) porphyrin and the active oxidant **4** is generated by the loss of methanol and iodobenzene from complex **3** (Scheme 2).[7c]

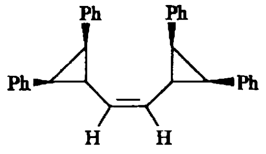


Scheme 2

Numerous mechanisms have been proposed for the oxygen transfer from oxoiron(IV) porphyrin π radical cations to alkenes.[3e] Almost all of which involve two steps with the formation of an intermediate. Collman and his co-workers[3a] followed the kinetics of the heterogeneous epoxidation of alkenes by perfluoroiodosylbenzene catalysed by $\mathrm{Fe^{III}}$TPFPP in dichloromethane. This system followed Michaelis–Menten kinetics and the rates were independent of the alkene concentration. They concluded that the alkene and the oxoiron(IV) porphyrin π radical cation were in rapid equilibrium with a metallaoxetane intermediate **5** (path a, Scheme 3) the breakdown of which to epoxide was rate determining. Under the conditions they used the reaction system was considered to be saturated in alkene and consequently the rate was zero-order in alkene concentration. A similar reaction mechanism was proposed for heterogeneous epoxidations catalysed by $\mathrm{Mn^{III}}$TPP and $\mathrm{Mn^{III}}$TMP.[13]

The involvement of a metallaoxetane intermediate, however, has been disputed by Traylor *et al.*[4c,7c,8a,14] and by Bruice and his co-workers.[8c,15] Perhaps most convincingly, molecular modelling of $\mathrm{Fe^{III}}$TDBPP-catalysed epoxidation shows that, for all but terminal alkenes, the formation of a metallaoxetane intermediate with this very sterically crowded catalyst would not be possible.[8c]

Bruice and his co-workers[8b] have also eliminated a carbon radical **6** (path b, Scheme 3)[4a,b,f,8b,16] as a required intermediate in the epoxidation using the (*Z*)-dicyclopropylalkene (**7**) as a hypersensitive radical probe. Epoxidation of **7** catalysed by iron(III) porphyrins gave the corresponding (*Z*)-epoxide as the sole oxygenated product. From the likely rate of rearrangement of an intermediate such as **6** from the alkene **7** ($>2 \times 10^{10}\ \mathrm{s^{-1}}$) they calculated that the conversion of **6** solely to the (*Z*)-epoxide would have to have a rate constant $>10^{12}\ \mathrm{s^{-1}}$. This effectively excludes **6** as a discrete intermediate.



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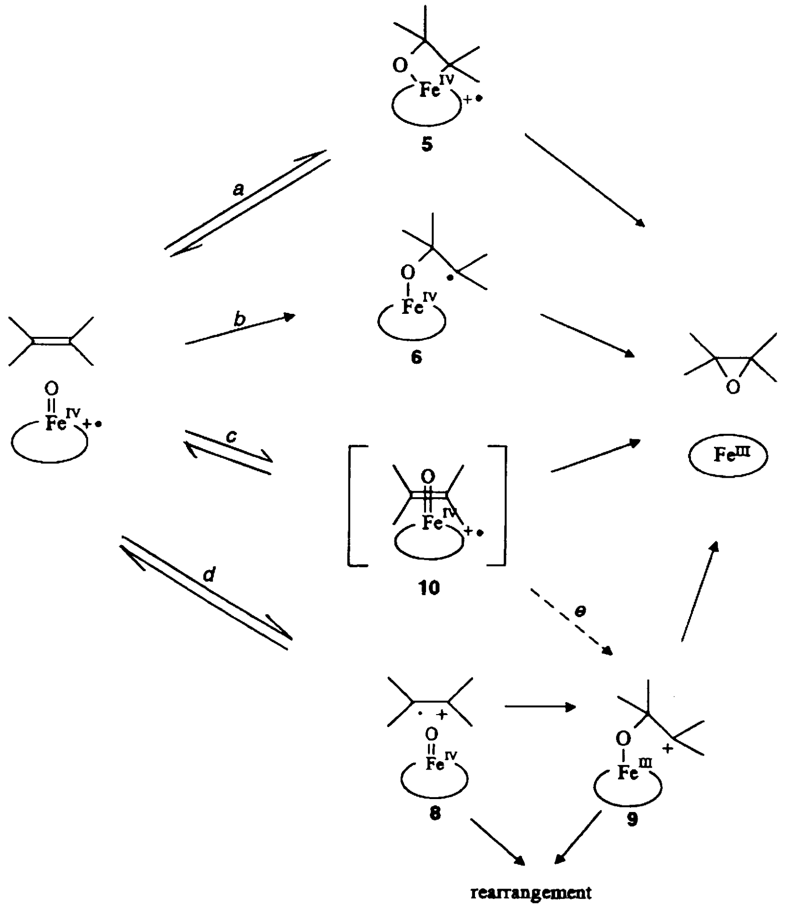
The involvement of cation radical and cationic intermediates in metalloporphyrin-catalysed epoxidations have also been proposed to account for the oxidative rearrangements observed with some alkenes (path d, Scheme 3).[3e,4c,d,f,7c,8a,17] Such a mechanism might be expected with alkenes with low oxidation potentials[8a,b] or with metalloporphyrins with electron-withdrawing substituents where the active oxidant has a high oxidation potential.[4c] However, it is unlikely to be the principal route for epoxidation of most alkenes.[8c,18]

