Metal-assisted Reactions. Part 21.[1] Epoxidation of Alkenes Catalysed by Manganese-porphyrins: The Effects of Various Oxidatively-stable Ligands and Bases

Antonio M. d'A. Rocha Gonsalves,[a] Robert A. W. Johnstone,*,[b] Mariette M. Pereira[a] and Jacqueline Shaw[b]

[a] Departamento de Quimica, Universidade de Coimbra, 3000 Coimbra, Portugal
[b] Department of Chemistry, University of Liverpool, Liverpool L69 3BX, UK

Porphyrin-catalysed epoxidation of alkenes with hydrogen peroxide has been shown to occur in the presence of non-oxidisable ligands and bases whereas previous work has suffered from destruction of base and ligand with concomitant excessive use of oxidant. The advantageous use of adducts of hydrogen peroxide is described.

Reaction of alkenes with oxidising agents to give epoxides (oxiranes), catalysed by a variety of metalloporphyrins, has been reviewed.[2-5] Thus, iodosoarenes,[6-8] hypochlorites,[10-11] alkyl hydroperoxides,[4,9] hydrogen peroxide,[12] oxygen[13] and other oxygen donors[14-16] have been utilised. The metalloporphyrins have been mainly those of iron or manganese complexed to a *meso*-tetrakisaryl porphyrin macrocycle. Of the above oxygen donors, hydrogen peroxide provides a reasonably cheap, readily available oxidant, giving only water as a by-product. However, it is necessary for efficient epoxidation that the hydrogen peroxide should be cleaved heterolytically to give an 'oxene' (Reaction 1a) rather than homolytically to give

$$HO-OH \underset{b}{\overset{a}{\rightleftharpoons}} \begin{matrix} [HO^+] + HO^- \\ 2HO^{\bullet} \end{matrix} \qquad (1)$$
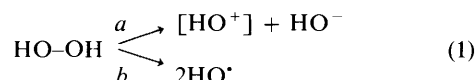
hydroxyl radicals (Reaction (1b). Formation of hydroxyl radicals leads to somewhat indiscriminate oxidation of organic substrates, with hydrogen abstraction being important. In reactions of type (1a), in which an oxene or its equivalent is involved, oxidation is much more selective and, with alkenes, leads directly to epoxides. There have been investigations concerning the hetero- and homo-lytic cleavage of hydroperoxides and hydrogen peroxide in the presence of various metalloporphyrins.[12] Broadly, it is found that epoxidation can be effected rapidly and in high yield through the use of manganese(III) tetrakis(2,6-dichlorophenyl)porphyrin chloride 1.[17] Unlike many metalloporphyrins used in attempted epoxidation, the manganese-porphyrin 1 is reasonably stable to oxidising conditions, although in our own and other work, attempts are being made to discover more stable catalysts.

Reactions of hydrogen peroxide with an alkene through the intermediacy of a porphyrin appears to require a ligand to the porphyrin metal (as in P450 enzyme systems[19]) and a base to promote formation of HO_2^- from H_2O_2. Up until now, the most successful system has employed imidazole as both ligand and base;[12] a few tertiary amines have been tried as bases but with little success.[12] A major drawback with the present epoxidising system is the rapid, oxidative destruction of imidazole and tertiary amines by hydrogen peroxide directly or *via* porphyrin oxo complexes. In the present work, the development of more oxidatively stable ligands and bases is described.

In most earlier work, acetonitrile has been used as solvent, with water from the aqueous H_2O_2 oxidant. As nitriles are known to form peroxyimidic acids which are themselves excellent epoxidising agents,[18] the use of acetonitrile was

avoided in the present systems. Finally, adducts of hydrogen peroxide have been shown to be attractive, stable sources of the oxidant, effectively free from water.

