Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide

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Contents

1. Introduction

Hydrogen peroxide is probably the best terminal oxidant after dioxygen with respect to environmental and economic considerations.[1-4] Indeed, in certain circumstances, it is better than oxygen insofar as O_2/organic mixtures can sometimes spontaneously ignite. As a result, epoxidation systems that use hydrogen peroxide in conjunction with catalytic amounts of cheap, relatively nontoxic metals are potentially viable for large-scale production of inexpensive products, and for specialized applications in development, process, and research. The literature


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Scheme 1. Hydrotalcite Epoxidations Using 30 % Hydrogen Peroxide: (a) With Benzonitrile as Peroxide Carrier; (b) with *iso*-Butyramide as Peroxide Carrier; and (c) the Presumed Mechanism of the Reaction Shown in part b
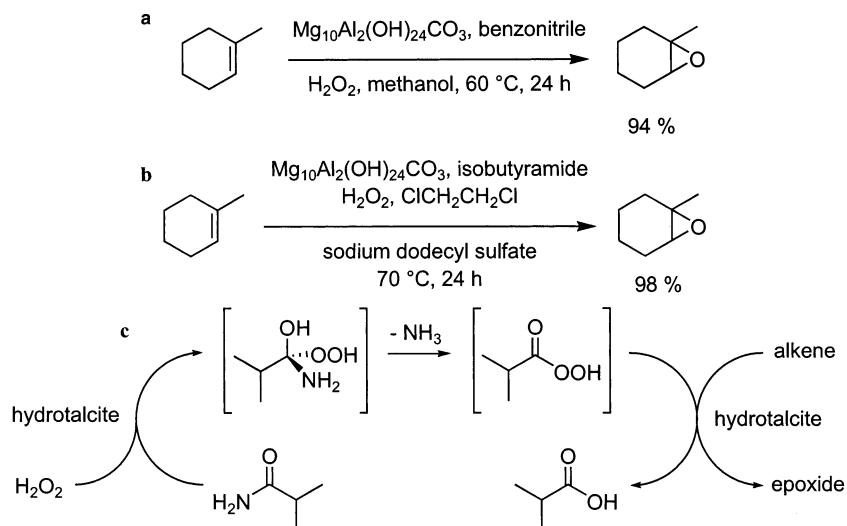
in this area is extensive and difficult to segregate into sharply delineated categories, but a fair way to attempt this is according to the catalyst precursors: "heterogeneous", "soluble metal oxides", and "homogeneous coordination complexes".[5] Organic catalysts designed for asymmetric epoxidation may also function with hydrogen peroxide as a terminal oxidant, but they are beyond the scope of this review.[6−9] The focus of this review is methods for the production of fine chemicals, but heterogeneous systems (more suitable for production of chemical commodities) are outlined for completeness.

2. Heterogeneous Systems

2.1. Zeolites and Hydrotalcite Systems

Heterogeneous systems for epoxidation of alkenes with H_2O_2 are typically mineral-type catalysts, including zeolites[10−12] or hydrotalcites.[13−16] Zeolites most commonly used for alkene oxidations feature four-coordinate titanium centers in microporous siliceous frameworks.[17−19] The first Ti-containing silicalite zeolite, TS-1, has a relatively small pore size of 5.5 Å. The small pore size of TS-1 precludes reactions of larger substrates[4] though the isomorph ZSM-5 or zeolites with larger pore sizes, such as Ti-β, have less severe limitations in this regard.[20−22] Zeolites such as TS-1 are most reactive toward terminal akenes and less reactive to *Z*-alkenes, and modified forms can allow for epoxidation of *E*-isomers.[11] For instance, Ti-MWW (a zeolite having large, 10-membered ring, channels in the siliceous framework, also known as MCM-22) mediates epoxidation of C_6-C_8 linear aliphatic alkenes with 30% H_2O_2 to produce a 4:1 rate preference in favor of *E*-alkenes over their *Z*-isomers. This preference is related to the larger pore size, which also allows formation of C_6-C_8 epoxides in 80−85% yield. However, such systems tend to be used at slightly elevated temperatures (e.g., 60−70 °C), which may lead to decomposition of sensitive products. Since TS-

1-type zeolites are inherently acidic, they are sometimes modified prior to use to prevent inactivation of the catalyst or epoxide-decomposition. Even with such modifications, zeolites are generally limited to production of small, fairly stable epoxides.