Most recently Bruice and his co-workers[18] have proposed that oxoiron(IV) porphyrin π radical cations react with alkenes



Scheme 3

via a charge-transfer complex **10** which collapses to epoxide by a concerted mechanism (path c, Scheme 3). Some leakage of the charge-transfer complex to the cationic intermediate **9** (path e, Scheme 3) is required to account for the rearrangement products and for porphyrin *N*-alkylation observed with some alkenes.[4c,d,f,7c]

The present kinetic study shows the electrophilic nature of the active oxidant, although it does not lead to an unambiguous assignment of the intermediate formed with the alkene. However, on the basis of the evidence in the literature (outlined above), the data will be interpreted in terms of the formation of a charge-transfer complex between the active oxidant and alkene, as proposed by Bruice and his co-workers (path c, Scheme 3). The overall mechanism for the iron(III) porphyrin-catalysed epoxidation of alkenes by iodosylbenzene in methanol can then be described by Scheme 4. The oxoiron(IV) porphyrin π radical cation is consumed not only in alkene epoxidation but also in the competing reactions of solvent oxidation and catalyst comproportionation. Because the concentration of methanol remains essentially constant the former non-productive oxidation occurs at a constant rate. The oxoiron(IV) porphyrin formed in the comproportionation is the dominant porphyrin species in these oxidation systems.[19] However, unlike oxomanganese(IV) porphyrins which can epoxidise alkenes,[4c] it is inactive and it is presumed that it can only be reactivated by the disproportionation of two oxoiron(IV) prophyrins.

The proposed reaction scheme is similar to that found for some enzymes where sequential binding and conversion of two species on an enzyme is required.[20] These reaction schemes are amenable to Michaelis–Menten kinetics, and rate equations of the form shown in eqn. (1) are found. Where X and Y are two

$$\frac{1}{V}=\frac{P}{[\mathrm{X}]}+\frac{Q}{[\mathrm{Y}]}+\frac{R}{[\mathrm{X}][\mathrm{Y}]} \qquad (1)$$

substrates, V is the rate of the reaction of one of them, Y, and P, Q and R are constants. As a result, these types of reaction can be identified by plotting $1/V$ *vs.* $1/[\mathrm{X}]$ and obtaining a series of straight line plots which vary in slope and intercept with the value of [Y]. This type of behaviour can be seen in the epoxidation of cyclohexene by the Fe$^{\mathrm{III}}$T4MPyP–PhIO–MeOH system where the enzyme is represented by Fe$^{\mathrm{III}}$T4MPyP and the substrates Ph(OH)OMe and cyclohexene. Plotting $1/V$ (where V is the initial rate of epoxidation) against 1/[cyclohexene] or 1/[PhIO] provides a series of straight line plots corresponding to different PhIO or cyclohexene concentrations respectively (Figs. 5 and 6), in agreement with the reaction scheme described above.