Results and Discussion

To examine the interactive effects of imidazole and hydrogen peroxide in a solvent system similar to that used by previous workers, alkenes in dichloromethane–acetonitrile were epoxidised with hydrogen peroxide using porphyrin 1 as catalyst. To obtain a controlled release of H_2O_2, it was added as its urea adduct, together with a small quantity of water. Further comment is made later on this use of H_2O_2 adducts. In this system, with a 1:10 molar ratio of porphyrin to imidazole, the rate of epoxidation of cyclooctene was very fast and gave a 98% yield of the corresponding epoxide (Fig. 1a). In this and all other epoxidations described here, yields of epoxides are based on the percentage conversion of alkenes, not oxidant. As seen from the figure, at about the same rate of epoxide formation, the amount of imidazole decreased rapidly, until about 20% of the original quantity remained. For a 1:20 molar ratio of porphyrin to imidazole, epoxidation was as fast as for a 1:10 ratio but the yield of epoxide reached only 84% and there was rapid elimination of imidazole from the system (Fig. 1b). With an even greater proportion of imidazole (1:60), the initial rate of epoxidation remained about the same as for the 1:10 and 1:20 ratios but the yield of epoxide again fell, this time to 75% (Fig. 1c). These results accord well with a mechanism in which oxidation of the imidazole base/ligand is competitive with alkene epoxidation to such an extent that, when the proportion of imidazole in the system is increased, it uses up more of the available supply of H_2O_2 and prevents complete epoxidation of the alkene. This conclusion was confirmed by addition of extra H_2O_2 after epoxidation had ceased; reaction recommenced and provided a 98% yield of epoxide whilst the amount of imidazole again fell (Fig. 1c). The rate of epoxidation appears to be largely independent of the concentration of imidazole and it is clear that, with a suitable excess of oxidant, all of the imidazole acting as base would be consumed. Thus, for rates of epoxidation of other alkenes which are less than the rate for cyclooctene, then more and more imidazole and oxidant must be provided if a reasonable yield of epoxide is to be achieved. Such a situation is inefficient in both imidazole and oxidant, particularly for large-scale application.