Hydrotalcite systems are more widely applicable than zeolites insofar as they can be used with a greater variety of substrates. These synthetic anionic clays are basic; in fact, they are basic enough to promote some nucleophilic epoxidations.[23] For example, $Mg_{10}Al_2(OH)_{24}CO_3$ and $Mg_{9.5}Al_{2.6}(OH)_{24.8}CO_3$ mediate epoxidations of α,β-unsaturated ketones with H_2O_2 in the absence of other inorganic bases.[15,24] The $Mg_{10}Al_2(OH)_{24}CO_3$ hydrotalcite system developed by Kaneda also gives high conversions and selectivities for electrophilic epoxidations, even when acid-sensitive epoxides are produced, Scheme 1. Unfortunately, this system requires more than one equivalent of an amide[13] or nitrile[14] additive to act as a peroxide carrier. This additive is converted into a carboxylic acid byproduct, which can complicate isolation of the desired epoxide. Epoxidations mediated by the Kaneda system can be accelerated using microwave-heating,[25] such that reaction times can be reduced from 1 day to 1 min. The Kaneda's epoxidation reaction is mechanistically similar to the Payne epoxidation, which is often used for industrial batch-type processes,[26] the major difference being that H_2O_2 activation is achieved using hydrotalcites at 60 °C rather than bicarbonate at room temperature (Payne).

Typical hydrotalcites used as catalysts in epoxidation reactions are polynuclear-alumina clays (i.e., $Mg_{10}Al_2(OH)_{24}CO_3$); however, simple alumina will also catalyze this reaction without amides or nitriles.[27−30] A variety of different alumina sources can absorb hydrogen peroxide onto that surface, forming an active oxidant (alumina-OOH) that can epoxidize unfunctionalized alkenes in low to modest yields at ambient temperatures.[27] Higher yields can be obtained by using anhydrous H_2O_2 in refluxing ethyl acetate, but the presence of a small amount of water is critical.[28−30] Aqueous 60% H_2O_2 can also be

1

2   **3**

M = Fe^{III} or Mn^{III}
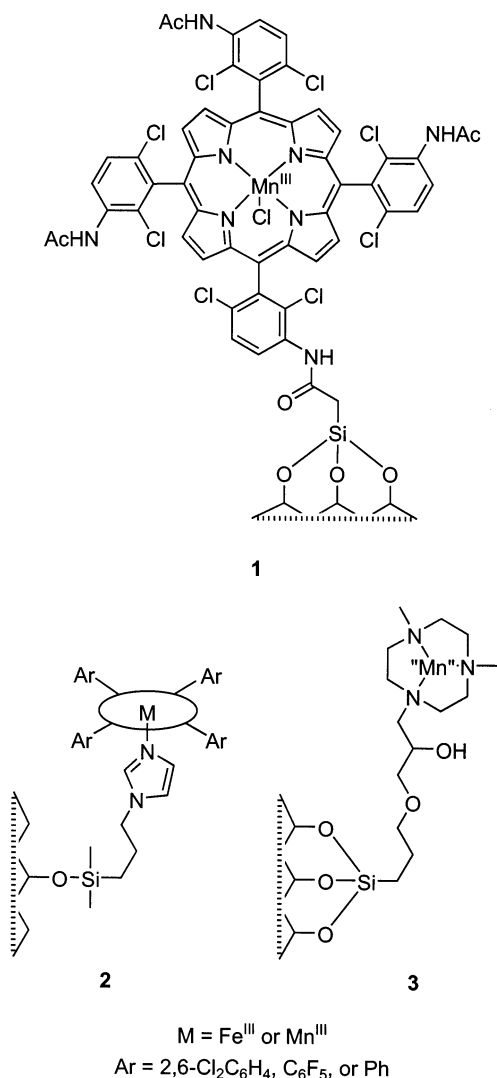
Ar = 2,6-Cl$_2$C$_6$H$_4$, C$_6$F$_5$, or Ph