$$\mathrm{Fe^{III}P + PhI(OMe)OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PhI(OMe)OFe^{III}P} \qquad (1)$$

$$\mathrm{PhI(OMe)OFe^{III}P \xrightarrow{k_2} OFe^{IV}P^{\bullet +} + PhI + MeOH} \qquad (2)$$

$$\mathrm{S + OFe^{IV}P^{\bullet +} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CT} \qquad (3)$$

$$\mathrm{CT \xrightarrow{k_4} Fe^{III}P + OS} \qquad (4)$$

$$\mathrm{OFe^{IV}P^{\bullet +} + MeOH \xrightarrow{k_5} Fe^{III}P + HCHO} \qquad (5)$$

$$\mathrm{Fe^{III}P + OFe^{IV}P^{\bullet +} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} 2\,OFe^{IV}P} \qquad (6)$$

Where $\mathrm{Fe^{III}P = Fe^{III}T4MPyP}$
$\mathrm{OFe^{IV}P = OFe^{IV}T4MPyP}$
$\mathrm{OFe^{IV}P^{\bullet +} = OFe^{IV}T4MpyP^{\bullet +}}$
S = cyclohexene
OS = epoxycyclohexane

Scheme 4 Proposed reaction scheme for the epoxidation of cyclohexene by the Fe$^{\mathrm{III}}$T4MPyP–PhIO system in methanol

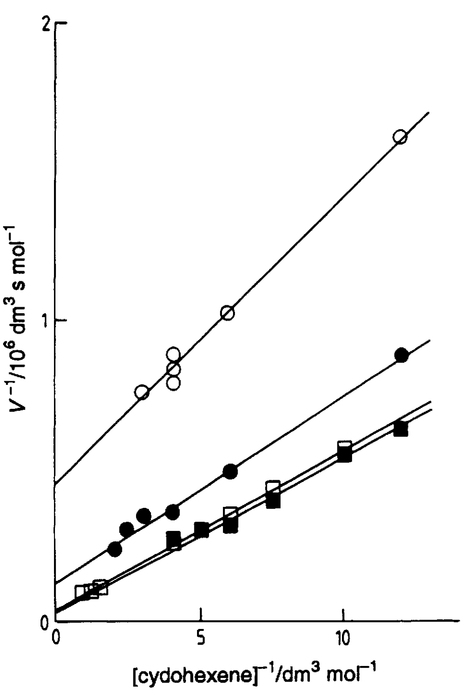


Fig. 5 Plot of $1/V$ *vs.* 1/[cyclohexene] for the epoxidation of cyclohexene with different iodosylbenzene concentrations: Fe$^{\mathrm{III}}$T4MPyP, 1.56×10^{-4} mol dm^{-3} in methanol total volume 3 cm^3, 4.5 °C; PhIO, (○) 1.7×10^{-2}; (●) 5.0×10^{-2}; (□) 13.3×10^{-2}; (■) 16.7×10^{-2} mol dm^{-3}

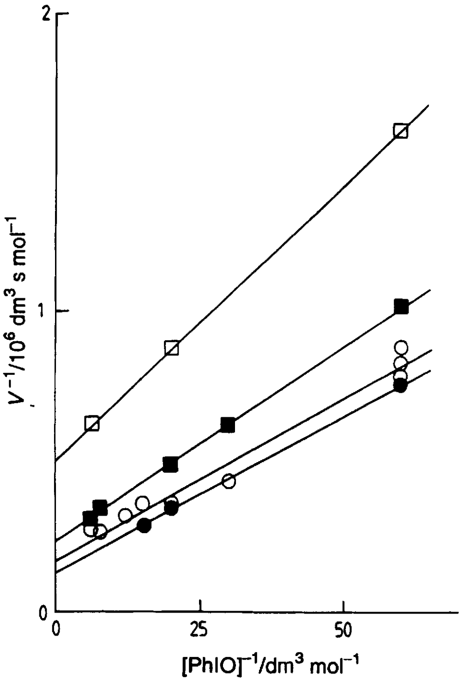


Fig. 6 Plot of $1/V$ *vs.* 1/[PhIO] for the epoxidation of cyclohexene with different cyclohexene concentrations: Fe$^{\mathrm{III}}$T4MPyP, 1.56×10^{-4} mol dm^{-3} in methanol total volume 3 cm^3, 4.5 °C; cyclohexene (□) 8.2×10^{-2}; (■) 16.5×10^{-2}; (○) 24.7×10^{-2}; (●) 33.3×10^{-2} mol dm^{-3}