Because of the possibility that the acetonitrile used as a cosolvent could participate in the epoxidation or destruction of imidazole through formation of acetylperoxyimidic acid (Payne-type oxidation[18]), these experiments were repeated but in a
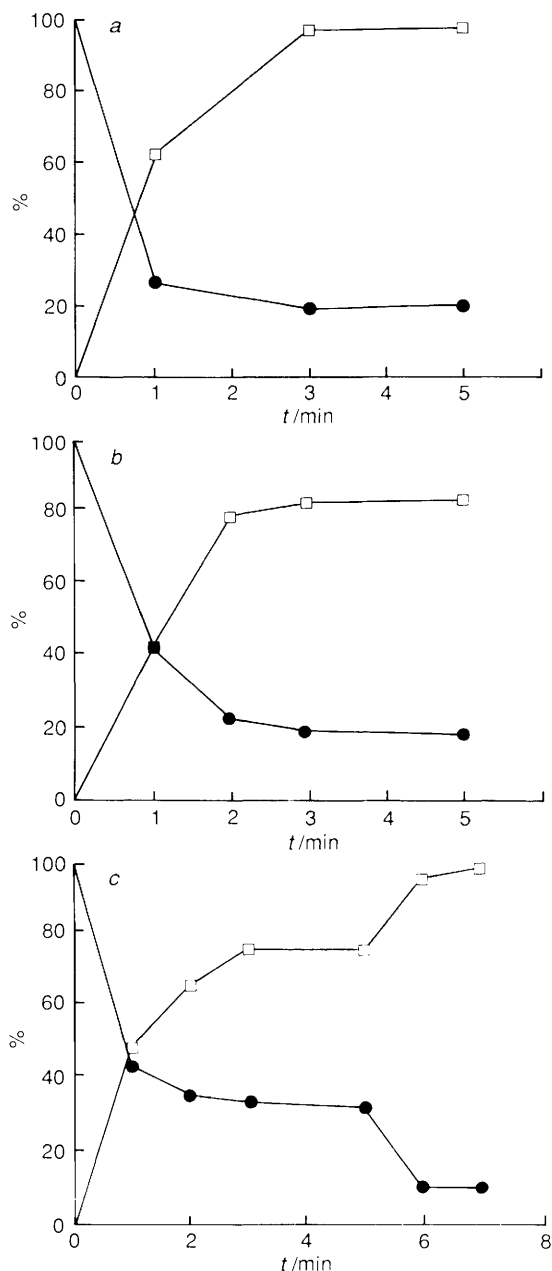
Fig. 1 Graphs showing the rates of disappearance of imidazole (●) and formation of cyclooctene epoxide (□) as the ratio of manganese porphyrin 1 to imidazole is changed from a 1:10, to b 1:20, to c 1:60 in the MeCN–CH$_2$Cl$_2$ solvent system. Experimental details as in the text.
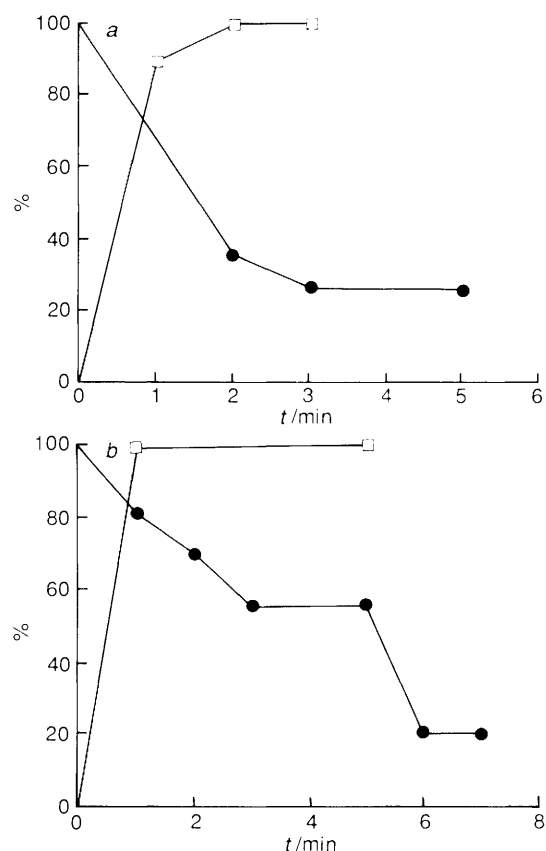

Fig. 2 Graphs showing the rates of disappearance of imidazole (●) and formation of cyclooctene epoxide (□) as the ratio of manganese porphyrin 1 to imidazole is changed from a 1:20, to b 1:60 in the MeOH–CH$_2$Cl$_2$ solvent system. Experimental details as in text.

methanol–dichloromethane solvent system. Comparatively, epoxidation in MeOH–CH$_2$Cl$_2$ was faster than in MeCN–CH$_2$Cl$_2$. Thus, for a 1:20 ratio of porphyrin to imidazole, epoxidation of cyclooctene was complete in 2 min (Fig. 2a) whereas, in MeCN–CH$_2$Cl$_2$, epoxidation ceased at 84% after 4 min. Similarly, for a 1:60 ratio, in MeOH–CH$_2$Cl$_2$ overall behaviour was similar to that in MeCN–CH$_2$Cl$_2$ except that epoxidation was faster and went to 100% completion (Fig. 2b). Addition of more hydrogen peroxide led to a further fall in the concentration of imidazole.