Figure 1. Strategies for attaching coordination complexes to modified silica.

used with the addition of a Dean–Stark apparatus; 1-*tert*-butylcyclohexene was epoxidized in 91% yield in 4 h using these conditions.[28] These types of systems have generally been tested on simple, unfunctionalized alkenes.

2.2. "Homogeneous Catalysts" Attached to Solid Supports

Heterogeneous catalysts may be constructed by attaching or impregnating homogeneous catalysts onto solid supports. This may be achieved by using ion-exchange resin to bind anionic catalysts,[31,32] encapsulating inorganic complexes onto chemically modified silica or zeolites,[12,16,33–35] or covalently binding coordination complexes onto modified silica. Figure 1 illustrates the latter approach in the context of porphyrin (**1** and **2**)[36,37] or triazacyclononane (**3**) complexes.[38–41]

Supported homogeneous catalysts tend to have reduced activities relative to their truly homogeneous analogues. However, this drawback can be offset by the advantages of easy catalyst recovery, reduction of trace metal contamination, and facile methods for parallel screening. Recent work illustrates how solid

phase techniques can be used to prepare supported, peptide-derived transition metal complexes (particularly Mn and Fe), which may then be screened for potential catalytic activities.[42–45]

3. Soluble Metal Oxides

3.1 Polyoxometalates

Polyoxometalates are salts composed of complex anions incorporated with two or more metal cations. They act as homogeneous epoxidation catalysts, but the conversions obtained, the selectivities for epoxide products, and the range of solvents that can be used for the reaction are mostly inferior compared to other methods.[46] For example, (R$_4$N)$_6$SiW$_{10}$Fe(OH$_2$)$_2$O$_{38}$ (where R = alkyl) salts epoxidize aliphatic alkenes slowly at 32 °C in acetonitrile but also mediate C–H activation of alkanes, causing lack of selectivity.[47] Better selectivities were obtained for some substrates using systems with (R$_4$N)$_9$Ni(OH$_2$)H$_2$F$_6$NaW$_{17}$O$_{55}$ but at 60 °C in biphasic systems that include halogenated solvents.[48]

3.2. Peroxotungstates

Systems derived from tungstic acid (H$_2$WO$_4$), phosphate, and ammonium or phosphonium counterions that act as phase transfer agents are prominent among simple, soluble metal oxide salts for catalytic epoxidation with H$_2$O$_2$.[49–60] They are nearly always formed in situ, but catalytically active complexes such as (R$_4$N)$_3${PO$_4$(W(O)(O$_2$)$_2$)$_4$} (Figure 2) have been

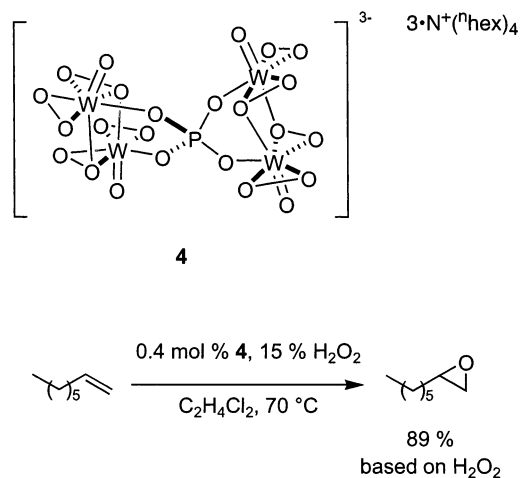**4**

89 %
based on H$_2$O$_2$

Figure 2. Venturello epoxidation catalyst.