Table 3 Values of the kinetic parameters for the epoxidation of aliphatic alkenes by iodosylbenzene catalysed by Fe^{III}T4MPyP in methanol at 4.5 °C

Substrate	$V_{max}/10^{-6}$ mol dm^{-3} s^{-1}	$CK_M/10^{-7}$ mol dm^{-3}	(V_{max}/CK_M)/s^{-1}
2,3-Dimethylbutene	168 ± 63	21.5 ± 9.1	78.0 ± 3.7
Norbornene	2.38 ± 0.18	0.62 ± 0.21	38.4 ± 10.2
Cyclopentene	55.0 ± 9.8	25.0 ± 5.4	21.9 ± 0.8
Cyclohexene	21.9 ± 4.9	10.8 ± 2.8	20.2 ± 0.6
Cyclooctene	14.8 ± 4.0	7.35 ± 2.64	20.1 ± 1.7
(*Z*)-4-Methylpentene	46.7 ± 10.6	23.4 ± 6.2	19.9 ± 0.8
(*E*)-4-Methylpentene	17.4 ± 10.4	43.8 ± 28.4	3.97 ± 0.21
(*E*)-Oct-2-ene	23.3 ± 5.6	34.6 ± 10.2	6.74 ± 0.37

Table 4 Values of the kinetic parameters for the epoxidation of styrene and substituted styrenes ($XC_6H_4CH{=}CH_2$) by iodosylbenzene catalysed by Fe^{III}T4MPyP in methanol at 4.5 °C

X	$V_{max}/10^{-6}$ mol dm^{-3} s^{-1}	$CK_M/10^{-6}$ mol dm^{-3}	(V_{max}/CK_M)/s^{-1}
4-NO_2	55.0 ± 8.7	4.15 ± 1.3	13.2 ± 2.0
4-CF_3	34.9 ± 3.7	2.84 ± 0.40	12.2 ± 0.4
3-Cl	41.9 ± 1.7	1.81 ± 0.09	26.3 ± 0.9
4-Cl	17.1 ± 2.1	0.37 ± 0.096	46.0 ± 6.2
H	12.8 ± 0.1	0.24 ± 0.025	53.1 ± 3.2

Derivation of the rate equation

Scheme 4 can be used to derive a rate equation for epoxidation. Under conditions where the system is saturated in oxidant, the rate eqn. (2) can be obtained by steady state treatment of the species $Fe^{III}P$, $OFe^{IV}P$ and the charge transfer complex (CT) by defining the following: (*a*) the total iron porphyrin concentration, $[FeP]_{total} = [Fe^{III}P] + [OFe^{IV}P] + [OFe^{IV}P^{\cdot +}] + [CT]$; (*b*) $K_M = (k_{-3} + k_4)/k_3$; and (*c*) V_{max} is the maximum rate when the system is saturated in both oxidant and substrate $\{V_{max} = k_4[FeP]_{total}\ (\text{limit } V, [S] \rightarrow \infty)\}$.

$$\frac{d[OS]}{dt} = V = V_{max}[S]/[S](1 + k_4/k_2) + K_M\{1 + k_5/k_2 + (k_5k_6/k_2k_{-6})^{\frac{1}{2}}\} + (K_M[S]k_4k_6/k_2k_6)^{\frac{1}{2}} \quad (2)$$

Eqn. (2) can be simplified to the more useful eqn. (3), where C is a constant $[1 + k_5/k_2 + (k_5k_6/k_2k_{-6})^{\frac{1}{2}}]$ that is dependent only on the oxidation system, by assuming $k_4/k_2 \ll 1$ and $(K_M[S]k_4k_6/k_2k_{-6})^{\frac{1}{2}}$ is negligible.

$$V = V_{max}[S]/([S] + CK_M) \quad (3)$$

Applying this analysis to the results from the epoxidation of cyclohexene (Table 1) allows reaction parameters CK_M and V_{max} to be determined from the double reciprocal plot of $1/V$ *vs.* 1/[cyclohexene], the gradient of the resulting straight line being CK_M/V_{max} and the *y*-intercept being $1/V_{max}$. The value of the rate constant k_4 may be determined from V_{max}.