It seems clear from these results that, with a limited amount of hydrogen peroxide, reaction ceases when the oxidant has been used up for both epoxidation and destruction of imidazole. As long as the rate of epoxidation is faster than the rate of oxidation of imidazole then the epoxidation can go to completion. If the rate of epoxidation is slower than the rate of destruction of imidazole then more hydrogen peroxide must be

added to the system which becomes inefficient in utilisation of the oxygen donor. Similarly, addition of extra oxidant leads to more imidazole being consumed and the system becomes inefficient in the use of this base/ligand. Finally, since there is faster epoxidation in MeOH–CH$_2$Cl$_2$, it seems that the acetonitrile does not react at a sufficiently fast rate through formation of acetylperoxyimidic acid to affect the overall porphyrin-catalysed epoxidation. Despite this, because some of the later examples of epoxidation are much slower than for cyclooctene, the MeOH–CH$_2$Cl$_2$ solvent system was retained in preference to MeCN–CH$_2$Cl$_2$.

As a first step to replacing imidazole, other bases were examined. Earlier reported work has shown that amines are only partially successful as bases because they are themselves oxidised. Thus, triethylamine, dicyclohexylamine and iso-propylamine led to fast removal of H$_2$O$_2$ and to only modest yields (40–50%) of epoxide.[12] Inorganic bases, being generally insoluble in non-aqueous systems, are not satisfactory in the system developed in the present work. However, tetrabutyl-ammonium hydroxide is a strong base, soluble in many organic solvents and which, when used in place of imidazole, allowed epoxidation to proceed. Whereas, with imidazole as both base and ligand, cyclooctene epoxide was obtained in 98–99% yield in 10 min, with tetrabutylammonium hydroxide only a 42% yield was attained in 24 h. Although this epoxidation was slow, the porphyrin 1 was stable to oxidation in the absence of imidazole. Addition of a small amount of imidazole (2.5:1 molar ratio to porphyrin) to this same mixture with tetra-butylammonium hydroxide speeded up the reaction consider-ably, so that a 98% yield of epoxide could be attained in only 2 h (Table 1). These results show that an alternative base to imidazole can be used but also that imidazole is a very

Table 1 Effects of various base/ligand combinations on the epoxidation of cyclooctene[a]

Base	Ligand	t/h	Yield epoxide (%)
TO[b] (0.74 × 10⁻⁴ mol)	TO (0.74 × 10⁻⁴ mol)	5	73
Bu₄N⁺OH⁻ (0.1 mmol)	TO (1.48 × 10⁻⁴ mol)	2 5	83 98
Na₂CO₃ (3.3 mmol)	TO (1.7 × 10⁻⁴ mol)	2 5	51 74
NaOAc (1.5 cm³ of MeOH saturated with NaOAc)	AO[b] (1.7 × 10⁻⁴ mol)	2	96
Bu₄N⁺OH⁻ (0.1 mmol)	Imidazole (18.5 × 10⁻³ mmol)	2	98
—	PPh₃O (226 × 10⁻³ mmol)	1	0.6
Bu₄N⁺OH⁻ (0.1 mmol)	PPh₃O (226 × 10⁻³ mmol)	1	37[c]
Bu₄N⁺OH⁻ (0.07 mmol)	2-Chlorophenol (1.44 × 10⁻⁵ mmol)	24	63

[a] Reaction conditions were identical with those described in Table 2 except that amounts of ligands and bases were varied as shown. [b] AO ≡ diisopropylethylamine N-oxide; TO ≡ triethylamine N-oxide. [c] If further H₂O₂ is added reaction proceeds further.

Table 2 Effect of various amines on the rate of formation and yield of cyclooctene epoxide[a]

Amine	Reaction t/h[b]	Yield epoxide[c] (%)
Imidazole	10 min	99
Triethylamine	1.25[d]	98
Triethylamine	1.0[e]	81
Diisopropylethylamine	1.25[d]	96
Diisopropylethylamine	1.0[e]	88
1,5-Diazabicyclo[4.3.0]non-5-ene	0.5	97
Aniline	2.0	0
N,N-Dimethylaniline	2.0	0

[a] Reactions were carried out with cyclooctene (1 mmol); 50% H₂O₂ (2 mmol) and manganese porphyrin 1; (7.4 × 10⁻³ mmol) in a mixture of CH₂Cl₂ (2 cm³), and MeOH (1.5 cm³) at room temperature. Amine (0.05 cm³) was added to the reaction, unless otherwise state. [b] These are approximate times taken to reach the yield stated. [c] Yields were calculated from gas chromatographic peak areas based on pre-calibration with internal standard. The only other product observed was starting material. [d] Rate of addition of amine was 0.83 mm³ min⁻¹ over 1 h. [e] After this time the reaction stopped.

favourable ligand for rapid epoxidation. In the next part of the work, ligands other than imidazole were investigated.