isolated and characterized crystallographically by Venturello and co-workers.[61] Tungsten catalysts of this type use H$_2$O$_2$ more efficiently than many other epoxidation catalysts, insofar as their unique chemistry favors oxygen transfer over peroxide disproportionation. Biphasic systems involving chlorinated solvents or, less commonly, aromatic solvents such as benzene were used for such reactions until Noyori showed that terminal aliphatic alkenes could be epoxidized at 90 °C without organic solvents by means of rapid-stirring, Figure 3.[62,63] Under these conditions, 1-dodecene was converted to its corresponding epoxide in 99% yield with only 1.5 equiv
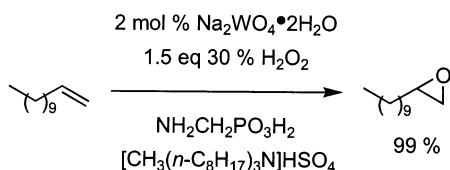
Figure 3. Noyori's solvent free epoxidation system.

H_2O_2. However, only simple aliphatic alkenes are usually cited as substrates; slightly acid-sensitive epoxides such as phenyl oxiranes are not stable to such reactions conditions, resulting in low yields.[62] This is common for systems with Lewis-acidic catalysts that use aqueous H_2O_2 at high temperatures. Due to the above limitations, such tungsten catalysts may only be used to produce relatively stable epoxides, particularly terminal aliphatic ones, despite their high conversions and selectivities.

The type of ammonium salt used with phosphate/ tungstic acid catalyst is important. For example, *n*-octylammonium hydrogen sulfate is critical in Noyori's work (Figure 3); chloride causes deactivation and other ammonium hydrogen sulfates produce catalysts that are not as effective or even completely inactive. It seems that the catalyst must have an appropriate partition coefficient, one that allows it to interact with both the aqueous oxidant and organic substrate. There is no reliable way to predict which ammonium salt is ideal, so selections are usually made through trial and error. The aminomethylphosphonic acid required in this system is relatively expensive.

Recoverable catalysts reduce product-impurities and costs, and both these factors are concerns with tungsten-based systems. To address these issues, the tungstic acid epoxidation catalyst shown in Scheme 2 was designed. The key to this system is the unique

Scheme 2. A Recoverable Phosphate/Tungstic Acid System Based on Catalyst Solubility
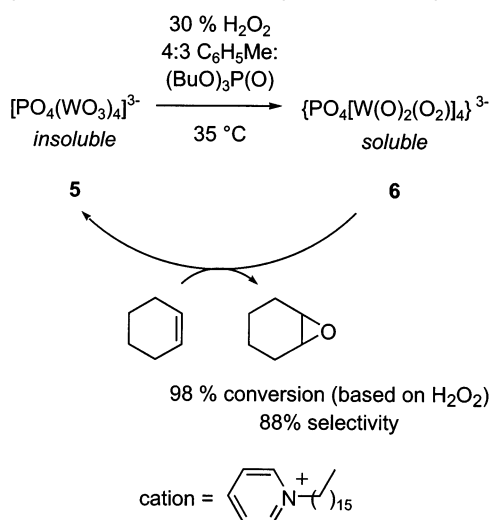
solubility properties of the catalyst **6**. This soluble material oxidizes propene with 30% H_2O_2 in xylene and tributyl phosphate at 35 °C, but the reduced form **5** precipitates from the medium once H_2O_2 is consumed.[64] Many ammonium cations were screened to find a system with such desirable solubility charac-
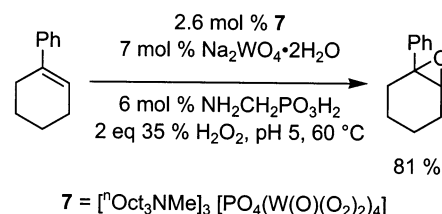
Figure 4. Phosphate/tungstic acid catalyst for the formation of acid sensitive epoxides.

