Kinetics of the iron porphyrin catalysed oxidation of cyclohexene with substituted iodosylbenzenes

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A quantitative kinetic study has been carried out on the iron porphyrin catalysed oxidation of cyclohexene with iodosylbenzenes bearing increasingly electronegative aryl substituents. The effect of increasingly electronegative substituents placed on the porphyrin aryl periphery has also been studied. A mixed solvent system (CH_2Cl_2–CH_3OH–H_2O, 80:18:2) ensured homogeneous conditions for determinations of the observed rate constants at 25 °C. Of the halogenated iron(III) porphyrin catalysts used, 5,10,15,20-tetra(pentafluorophenyl)porphyrinatoiron(III) chloride exhibited sufficient stability to obtain comparative values for oxidant uptake from iodosylbenzene through to pentafluoroiodosylbenzene. Increasingly electronegative iodosylbenzene substituents are seen to increase dramatically the rate of porphyrin activation, demonstrated as the rate determining step of the cyclohexene oxidation process. The effects of the iodosylbenzene substituents on a proposed iron porphyrin–iodosylbenzene transition state are discussed.

The study of oxygen atom transfer oxidations with metalloporphyrins has received much attention, fundamentally due to the similarities with the action of the heme proteins, particularly cytochrome P-450. The mechanism of epoxidation catalysed by metalloporphyrins is therefore of exceptionally broad interest, but remains controversial.[1] Catalytic cycles containing a high-valent iron-oxo species as the intermediates predominate, but direct evidence has frequently been difficult to obtain. It is the latter, coupled with competing reactions that has made kinetic studies of the system fraught with problems.

The oxidative destruction of the metalloporphyrin catalyst is reduced by the incorporation of substituents on the aryl rings, preventing aggregation and improving turnover.[2a–c] High turnovers with an *ortho*-fluoro substituted iron porphyrin were noted,[3] subsequent perfluorination lead the way to an initial kinetic study of PFIB† mediated olefin oxidation in a heterogeneous media.[4] Although not completely understood, the electronic effects of the substituents seem often to outweigh the steric considerations.[2a] Electronic effects induced by substituents on the iodosylbenzene aryl ring have also been shown to play a role, increasing electronegativity producing a corresponding yield of substrate oxidation products.[5]

A further improvement was seen, in that adding methanol to an otherwise heterogeneous suspension of iodosylbenzene in chloroform, produced a homogeneous oxidant that enabled a preliminary kinetic analysis of olefin oxidation to be made[6] at 25 °C.

In this paper are reported the results of studies utilising this homogeneous solvent system. Quantitative kinetic data is presented on the effects of electronegative substituents on both the iron porphyrin and iodosylbenzene moieties.

Results

Stability of the iron porphyrins

PhIO (10 mg) was added to the iron porphyrin (1.80×10^{-5} mol dm^{-3}) in dichloromethane (2 cm^3). After stirring at 25.0 °C while protected from light, the decrease in Soret absorption was evaluated (Table 1).

The oxidation of Fe(TPP)Cl produces a pronounced decrease in the Soret maxima and a shift from 418 to 411 nm.[7] Some recovery is seen on the addition of aqueous HCl (10 mol dm^{-3}, 500 μl), further evidence of $[Fe(TPP)]_2O$ as the main degradation product from Fe(TPP)Cl.[8] When PhIO addition was performed in an NMR tube (5 mm o.d., $CDCl_3$, Me_4Si) the characteristic broad pyrrolic-H signal of Fe(TPP)Cl (δ 80.5) diminished and a broad singlet (δ 13.5) appeared.[7] The latter is comparable to that of the synthetic dimer $[Fe(TPP)]_2O$. A far greater stability is exhibited by the substituted porphyrins which, under the conditions used in the kinetic runs below, show no degradation.

Table 1 Stability of the iron porphyrins to PhIO

Iron porphyrin	Soret/nm	Decrease in Soret absorbance after 1 h (%)
Fe(TPP)Cl	418	85.2[a]
Fe(TDClPP)Cl	417	6.8
Fe(TDFPP)Cl	419	6.2
Fe(TPClPP)Cl	410	3.4
Fe(TPFPP)Cl	406	1.3

[a] Figure reached almost instantaneously.