Earlier work has shown that several common tertiary amines appear to be ineffective for epoxidation because of their easy oxidation to N-oxides.[12] In the present work, the effect of a small range of tertiary amines and their N-oxides was examined (Tables 2, 3); some of the amines were sterically highly hindered and were not expected to be easily oxidised directly by hydrogen peroxide. Whereas imidazole enabled complete epoxidation of cyclooctene in 10 min, in contrast, triethylamine gave an 81% yield in 1 h, the reaction going no further. By slow addition of the triethylamine to the reaction mixture, complete epoxidation could be accomplished in 1.25 h. When triethylamine was added all at once at the beginning of epoxidation, it was itself oxidised and became ineffective as a base. When an excess of amine is always present, as by its gradual addition to the reaction mixture, then epoxidation proceeds rapidly and to completion. This effect may be connected with the ligand properties of amines. An excess of

Table 3 Effects of amine and amine oxide on epoxidation of cyclooctene[a]

Oxygen donor	Base	Ligand	t/h[c]	Yield epoxide[d] (%)
AO[b]	AO	AO	3	0
AO	A	AO	3	0
Aq. H₂O₂ (50%)	AO	AO	18	67
Aq. H₂O₂ (50%)	A	AO	1	88

[a] Reaction conditions were identical with those described in Table 2. [b] A ≡ diisopropylethylamine; AO ≡ diisopropylethylamine N-oxide. [c] Time at which reaction mixture was sampled. [d] The remainder was starting material.

amine added at the beginning of reaction may lead to some of the porphyrin being present as a bis-amine complex having no catalytic activity. A similar effect was observed with diisopropylethylamine, a hindered amine of similar basicity to that of triethylamine (Table 2). It was not expected that the hindered base would be oxidised so rapidly in the reaction medium because its reaction with hydrogen peroxide alone is very slow. In the presence of the porphyrin 1, oxidation of diisopropylethylamine proceeded quickly to give the N-oxide, identified by GC-MS comparison with an authentic specimen. The strong base, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) gave a 97% yield of epoxide in 30 min, almost as fast as with the reactions using imidazole as base (Table 2). In contrast, the weaker bases aniline and N,N-dimethylaniline provided almost no epoxidation. From these results, it appears that tertiary amine bases other than imidazole can be used and that they may also provide good ligands but there are complications. Firstly, N-oxides, formed by direct oxidation with H₂O₂, might themselves be sufficiently basic to form HO₂⁻. Therefore, even if an amine is rapidly oxidised to its N-oxide, in the latter form, it might still be a base in the porphyrin system. Secondly, an N-oxide might itself be an oxygen donor to the porphyrin, rather than the primary oxidant, H₂O₂. Thirdly, the N-oxide could provide, electronically, quite a different ligand for the porphyrin compared with any initially introduced tertiary amine. Therefore, experiments were carried out to examine the effects of tertiary amine oxides on rates of epoxidation with H₂O₂.