teristics. Tributyl phosphate is not an ideal solvent with respect to environmental considerations, so the system could be improved in that respect. Another method to recover Venturello tungsten catalysts is to support them on ion-exchange resins.[31,32] The anion $\{PO_4[W(O)(O_2)_2]_4\}$ supported on Amberlite IRA-900 resin by ion exchange[61] gives a heterogeneous system for the epoxidation of a variety of commercially interesting epoxides; high yields are obtained using only 2 equiv of 30% H_2O_2 in acetonitrile at 38 °C.

None of the systems mentioned above are suitable for preparing acid-sensitive epoxides such as that from 1-phenylcyclohexene, but a modification developed by Jacobs addresses this.[31] The Venturello anion was combined with the Noyori's optimal ammonium cation to form an epoxidation catalyst for use in a biphasic reaction with (aminomethyl)phosphonic and tungstic acids at pH 5, Figure 4. Under such conditions, 1-phenylcyclohexene was epoxidized in 81% yield and successfully isolated from the reaction mixture. Experimentally the reaction has some drawbacks. Solutions of catalyst and reagents must be adjusted to appropriate pH's prior to mixing, the optimal reaction conditions are substrate dependent, and relatively large quantities of tungsten are required.

In general, the tungstate/phosphate systems discussed in this section are effective catalysts. Application of these systems tends to be restricted by toxicity factors related to tungsten catalysts and some of the solvents (often chlorinated media), though the catalysts are active and selective.

3.3. Peroxomolybdates

Molybdenum catalysts (e.g., $[NMe_4]_2[(PhPO_3)\{MoO-(O_2)_2\}_2\cdot\{MoO(O_2)_2(H_2O)\}]$, $[(NH_4)_6Mo_7O_{24}\cdot4H_2O]$, etc., similar to peroxotungstates), have been prepared and investigated for the epoxidation of alkenes with H_2O_2.[59,65-70] They give low turnovers and selectivities for the desired products, and their reactions are performed under harsh conditions. Soluble molybdenum oxide complexes are often used in stoichiometric quantities in which an active oxidant is generated from 30% H_2O_2 and commercially available ammonium molybdate. Some peroxomolybdate complexes bearing a chiral bidentate α-hydroxyamide or a chiral monodentate amine *N*-oxide ligand have been prepared and tested in asymmetric epoxidations,[71,72] but the resulting complexes have to be used in stoichiometric quantities to afford low enantioselectivity and yields.

Scheme 3. Catalytic Cycle in Methyltrioxorhenium Mediated Epoxidations with Hydrogen Peroxide

Figure 5. Additives in methyltrioxorhenium epoxidations with 30% hydrogen peroxide.
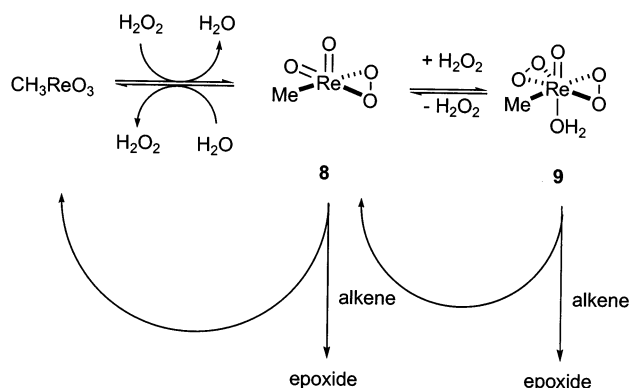
3.4. Methyltrioxorhenium