Assuming that the above analysis holds for all the other alkenes (Tables 1 and 2), their reaction constants may also be calculated (Tables 3 and 4). These results can be compared with the V_{max} values obtained by Collman and his co-workers using the heterogeneous systems $Mn^{III}TPP{-}OCl^-$, $Mn^{III}TMP{-}OCl^-$ and $Fe^{III}TPFPP{-}C_6F_5IO$.[3a,13a,b] For the limited number of substrates in common (cyclohexene, styrene and norbornene), the V_{max} values at 22 °C are 10–100 times greater than those from the present study at 4.5 °C. No direct comparison of the magnitude of K_M values can be made because of the correction factor C in this work ($C > 1$ by definition). The relative values found for different substrates show similar trends in this work to those of Collman and his co-workers but do not correlate exactly, possibly due to different combinations of electronic and steric factors working in the different systems.

An examination of the results from the epoxidation of the aliphatic alkenes shows that particular levels of reactivity (V_{max}/CK_M) are characteristic of a particular arrangement of alkyl groups on an aliphatic double bond. (*Z*)-Dialkylalkenes have, with the exception of norbornene, $V_{max}/CK_M \approx 20$ s^{-1} whilst the corresponding (*E*)-alkenes have $V_{max}/CK_M \approx 5$ s^{-1}. The more highly substituted 2,3-dimethylbut-2-ene has a higher reactivity. We observed a similar order of reactivity from product studies from competitive epoxidations with the heterogeneous $Fe^{III}TPP{-}PhIO$ system in dichloromethane.[4a] The results are consistent with a higher reactivity correlating with a higher electron density on the alkene. Ignoring the steric effects, the reactivity would be expected to increase in a stepwise manner for mono-, di-, tri- or tetra-alkylalkenes. However, the five-fold difference in reactivity between the (*Z*)- and (*E*)-4-methylpent-2-ene shows that steric effects are important. Previous work[4a,b,9b] using heterogeneous iron(III) porphyrin–PhIO systems in CH_2Cl_2 have reported this difference in reactivity between (*Z*)- and (*E*)-alkenes in competitive reactions. The reported Z:E reactivities being 5.8:1 for but-2-enes[4b] and 13–14:1 for 4-methylpent-2-enes.[4a,9b] The higher reactivity of 2,3-dimethylbut-2-ene than (*Z*)-dialkylalkenes shows that the electronic effects dominate the steric effects.

The exception to these results is norbornene, which is twice as reactive as would be expected from these arguments. The high reactivity of norbornene towards electrophiles has been noted previously, as has its strong preference for *exo*-addition.[4b,c,21] In the present study no *endo*-product (*exo*:*endo* > 100) was observed. Traylor and his co-workers[4c] in their studies of iron porphyrin-catalysed epoxidation of norbornene obtained *exo*:*endo* product ratios ranging from 3 for the most active oxidant system to 58 to Fe^{III}TPP. This would suggest that the active oxidant from Fe^{III}T4MPyP in methanol is relatively unreactive.

Although the reactivity of an aliphatic alkene is determined largely by its alkyl substituents this cannot be assigned solely to either the interaction of the substrate with the active oxidant (CK_M) or to the subsequent breakdown of the intermediate to products (V_{max}). The CK_M values show that (*E*)-substituted dialkylalkenes complex less strongly (larger CK_M values) than their (*Z*)-counterparts although there is a considerable variation within the latter class of compounds.

The V_{max} values tend to vary inversely with the value of CK_M for a particular class of alkene, thus keeping the reactivity approximately constant. This suggests that the factors which inhibit the association of the alkene with the active oxidant also accelerate the breakdown of the resulting intermediate to products. The overall reactivity (V_{max}/CK_M) appears to follow the association of substrate and oxidant ($1/CK_M$) more closely than the rate at which the intermediate breaks down (V_{max}).

Norbornene again appears to be different from other aliphatic alkenes in that it interacts much more strongly with the active oxidant and the intermediate formed breaks down to the epoxide much less readily. Similar observations were made by Collman and his colleagues[8a] in the heterogeneous $Fe^{III}TPFPP{-}C_6F_5IO$ system, where norbornene was found to bind to the active oxidant 300 times more strongly than (*Z*)-cyclooctene.