Epoxidation of cyclooctene was attempted, using porphyrin 1 and diisopropylethylamine N-oxide in the triple functional mode of possible base, ligand and oxygen donor (Table 3). No formation of epoxide was observed after 3 h, and therefore at least one of these functions was not operating. With both diisopropylethylamine and its N-oxide present, again no epoxidation could be observed in 3 h. These results indicate that, in this system, with porphyrin 1, the N-oxide does not act as an oxygen donor. Addition of H₂O₂ to diisopropylethylamine and its N-oxide, with cyclooctene and porphyrin 1 afforded rapid conversion into epoxide (Table 3), showing that the amine and its N-oxide must act in their simple respective functional roles of base and ligand. Diisopropylethylamine N-oxide alone can act as a ligand and, to some extent as a base, as illustrated by the slow epoxidation of cyclooctene (18 h) when the N-oxide was used without the tertiary amine as base (Table 3). However, this rate of epoxidation is considerably less than the rate observed when a free amine is present (Table 2) and it may be concluded that, whereas an N-oxide can be a good ligand for the porphyrin, it is not sufficiently basic in the present epoxidation system using H₂O₂ to provide rapid epoxidation. The conclusions that N-oxides were insufficiently basic and were not oxygen donors but were good ligands were confirmed by the next experiments.

Using the same standard experimental conditions (cyclo-

Table 4 Examples of alkene epoxidation using tetrabutyl ammonium hydroxide as base and triethylamine N-oxide as ligand[a]

Amine	Reaction t/h[b]	Yield epoxide[c] (%)
Cyclooctene	5	98
Oct-1-ene	24	72[b]
1-Methylcyclohexene	2.5	89
trans-Oct-4-ene	24	24
Limonene	3.5	89[c]

[a] Reaction conditions: alkene (1 mmol); manganese porphyrin 1 $(7.4 \times 10^{-3}$ mmol); H_2O_2 (50% aqueous, 0.15 cm^3); $Et_3N^+-O^-$ (20 mg, 1.7×10^{-4} mol); $Bu_4N^+OH^-$ (0.1 mmol) in solvent mixture of CH_2Cl_2 (2 cm^3) and MeOH (1.5 cm^3). Reaction carried out at room temperature. [b] Further H_2O_2 added after 17 h. [c] Ratio of epoxides:

0.69 0.18 0.12
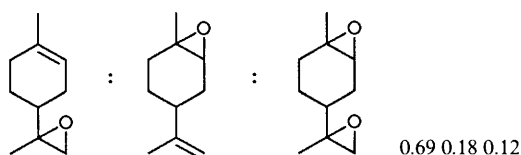
Table 5 Use of H_2O_2 adducts for epoxidation of cyclooctene.[a]

Adducts $(A \cdot H_2O_2)$ A	Base	t/h	Yield epoxide (%)
Na_2CO_3[b]	$Bu_4N^+OH^-$	2.0	91
Na_2CO_3[b]	—	4.5	90[c]
H_2NCONH_2[b]	$Bu_4N^+OH^-$	24	89[c]
Me_3NO	$Bu_4N^+OH^-$	17	22
Me_3NO[d]	$Bu_4N^+OH^-$	21	96[d]
Ph_3PO	$Bu_4N^+OH^-$	3	21[e]

[a] Alkene (1 mmol); $Et_3N^+-O^-$ (20 mg, 1.7×10^{-4} mol); $A \cdot H_2O_2$ (2.5 equiv. as H_2O_2); $Bu_4N^+OH^-$ (0.1 mmol); CH_2Cl_2 (2 cm^3), MeOH (1.5 cm^3) and manganese porphyrin 1 $(7.4 \times 10^{-3}$ mmol). Reaction was carried out at room temperature. [b] With addition of H_2O (0.2 cm^3) to solvent system. [c] More H_2O_2 adduct was added at the half way stage. [d] More H_2O_2 (aqueous 50%) was added to previous reaction after 17 h. [e] No more adduct or aqueous H_2O_2 was added in this instance.

octene, porphyrin 1, H_2O_2), epoxidation was attempted with a variety of amine N-oxide/base combinations (Table 1). With triethylamine N-oxide as both base and ligand, a 73% yield of cyclooctene epoxide was obtained in 5 h. Addition of tetrabutylammonium hydroxide as base, with the same N-oxide as ligand, gave about the same yield of epoxide in 2 h and a 98% yield in 5 h. These conditions, in contrast to the use of imidazole alone, form the basis of a manganese-porphyrin catalytic epoxidation system, in which the ligand and base are not oxidised and could be reused if necessary. Thus, amine N-oxides can be used as ligands but are not satisfactory as bases in this system. However, other non-oxidisable bases can be used (Table 1). Sodium carbonate and sodium acetate both afford rapid high yields of cyclooctene epoxide, with the acetate being particularly good.