Rates of cyclohexene oxidation obtained with the stable porphyrins

Following the loss of PFIB (1×10^{-3} mol dm^{-3}) at 285 nm during CHE (0.5 mol dm^{-3}) oxidation at 25.0 °C, a linear relationship is seen between the observed rate constant (k_{obs}) and the porphyrin concentration (Fig. 1).

Under the reaction conditions, CHE oxidation is first order with respect to the iron porphyrin. Linearity is not well maintained beyond the plotted limits of the iron porphyrin concentration. The system reaches a saturation limit beyond approximately 10^{-4} mol dm^{-3}, where the large k_{obs} precludes an accurate determination by the techniques available. On

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† *Abbreviations:* Fe(TPP)Cl, 5,10,15,20-tetraphenylporphyrinatoiron(III) chloride; Fe(TDClPP)Cl, 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrinatoiron(III) chloride; Fe(TDFPP)Cl, 5,10,15,20-tetra(2,6-difluorophenyl)porphyrinatoiron(III) chloride; Fe(TPClPP)Cl, 5,10,15,20-tetra(pentachlorophenyl)porphyrinatoiron(III) chloride; Fe(TPFPP)Cl, 5,10,15,20-tetra(pentafluorophenyl)porphyrinatoiron(III) chloride; PhIO, iodosylbenzene; 4-FIB, 4-fluoroiodosylbenzene; 3-ClIB, 3-chloroiodosylbenzene; 3-FIB, 3-fluoriodosylbenzene; DClIB, 2,6-dichloroiodosylbenzene; DFIB, 2,6-difluoroiodosylbenzene; 2-ClIB, 2-chloroiodosylbenzene; 2-FIB, 2-fluoroiodosylbenzene; PFIB, pentafluoroiodosylbenzene; CHE, cyclohexene; CHEO, cyclohexene oxide.

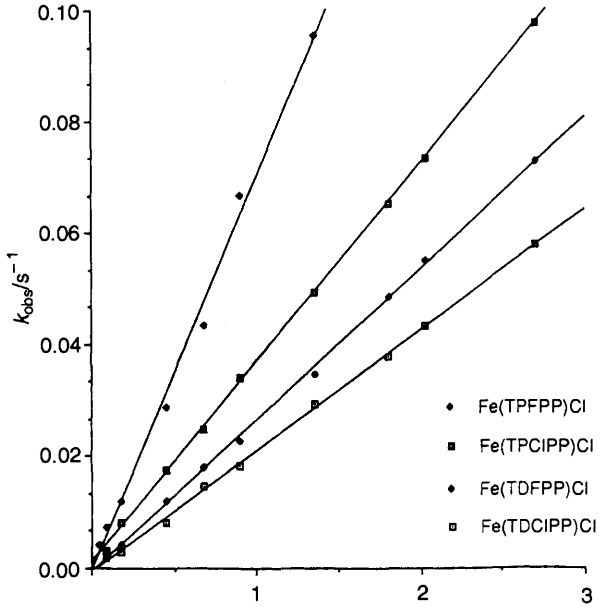


Fig. 1 Dependence of the observed rate constant (k_{obs}) on the concentration of iron porphyrin

completion, the porphyrins are found to be intact by virtue of their UV–VIS spectra. The unsubstituted Fe(TPP)Cl undergoes instantaneous bleaching under the conditions used here, forestalling the making of any kinetic comparisons.

Derived second order rate constants, k_2 ($k_2 = k_{obs}/$[porphyrin]) demonstrate an ascending order of catalyst efficiency with respect to the total electronegativity of the aryl substituents. The catalysts Fe(TDClPP)Cl, Fe(TDFPP)Cl, Fe(TPClPP)Cl and Fe(TPFPP)Cl yield values of k_2 ($10^4 k_2$/dm^3 mol^{-1}) of 0.21, 0.25, 0.37 and 0.73, respectively (all values ±0.01).