The discovery of methyltrioxorhenium, $MeReO_3$ or MTO, epoxidations by Herrmann and co-workers' is a milestone in this area. A variety of alkenes was epoxidized with anhydrous H_2O_2 in [t]BuOH or THF at room temperature or below using 0.1–1.0 mol % of this catalyst in *tert*-butyl alcohol or THF.[73,74] This innovation inspired a variety of research efforts, including a switch to 30% hydrogen peroxide as oxidant,[75] mechanistic studies,[75–81] and theoretical simulations of involved intermediate and transition states, Scheme 3.[82,83] With a few exceptions, MTO does not undergo redox chemistry during catalytic reactions; it remains in the +VII oxidation state. MTO activates H_2O_2 through an equilibrium formation of the η^2-peroxo species **8** and **9**. The structure of **9** was confirmed crystallographically, and the methyl resonances of **8** and **9** were detected by both ^{1}H and ^{13}C NMR.

The main disadvantage in MTO/H_2O_2 epoxidations is that they are inherently acidic and this tends to cause ring opening of sensitive epoxides to diols. None of the procedural-modifications to MTO-mediated epoxidations satisfactorily addressed the issue of acidity until Sharpless and co-workers tested pyridine in the system.[84] This additive confers two important effects. First, it makes the medium slightly basic, thus protecting acid-sensitive epoxides from ring opening, and second it accelerates the rate of the desired epoxidation reaction. Herrmann had previously investigated the use of nitrogen bases in MTO-catalyzed epoxidations but did not observe significant ligand-accelerated catalysis[85] because the amines used were oxidized to amine *N*-oxides under the reaction conditions.[86,87] Besides decomposing during the reaction, amine *N*-oxides also served as weaker donor ligands than the corresponding amines, resulting in less selective and active complexes. The pK_a of the amine used is important in achieving ligand-accelerated catalysis since the extent of interaction between the rhenium and amine can be correlated to the latter's pK_a; more basic amines tend to deactivate the MTO. Sharpless' discovery hinges on the use of the right base in the correct quantities to ensure high catalytic activity and diminished epoxide ring-opening. Other nitrogen donors beside
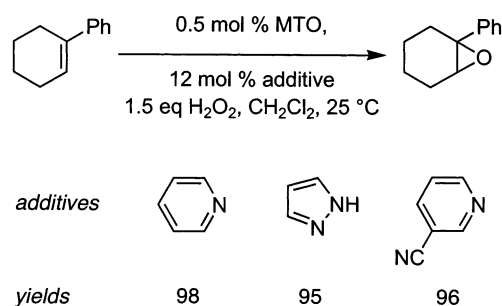
pyridine,[84,88–90] notably pyrazole[91–93] and 3-cyanopyridine,[94,95] have now been investigated as additives in methyltrioxorhenium-mediated epoxidations, Figure 5. Despite these studies, the effects of the basic additives are still a matter for conjecture. They seem to function as phase transfer catalysts. The most effective ones are resistant to oxidation themselves, and not so basic that catalyst decomposition is favored over the desired epoxidation event. Basic characteristics of the additives are crucial because if they are too basic then MTO decomposes to catalytically inert perrhenic acid and methanol. For these reasons, pyrazole and 3-cyanopyridine tend to be preferred.

There are relatively few disadvantages of MTO/base systems in epoxidation. In some cases it can be difficult to separate the additive from the product; for instance, separation of acid-sensitive epoxides from bases having similar boiling points can be experimentally difficult since the product may not survive treatment of the crude reaction mixture with acid or exposure to silica. With few exceptions,[96–98] additives only work when used in an aprotic media like nitromethane or chlorinated solvents, but such solvents are not suited for large-scale reactions due to the risk of explosions and toxicity issues. Nevertheless, MTO-catalyzed epoxidations are a very attractive option, particularly for small-scale epoxidation reactions. MTO has been used to epoxidize a variety of different alkenes with aliphatic and aromatic substituents.