The epoxidation of substituted styrenes was investigated since the steric effects of each substrate should be essentially constant, thus allowing the electronic effects to be quantified. The results show that the interaction of a particular styrene with the active oxidant increases (CK_M decreases) and the rate of

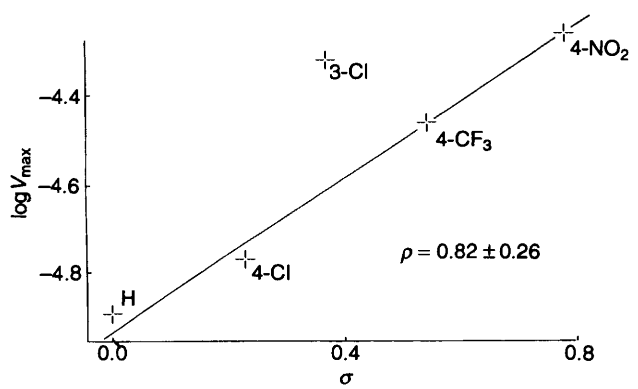


Fig. 7 Hammett plot of log V_{max} *vs.* σ for the Fe^{III}T4MPyP-catalysed epoxidation of styrenes by iodosylbenzene in methanol at 4.5 °C

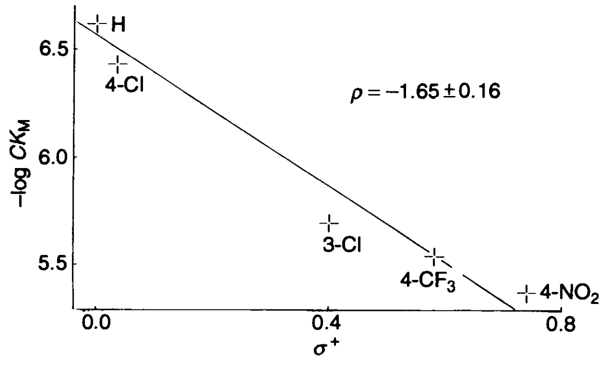


Fig. 8 Hammett plot of −log (CK_M) *vs.* σ^+ for the Fe^{III}T4MPyP-catalysed epoxidation of styrenes by iodosylbenzene in methanol at 4.5 °C

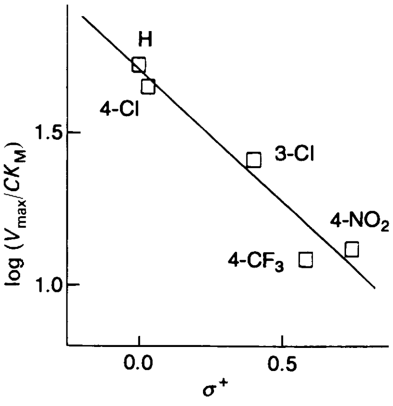


Fig. 9 Hammett plot of log (V_{max}/CK_M) *vs.* σ^+ for the Fe^{III}T4MPyP-catalysed epoxidation of styrenes by iodosylbenzene in methanol at 4.5 °C

reaction of the intermediate (V_{max}) decreases as the substituent on the styrene becomes more electron-donating, with the exception of the two most reactive substrates, 4-methoxy- and 4-methyl-styrene. For these two substrates the rate of epoxidation was first-order in the substrate concentration at all concentrations used, with no saturation kinetics being observed. These styrenes, and other more electron-rich styrenes with higher but unquantified rates of reaction (for example, 3,4-dimethoxystyrene and 4-methoxy-β-methylstyrene) are believed to react by a different mechanism from the other alkenes in this study (*vide infra*).

The results (V_{max}, CK_M and V_{max}/CK_M) from the less reactive styrenes can be correlated with Hammett σ or σ^+ values (Figs. 7–9; Table 4).

No improvement in the Hammett plots is obtained when a dual parameter equation accounting for any radical stabilisation is used.[22] The value of $\rho^+ = -0.88$ obtained for the reactivity (V_{max}/CK_M) compares well with the value of ρ^+ obtained from competitive oxidations and product studies using heterogeneous iron(III) porphyrin–PhIO systems (Table 5).