Rates of cyclohexene oxidation obtained with increasing iodosylbenzene concentration

Following the loss of the iodosylbenzene at 285 nm during CHE (0.5 mol dm^{-3}) oxidation catalysed by Fe(TPFPP)Cl (9×10^{-6} mol dm^{-3}) at 25.0 °C, a linear relationship is seen between the observed rate constant (k_{obs}) and the concentration of the iodosylbenzene (Fig. 2).

Under the reaction conditions, CHE oxidation is first order with respect to the iodosylbenzene. Linearity is not maintained beyond the limits of the displayed plot. Above 10^{-3} mol dm^{-3} [iodosylbenzene] extensive bleaching of the porphyrin occurs, leading to a complete loss of catalytic activity. Partial restoration of activity, and the reappearance of the characteristic red colouration indicative of the active species,[9] is effected by mild acidification. Dimerisation of the porphyrin is therefore suggested as one of the major destructive pathways.

Rates of cyclohexene oxidation obtained with differing iodosylbenzene aryl substituents

Following the loss of the iodosylbenzene (1×10^{-3} mol dm^{-3}) at 285 nm during CHE (0.5 mol dm^{-3}) oxidation catalysed by Fe(TPFPP)Cl at 25.0 °C, linear relationships are seen between the observed rate constant (k_{obs}) and [Fe(TPFPP)Cl] for a range of substituted iodosylbenzenes (Fig. 3).

Iodosylbenzenes with a range of substituent electronegativities, all follow a first order relationship under the reaction conditions. Below an iodosylbenzene concentration of 1×10^{-4} mol dm^{-3} less reliable k_{obs} values are obtained, oxidation of the catalyst over time appears to become a contributing factor. The derived second order rate constants, k_2' ($k_2' = k_{obs}$/[iodosylbenzene]) are given (Table 2) for CHE (0.5 mol dm^{-3}) oxidation at 25.0 °C catalysed by Fe(TPFPP)Cl (9×10^{-6} mol dm^{-3}).

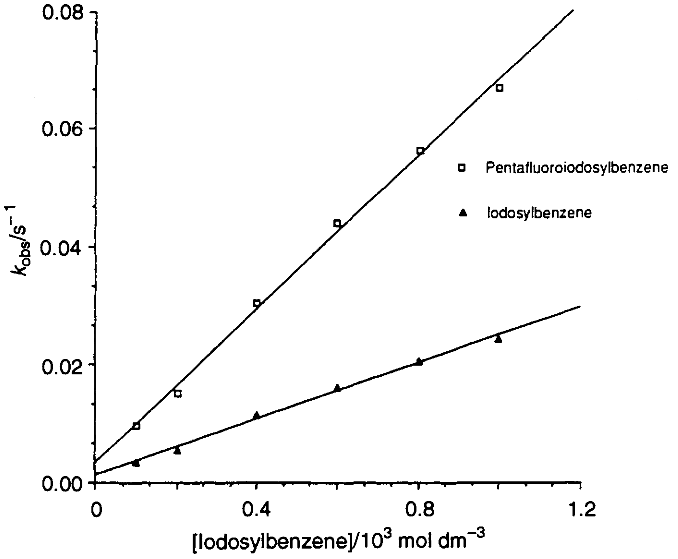


Fig. 2 Dependence of the observed rate constant on the concentration of iodosylbenzene