3.5. Other Metal Oxides

Other than $MeReO_3$, soluble metal oxides for alkene epoxidation using H_2O_2 have relatively major limitations.[5,99] For instance, tetraperoxoniobate, ${Nb(O_2)_4}^{3-}$, is a catalyst, but it produces relatively poor conversions and selectivities for the desired epoxide product;[100] other peroxyniobium complexes have similar activities.[101] Reactivity profiles such as this are characteristic of systems that operate via production of free hydroxyl radicals, i.e., "Fenton chemistry".[102,103]

4. Metal Oxides Generated in Situ

4.1. Selenium and Arsenic Compounds

Some selenium[104–107] and arsenic[108–110] compounds in perfluorinated solvents are surprisingly active and selective epoxidation catalysts. Epoxidation of electron-
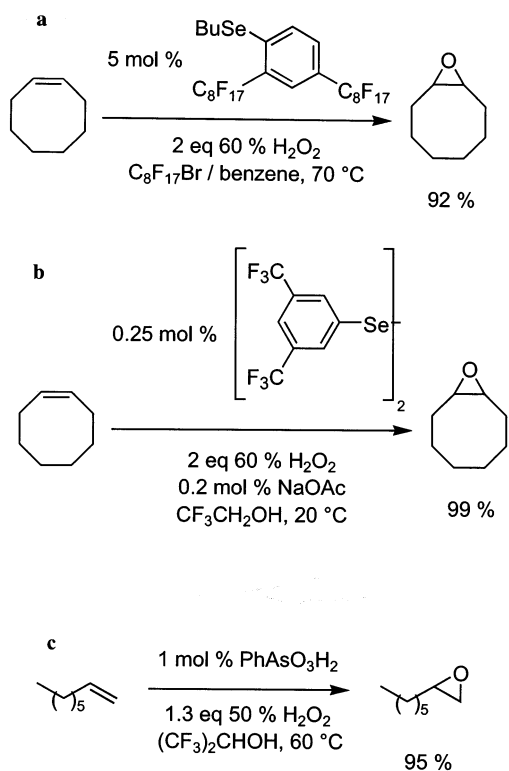
Figure 6. Selenium/arsenic-based catalysts for the epoxidation of alkenes: (a) phenylselenide catalyst, (b) diselenide catalyst, and (c) benzenearsonic acid.

rich alkenes by H_2O_2 in perfluorinated solvents at 80 °C occurs in the absence of catalysts,[111,112] but addition of diselenide and arsenic catalysts allows epoxidation to be achieved at lower temperatures and shorter times. The phenylselenide, diselenide, and arsenic systems can epoxidize alkenes with only 2 equiv or less of H_2O_2 (Figure 6). While most systems involving these catalysts require temperatures of 60–70 °C, the diselenide system catalyzes epoxidations at room temperature. The mechanism of this process involves in situ oxidative formation of selenic acids or oxides that further react with H_2O_2 to form peroxyselenic acids.[105,106,113] Peroxyselenic acid is the active epoxidizing agent, so the diselenide and phenylselenide compounds are catalyst precursors. The mechanism of benzenearsonic-acid-catalyzed epoxidations is similar, occurring via formation of phenylperarsonic acid.

Tertiary arsines can serve as cocatalysts in perrhenic acid ($HReO_4$)-catalyzed epoxidations.[114] Rhenium compounds, other than MTO, tend not to be efficient epoxidation catalysts with H_2O_2 because their Lewis acidities, and/or the acidic media they require for catalytic activity, lead to formation of diols.[114,115] Diphenylmethylarsine attenuates the acidity of the rhenium salts and allows a greater variety of solvents to be used such that epoxides form without any ring opening. Perrhenic acid (1 mol %) and diphenylmethylarsine (1.5 mol %) with 60% H_2O_2 in trifluoroethanol can epoxidize terminal and cyclic alkylalkenes in high yields at 75 °C. Interestingly, tertiary arsines are the most useful cocatalysts tested. The next best is triphenylantimony, which produces less than half the amount of epoxide.