Groves and Watanabe [3c] in their study of alkene epoxidation by oxoiron(IV) tetramesitylporphyrin π radical cation in CH$_2$Cl$_2$ at −50 °C detected an intermediate prior to epoxide formation. A Hammett study of the rate of formation of this intermediate gave a ρ^+ value of −1.9. This compares well with the $\rho^+ = -1.65$ obtained from the CK_M values in the present study, particularly when the lower temperature of the earlier study is taken into account.

The ρ values for the formation and breakdown of the intermediate charge-transfer complex show that while the interaction of substituted styrenes with the active oxidant is strongly favoured by electron-donating groups, the breakdown step is accelerated by electron-withdrawing groups. The formation of the charge-transfer complex dominates the overall reaction as can be seen from the negative ρ^+ value for the reactivity correlation (Fig. 9). The size of the negative ρ^+ value for the interaction of substrate and active oxidant (Fig. 8) indicates a substantial build up of positive charge on the alkenic carbons occurs in the intermediate which is reduced in the transition state of the breakdown of the intermediate to the epoxide, as shown by the positive ρ value for this step (Fig. 7). Although these data are consistent with the mechanisms a, c and d in Scheme 3, as described above, other investigations identify path c, as the general mechanism for epoxidation by oxoiron(IV) porphyrin π radical cations. Thus the alkene acts as the electron-donor and the electrophilic oxidant as the acceptor in the charge-transfer complex **10** formed in the first step. The concerted reaction of this complex to give the epoxide and iron(III) porphyrin in the second step leads to removal of the positive charge on the alkene.

4-Methyl- and 4-methoxy-styrene, which did not show saturation kinetics in the substrate, are the most electron rich of the monosubstituted styrenes studied. It is possible for these

Table 5 Comparison of the ρ values for the epoxidation of styrenes by metalloporphyrin oxidation systems

Catalyst	Oxidant	Solvent	T/°C	Method	ρ	Ref.
Fe^{III}TPP	PhIO	CH$_2$Cl$_2$	Room temp.	Competit.[a]	−0.93	4(*a*)
Fe^{III}TDCPP	C$_6$F$_5$IO	CH$_2$Cl$_2$–MeOH–H$_2$O	Room temp.	Competit.[a]	−0.84	3(*e*)
Fe^{III}TDCPP	PhIO	CH$_2$Cl$_2$	20	Competit.[a]	−0.94	9(*b*)
Fe^{III}TMP	3-Cl-C$_6$H$_4$CO$_3$H	CH$_2$Cl$_2$	−50	Kinetic[b]	−1.9[c]	3(*c*)
Fe^{III}T4MPyP	PhIO	MeOH	4.5	Kinetic[b]	−0.88[d]	This study
					0.82[e]	This study
					−1.65[f]	This study

[a] Relative rates from product ratios from competitive reactions. [b] Rate constants from kinetic measurements. [c] ρ Value for rate of reaction of oxoiron(IV) porphyrin π radical cation and styrene to form intermediate. [d] ρ-Value from V_{max}/CK_M. [e] ρ-Value from V_{max}. [f] ρ-Value from CK_M.

Table 6 Experimentally measured and calculated rates of epoxidation of styrene and 3-chlorostyrene by iodosylbenzene in a competitive reaction catalysed by $Fe^{III}T4MPyP$ in methanol at 4.5 °C

Substrate	$V_c = f_c V_{max}{}^a$/ 10^{-6} mol dm^{-3} s^{-1}	V_c(experimental)/ 10^{-6} mol dm^{-3}
Styrene	11.3	13.3
3-Chlorostyrene	5.65	4.66

[a] Calculated V_c where f_c given by eqn. (4).

substrates that the initial reaction with the active oxidant involves the formation of an alkene radical cation rather than a charge-transfer complex. In agreement with this conclusion the half wave oxidation potentials reveal that these styrenes would be expected to be more readily oxidised by electron transfer than styrene or cyclohexene. Furthermore, 3,4-dimethoxystyrene which was very rapidly oxidised by $Fe^{III}T4MPyP–PhIO$ would be more reactive still.