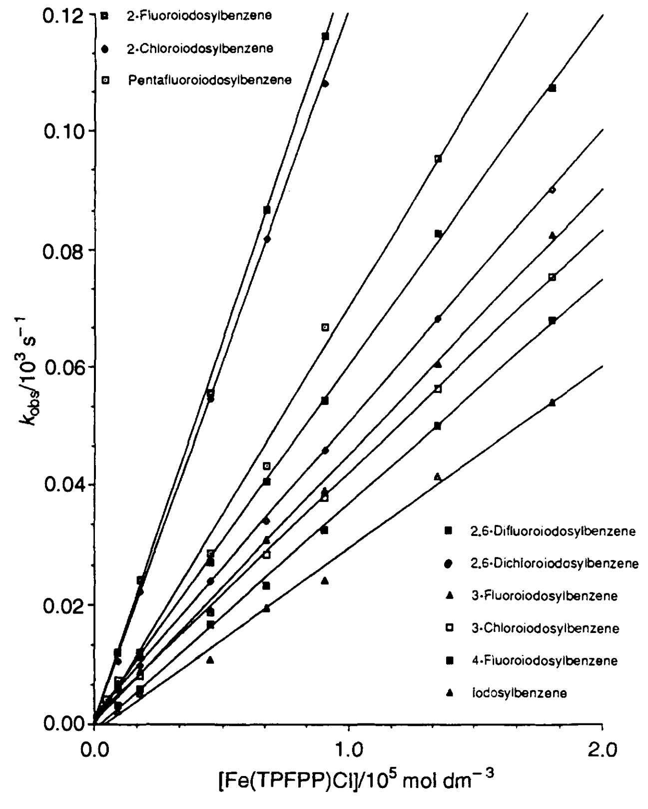


Fig. 3 Dependence of the observed rate constant on the nature of the iodosylbenzene

Rates of cyclohexene oxidation obtained in the presence of a species competing for the iron centre

The loss of PFIB (1×10^{-3} mol dm^{-3}) during CHE (0.5 mol dm^{-3}) oxidation at 25.0 °C catalysed by Fe(TPFPP)Cl (9×10^{-6} mol dm^{-3}) was monitored with respect to an increasing imidazole (ImH) concentration (Fig. 4). Exclusion

Table 2 Derived second order rate constants

Iodosylbenzene	k_2'/mol^{-1} dm^3 s^{-1}
2-FIB	116.10
2-ClIB	108.00
PFIB	66.70
DFIB	54.40
DClIB	46.10
3-FIB	37.90
4-FIB	32.50
PhIO	24.10

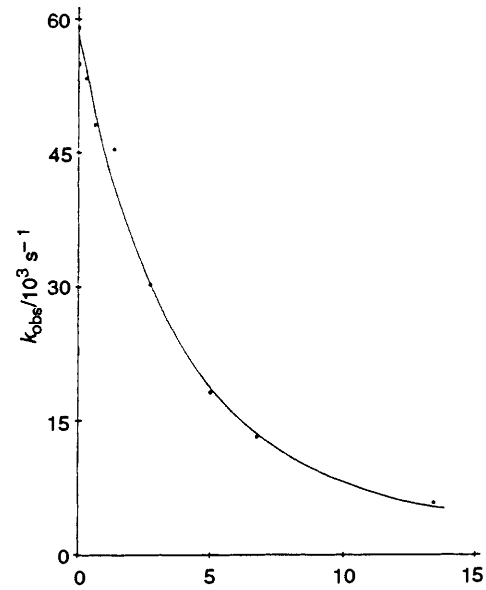


Fig. 4 Effect of increasing imidazole concentration on the observed rate constant for CHE oxidation

of CHE results in a negligible consumption of PFIB under the same conditions (k_{obs} 10^{-5} s^{-1}), directly comparable to that obtained under control experiments where no identifiable substrate was available. Loss of iodosylbenzene to the iron porphyrin is therefore the only process to have a significant affect upon k_{obs}.

Yields of CHEO obtained

The main product at the completion of the iodosylbenzene consumption is CHEO under all the previously described conditions, with minor amounts of cyclohex-2-en-1-one and cyclohex-2-en-1-ol. Since CHE is present in large excess, the yield of CHEO was evaluated on the initial iodosylbenzene concentration. A large excess of CHE prevents the oxidation of methanol, as the accumulation of high-valent iron intermediates becomes prevalent at low substrate concentrations. The yields of CHEO from the PFIB mediated oxidation of CHE (0.5 mol dm^{-3}) catalysed by the stable iron porphyrins (9×10^{-6} mol dm^{-3}) at 25 °C, are shown below (Table 3), along with the yields of CHEO produced under Fe(TPFPP)Cl (9×10^{-6} mol dm^{-3}) catalysis with the substituted iodosylbenzenes.