Ligands other than amine oxides can be used as, for example, phenols and triphenylphosphine oxide (Table 1). 2-Chlorophenol (or its anion in the presence of base) with tetrabutylammonium hydroxide provided slow epoxidation and triphenylphosphine oxide with the same base gave 37% of

* In independent work, we have found that addition of the adducts to a variety of solvents and estimation of 'available oxygen' in solution at intervals of time, show that the adducts release H_2O_2 until an equilibrium is set up. This position of this equilibrium depends on the natures of the adduct and solvent. Catalytic amounts of water speed up the approach to equilibrium (see ref. 20).

epoxide in 1 h, although this reaction proceeded further on addition of more H_2O_2.

Some examples are shown in Table 4 of epoxidation of alkenes other than cyclooctene using H_2O_2 with triethylamine N-oxide as ligand, tetrabutylammonium hydroxide as base and the manganese porphyrin 1 as catalyst. Yields of epoxides are good, although rates vary considerably. In 24 h, oct-1-ene afforded a 54% yield of its epoxide; addition of more H_2O_2 increased the yield to 72%. Evidently, a problem with the slower reactions appears to be general loss of H_2O_2 through decomposition so that epoxidation ceases until more oxidant is added.

Sources of H_2O_2, other than an aqueous solution, can be used advantageously. Some compounds **A**, such as sodium carbonate, urea, triphenylphosphine oxide and trimethylamine-N-oxide, form adducts $(A \cdot xH_2O_2)$ with hydrogen peroxide which are stable, easily prepared anhydrous sources of the oxidant. With solvent, the adducts dissociate to an extent which is dependent on the nature of the adduct and the solvent (Reaction 2). Because of this dissociation, such adducts provide

$$A \cdot xH_2O_2 \rightleftharpoons A + xH_2O_2 \qquad (2)$$
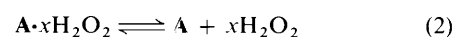
a convenient source of anhydrous H_2O_2.* The usual handling precautions for H_2O_2 should be taken. The non-oxidising part of the adduct **A** may be neutral, basic or acidic and, furthermore, may be also a suitable ligand for the porphyrin. For example, sodium percarbonate $(Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$; an adduct, not a peracid as its common name would imply) can act as a base, whilst trimethylamine N-oxide could provide a ligand, as discussed above. As shown in Table 5, with sodium percarbonate $(A \equiv Na_2CO_3)$ and tetrabutylammonium hydroxide, epoxidation of cyclooctene was almost complete in 2 h. However, if the ammonium base is omitted, a high yield of epoxide is still obtained, but in 4.5 h. In this case, the Na_2CO_3 must be acting as the base as well as provider of H_2O_2 through its adduct. For this last reaction, addition of a catalytic quantity of water was found to be advantageous, the biphasic (liquid–solid) reaction proceeding very slowly in its absence. Catalytic effects of water on heterogeneous (biphasic) reactions have been reported.[20] The H_2O_2 adduct with trimethylamine in the presence of base afforded only 22% of epoxide after 17 h but addition of a small quantity of aqueous H_2O_2 caused the reaction to go to completion in only 4 h. This effect may be due to the same catalytic effect of water but possibly also to the ligand effect of trimethylamine N-oxide; to add sufficient H_2O_2 to the reaction mixture, the molar ratio of N-oxide to porphyrin was about 270:1 and, at this level, much of the porphyrin could become catalytically inactive through having two ligands to the central metal rather than one.