When two alkenes are oxidised together by the metalloporphyrin system each alkene should competitively inhibit the epoxidation of the other. This was investigated with styrene and 3-chlorostyrene under conditions where the reaction kinetics were saturated in both the substrates and in the oxidant. Using the V_{max} and CK_M values from the single substrate reactions, the competitive rates for each substrate (V_c) can be calculated by multiplying V_{max} by a factor (f_c) [eqn. (4) (c and c′ represent

$$f_c = (CK_M)_c{}^{-1}/[(CK_M)_c{}^{-1} + (CK_M)_{c'}{}^{-1}] \quad (4)$$

the two competitive styrene substrates)] to allow for the relative binding abilities of each substrate to the active oxidant. The values of V_c calculated in this way are in good agreement with the experimental values obtained from the competitive reactions (Table 6). This study also shows that the competitive rate of epoxidation of styrene is approximately three times that of 3-chlorostyrene whereas in the non-competitive reactions the V_{max} value of 3-chlorostyrene is greater than that of styrene. This reversal arises from the much stronger complexing of styrene ($CK_M = 0.242 \times 10^{-6}$ mol dm^{-3}) than that of 3-chlorostyrene ($CK_M = 1.81 \times 10^{-6}$ mol dm^{-3}) with the active oxidant which ensures that the rate of epoxidation of styrene is virtually unaffected by the presence of 3-chlorostyrene, whereas the epoxidation of 3-chlorostyrene is drastically inhibited by styrene. An analogous reversal of reactivity was observed by Collman *et al.*[13b] in the competitive epoxidation of styrene and indene by the $Mn^{III}TPP–OCl^-$ system in CH_2Cl_2.

Experimental

Materials

All reagents were commercially available and used without further purification unless otherwise stated. The purities of the aliphatic alkenes were checked by GC and, where trace oxidation products were detected, they were purified by passage through a column packed with neutral alumina.

All the styrenes, except 4-trifluoromethyl- and 3,4-dimethoxystyrene, were available or had been previously prepared[4a,23] and were purified by distillation to remove any impurities or autoxidation inhibitors. 4-Trifluoromethylstyrene was prepared in two stages from 4-trifluoromethylbenzaldehyde *via* 1-(4-trifluoromethylphenyl)ethanol using methylmagnesium iodide followed by dehydration of the alcohol with phosphoric acid, bp 48–50 °C/21 mmHg (lit.,[24] 69.4 °C/27 mmHg). 3,4-Dimethoxystyrene was obtained in low yield by the copper-catalysed decarboxylation of 3,4-dimethoxycinnamic acid.[25] All the epoxides, except (*E*)-2,3-epoxyoctane and 4-trifluoromethylstyrene oxide, were commercially available or had been previously prepared and were checked by GC and ^1H NMR analyses. The two epoxides that were unavailable were prepared by a standard procedure using 3-chloroperoxybenzoic acid.[26]

Iodosylbenzene was prepared from iodosylbenzene diacetate following Saltzmann and Sharefkin[27] and its purity was checked by iodometric titration.

Iron(III) tetra(4-*N*-methylpyridyl)porphyrin pentachloride was prepared as described previously.[28]

Methanol was dried by refluxing over magnesium turnings in the presence of a trace of iodine, distilled and stored over molecular sieves (3A).

Instrumentation

GC Analyses were carried out with a Pye Unicam 204 gas chromatograph fitted with a flame ionisation detector. The results were recorded and processed on a Trivector Trilab 2000 data station. The glass columns used for the analyses of the product mixtures were packed with diethyleneglycol adipate polyester (10%, w/w) and with SE30 (20%, w/w) on Celite (100–120 mesh), and with OV1 (3%, w/w), OV17 (10%, w/w) and OV225 (1 and 10%, w/w) on Gas ChromQ (100–120 mesh).

For GC–MS analyses a Pye 104 chromatograph was coupled to an AEI MS30 mass spectrometer.

Oxidation procedure

The oxidant (PhIO) was dissolved in dry methanol (2.5 cm^3) containing the internal standard for GC analysis and immersed in a water bath maintained at 4.5 ± 0.5 °C. After 10 min the substrate was added as a pure liquid or, if a solid, as a solution in methanol. Finally the catalyst in dry methanol (0.5 cm^3) was added and the solution was rapidly mixed. Samples (1 µl) were removed at timed intervals and analysed directly by GC. Five or six readings were taken for each reaction and used to calculate the initial rate of epoxide formation.

In the competitive reaction with styrene and 3-chlorostyrene, the two substrates were added together in equimolar amounts and the total reaction volume was 3 cm^3.

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