Discussion

The principal effect of placing substituents on the aryl rings of the iron porphyrins is to produce stable oxidation catalysts. It has been known that the addition of large substituents to the porphyrin prevent intermolecular self-oxidation and restrict the access to the oxidant,[10] however, steric constraints are not the only criteria evident here. Ease of oxidant approach has to be balanced with the need to restrict porphyrin dimer formation. On purely steric grounds Fe(TPClPP)Cl should be more resistant to dimer formation than Fe(TPFPP)Cl, the latter is however catalytically considerably more efficient. The observations are in keeping with the transfer of oxygen from the iodosylbenzene to the iron porphyrin as being the rate determining step. Oxygen transfer from a cyclic iron-oxo intermediate, as the rate determining step, has been suggested for heterogeneous PhIO catalysis.[4] Attempts to use iron porphyrin systems with only steric restraints placed on the aryl periphery (2′,4′,6′-trimethyl, 2′,4′,6′-trimethoxy and α^4-2-pivalamidophenyl) were unsuccessful due to rapid bleaching of the catalyst. Electron withdrawal from the catalytic centre appears to stabilise the iron-oxo intermediate above that of steric considerations.

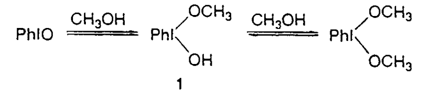
Table 3 Yields of CHEO at completion

Catalyst	Oxidant	Yield[a] (%)
Fe(TPFPP)Cl	PFIB	82
Fe(TPClPP)Cl	PFIB	78
Fe(TDFPP)Cl	PFIB	78
Fe(TDClPP)Cl	PFIB	75
Fe(TPFPP)Cl	2-FIB	86
Fe(TPFPP)Cl	2-ClIB	85
Fe(TPFPP)Cl	PClIB	82
Fe(TPFPP)Cl	DFIB	84
Fe(TPFPP)Cl	DClIB	82
Fe(TPFPP)Cl	PhIO	79

[a] Yields based on the initial [iodosylbenzene] (1×10^{-3} mol dm^{-3}).

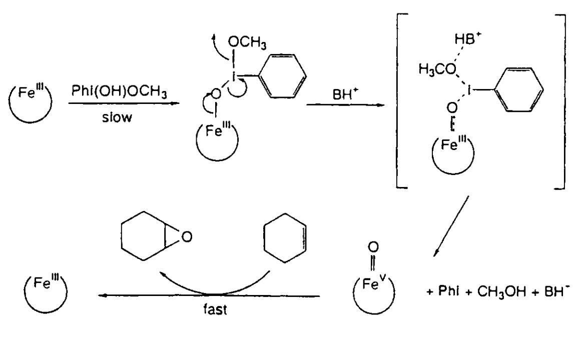
Similar considerations are evident from the results obtained with the substituted iodosylbenzenes. Fundamentally, the more electronegative the aryl substituents, the faster the oxygen transfer.

In aqueous methanolic solution, there is evidence to support **1** as being the oxidising species[11] (Scheme 1).



Scheme 1

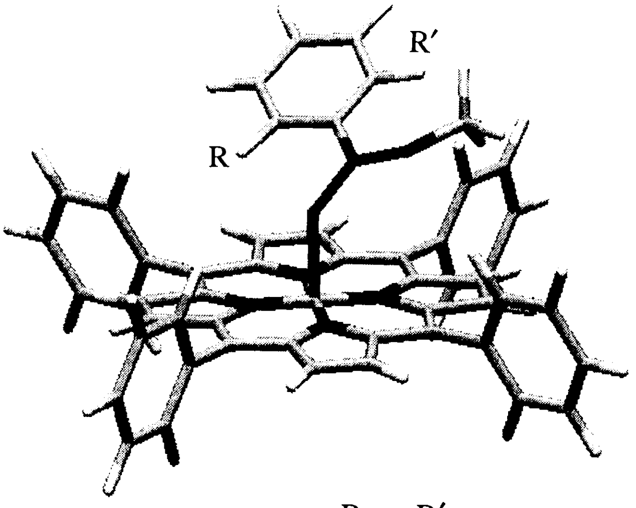
This work agrees with the previously proposed iodosylbenzene mediated oxidation pathway under homogeneous conditions, for all the oxidants and catalysts used in the kinetic determinations[6] (Scheme 2).