Conclusions

For the epoxidation of alkenes with hydrogen peroxide, catalysed by manganese-porphyrin 1, tertiary amine N-oxides can be used as stable ligands in place of the easily destroyed imidazole used previously. Further, the use of imidazole as base can be avoided through use of tetrabutylammonium hydroxide or other bases such as sodium carbonate or sodium acetate. Adducts of hydrogen peroxide provide convenient stable sources of the oxidant and can also provide the base and/or ligand needed in the epoxidation medium. The adducts are particularly useful for reactions in which the concentration of H_2O_2 in solution needs to be controlled at a fixed level.

Experimental

For the identification of products of reaction, these were prepared independently and characterised by the usual methods

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(m.p., NMR, MS, IR *etc.*), all being known compounds. The course of a reaction was followed by removing aliquots at intervals and examining the products of reaction by gas chromatography, using internal standards precalibrated against authentic materials. Gas chromatography–mass spectrometry was carried out to help confirm the identities of reaction products by comparison of mass spectra with authentic specimens. In some instances, reactions were carried out on a larger scale and the epoxides were isolated as further confirmation of identity and yield.

Gas chromatography. This was carried out on a Dani 3800 instrument using a capillary column (25 m × 0.3 mm, i.d.) and tridecane as internal standard. Typically, for cyclooctene, the GC analysis was run at 100 °C for 2 min after which the temperature was increased at 10 °C min^{-1} up to 250 °C.

Gas chromatography–mass spectrometry. This was carried out using a VG 7070E mass spectrometer with electron-impact ionisation at 70 V. Total ion current chromatograms were compared with gas chromatograms obtained as above. Mass spectra of reaction products were compared with mass spectra of authentic materials.

Preparation of Adducts of Hydrogen Peroxide.—These were synthesised from aqueous hydrogen peroxide and the addend, by literature procedures: triphenylphosphine oxide,[21] amine *N*-oxides.[22] Samples of sodium percarbonate and urea hydrogen peroxide were obtained commercially (Interox, Widnes, UK).

General Procedure for Oxidations using Triethylamine N-Oxide as Ligand and Tetrabutylammonium Hydroxide as Base.— In a typical reaction, the alkene (1 mmol), manganese porphyrin **1** (7.4 × 10^{-3} mmol), triethylamine *N*-oxide (1.7 × 10^{-4} mol) and tetrabutylammonium hydroxide (0.1 mmol) were dissolved in a mixture of CH_2Cl_2 (2 cm^3) and MeOH (1.5 cm^3) at room temperature. Reaction was initiated by addition of H_2O_2 (aqueous solution or adduct; 2 mmol) and was continued at room temperature (with stirring where the adduct was used) until epoxidation was complete, as monitored by GC.

Reaction Conditions for Results Shown in Figs. 1(a–c).— Reactions were carried out as described above for the general procedure but using the following amounts: cyclooctene (1 mmol), manganese porphyrin **1**; (2.2 × 10^{-5} mmol), urea·H_2O_2 (2.8 mmol as H_2O_2), H_2O (0.2 cm^3), MeCN (4 cm^3) and CH_2Cl_2 (4 cm^3). The quantity of imidazole was dependent on the ratio of imidazole to manganese porphyrin as given in the Figs. The reaction was monitored by removing aliquots at intervals, destroying excess of H_2O_2 by addition of a small amount of palladium-on-charcoal (10% w/w) and analysing for appearance of epoxide and disappearance of imidazole by GC, using tridecane and hexadecane as respective internal standards.

Reaction Conditions for Results Shown in Figs. 2(a,b).—These reactions were carried out exactly like those for Figs. 1(*a–c*) except that a mixture of MeOH (4 cm^3) and CH_2Cl_2 (4 cm^3) was used in place of the solvent system, $CH_3CN–CH_2Cl_2$.

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