Scheme 2

Further evidence that the coordination of **1** with the iron porphyrin is rate determining is revealed with the presence of imidazole competing for the iron coordination site. The results are consistent with the provision of a fifth, and at higher imidazole concentrations, a sixth coordinating ligand.[12]

Generally, the oxidation of CHE (0.5 mol dm^{-3}) under the experimental conditions in CH_2Cl_2–CH_3OH–H_2O (80:18:2) is



	R	R′
2a	H	H
2b	F	H
2c	H	F
2d	F	F

Fig. 5 Proposed iron porphyrin–iodosylbenzene transition state model

Table 4 Mechanical considerations of the proposed intermediate

Structure	E/kJ mol^{-1}	O–I–$C_{(ar)}$–$C_{(ar)}$ torsion/deg.
2a	1193.8	9.7
2b	1229.4	11.3
2c	1244.2	9.9
2d	1274.9	10.8

seen to be very rapid. Values for $t_{\frac{1}{2}}$ range from 6 s ([Fe(TPFPP)Cl] 9 × 10^{-6} mol dm^{-3} with [2-FIB] 1 × 10^{-3} mol dm^{-3}) to 29 s (similarly with [PhIO] 1 × 10^{-3} mol dm^{-3}) for example. The reaction is first order in both the iodosylbenzene and in the iron porphyrin, essentially independent of cyclohexene concentration. The kinetics of CHE oxidation are described in eqn. (1).

$$\frac{d[\text{CHEO}]}{dt} = \frac{-d[\text{Iodosylbenzene}]}{dt} = k[\text{Iron porphyrin}][\text{Iodosylbenzene}] \quad (1)$$

The results do not provide direct evidence concerning the mechanism of oxygen transfer to the alkene. The Fe^{V}=O intermediate is extremely unstable, since the transfer of oxygen to the alkene is much faster than the formation of the suggested iron porphyrin–iodosylbenzene complex.

Steric considerations of the iron porphyrin–iodosylbenzene complex are represented by the minimised structure below (Fig. 5). The model was constructed using the program MacroModel,[13] under Unix,[14] based upon the coordinates of benzenesulfinato-5,10,15,20-tetraphenylporphyrinatoiron(III)[15] sourced from the CSD.[16] The program SPARTAN[17] was then utilised for a conformer search around the Fe–O–I–Ph torsion in 5 degree steps, using SYBYL[18] (Tripos) forcefields. The resulting conformer was assigned Gasteiger charges and minimised (PRCG). Fluoro substituents were placed on the iodosylbenzene and the resulting conformer similarly minimised (gradient criterion 0.005 kJ mol^{-1}–A in all cases), producing the listed O–I–$C_{(ar)}$–$C_{(ar)}$ torsions and global energies (Table 4).

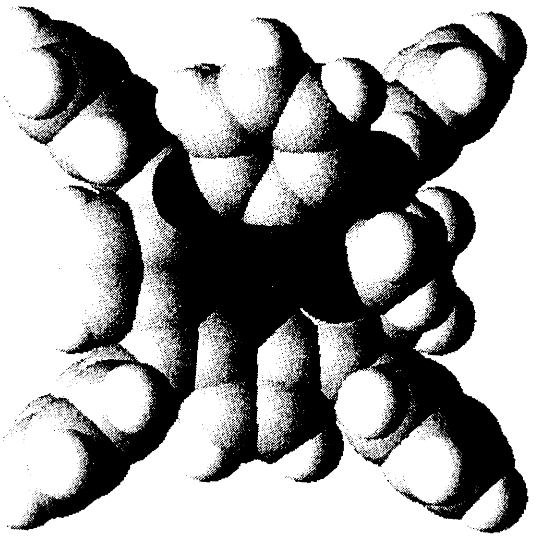


Fig. 6 Transition complex **2d** from above

The formation of the *transoidal* **2c** over **2b** can be expected on consideration of torsional strain, which in the former approaches that of the unsubstituted **2a**. Adoption of the *cisoidal* **2b** results in unfavourable conjugative dipole effects, primarily from the oxygen (Fe–O) lone pair, despite a conducive ‘pocket’ formation clearly seen from CPK view of **2d** (Fig. 6). A further conjugative dipole effect arises with electronegative substituents placed on the aryl porphyrin periphery.

The steric effects of fluorine substitution, well known as an important consideration with the porphyrin system,[19] can therefore be proposed as partially explaining the kinetic effects seen. A computational investigation, based upon *ab initio* calculations is currently underway.

Experimental

Materials

All materials were commercially available from Aldrich Chemical Co., unless otherwise stated.

The free porphyrins, $TPPH_2$, $TPClPPH_2$ and $TPFPPH_2$ were prepared by standard methods[20] prior to metallation.[21] For $TDClPPH_2$ and $TDFPPH_2$ the Rothemund route had to be followed,[22] prior to the above metallation procedure. The μ-oxo dimer, $[Fe(TPP)]_2O$, was prepared[23] from the base hydrolysis of Fe(TPP)Cl and found comparable to that produced from the action of PhIO.

Both PhIO and PFIB were prepared by the hydrolysis of their requisite acetates.[24] Diazotisation of 2,6-difluoroaniline[25] produced the iodo-dichloride, subsequent hydrolysis[26] gave DFIB. For the other iodosylbenzenes, 2-FIB, 3-FIB, 4-FIB, 2-ClIB, 3-ClIB and DClIB were prepared by hydrolysis of their respective iodo-dichlorides.[26] It should be noted that all the iodosylbenzenes are explosive if heated.[27] As one criteria of purity, the iodosylbenzenes were titrated against sodium thiosulfate,[28] available oxygen was found to be greater than 99% in all cases. All the iodosylbenzenes were refrigerated and used within 24 h.

Cyclohexene was stirred over P_2O_5, then distilled over metallic sodium under nitrogen. The distillate was then passed through a pre-baked (110 °C) alumina column. Impurities were evaluated by GC (less than 0.5%). CHEO was prepared from the epoxidation of CHE with *m*-CPBA in dichloromethane as described.[29]

Dichloromethane (BDH analytical grade) was dried over $CaCl_2$ and distilled from P_2O_5 under nitrogen, final purification as for CHE. Water was double distilled and passed through an 'Elgacan^{TM}' C144 cartridge. Methanol 'Gold Label' was used as supplied.

Methods

Kinetic measurements were carried out on a Pye-Unicam SP6-450 UV–VIS spectrophotometer, incorporating a thermostatted sample chamber. Data manipulation was performed on an interfaced Sinclair ZX Spectrum microcomputer, running 'in house' software.

In a typical determination, a solution of Fe(TPFPP)Cl (1 cm^3, 2.7×10^{-5} mol dm^{-3}) in CH_2Cl_2–CH_3OH–H_2O (80:18:2) and CHE (152 μl) (1 μl = 1 mm^3) in CH_2Cl_2–CH_3OH–H_2O (80:18:2) (1 cm^3) was placed in a quartz UV cell (1 cm pathlength, capacity 3 cm^3) positioned in the thermostatted (25.0 °C) cell holder within the spectrophotometer. The solution was allowed to equilibrate (determined by in-cell thermocouple) whereupon a fresh thermostatted (25.0 °C) solution of PhIO (1 cm^3, 0.03 mol dm^{-3}) in CH_2Cl_2–CH_3OH–H_2O (80:18:2) was rapidly added and mixed. Readings at 285 nm‡ (up to 4 per second) were taken to generate a linear $\ln(A_t - A_\infty)$ *vs.* time plot. From an estimate of the half-life so obtained, Guggenheim's method was used to generate a linear plot (slope = $-k_{obs}$). At least four determinations of k_{obs} were made for each system change, until the rate constant could be quoted to ±4%, the mean was then calculated.

GC analyses of CHE oxidation products were performed using a Perkin-Elmer Sigma 3B chromatograph coupled to a Spectra Physics Minigrator. The column consisted of 10% Carbowax on WHP 100–120 mesh, 3 mm i.d., 2 m length, held at 95 °C.

Acknowledgements

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‡ Between 250 and 350 nm, the absorptions of iodosylbenzenes in alcohols exceed those of either iodobenzenes or the iron(III) porphyrins.[6]