Scheme 4. Catalytic Cycle for Manganese Sulfate Mediated Epoxidations
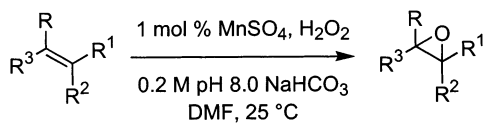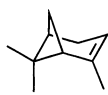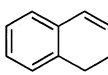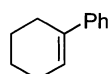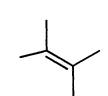

HCO_4^- = peroxymonocarbonate
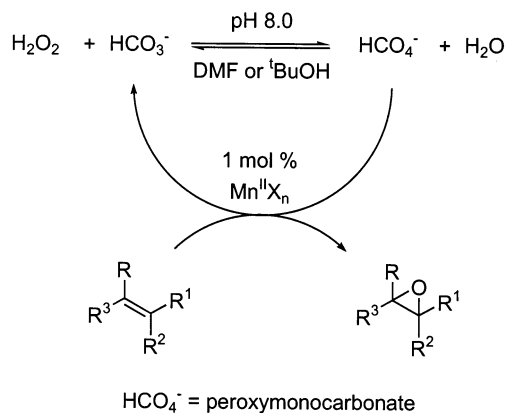
All the systems mentioned in this section utilize perfluorinated solvents to obtain high yields of epoxide. The perfluorinated solvent activates H_2O_2 by serving as a hydrogen bond acceptor prior to its reaction with the catalyst.[112] Despite their remarkably efficient catalytic abilities, these systems are therefore limited by environmental concerns regarding fluorinated media and safety issues related to high concentrations of H_2O_2.

4.2. Simple Metal Salts

Parallel screening led to a method wherein epoxidation is promoted by catalytic amounts (1.0–0.1 mol %) of manganese (2+) salts with 30% H_2O_2 as a terminal oxidant.[116] More than 30 d-block and f-block transition metal salts were screened for epoxidation activity under similar conditions (all in the presence of bicarbonate); only chromium (2+) chloride and iron (3+) sulfate exhibited some activity, and $MnSO_4$ gave the highest activity (Scheme 4). Bicarbonate is an essential component in this transformation. It forms peroxymonocarbonate ion, HCO_4^-, in this system; the presence of this intermediate was observed using NMR on mixing H_2O_2 and HCO_3^-. Such equilibria had previously been observed by Richardson et al. for formation of HCO_4^- from H_2O_2 and bicarbonate in other solvents,[117] and HCO_4^- without metal was found to be a moderately active epoxidizing agent in aqueous acetonitrile.[118] Uncatalyzed epoxidation by bicarbonate/H_2O_2 mixtures is slow in the solvents used in Mn-catalyzed processes, i.e., DMF and ^{t}BuOH. The inference from these observations is that the formed HCO_4^- reacts with Mn ions to produce active epoxidation reagent. EPR studies show that although Mn (2+) is initially consumed in the catalytic reaction, it is regenerated toward the end of the process when H_2O_2 is spent.[119] The implication of such findings is that Mn (2+) is first oxidized to Mn (4+), and then reduced once again in the catalytic cycle; these salts do not simply act as Lewis acids. A variety of aryl-substituted, cyclic, and trialkyl-substituted alkenes were epoxidized under these conditions, but monoalkyl alkenes were shown to be unreactive.

To improve the substrate scope of the Mn-mediated process and to increase the efficiency of H_2O_2 consumption, catalytic amounts of 68 diverse compounds

Table 1. Manganese Mediated Epoxidations Using 30 % Hydrogen Peroxide without and with Catalytic Salicylic Acid

| substrate	no additive		4 mol % salicyclic acid	
	eq H_2O_2	yield %	eq H_2O_2	yield %
(camphene-type alkene)	10	59	5	89
(dihydronaphthalene)	10	78	5	97
(1-phenylcyclohexene)	10	93	5	95
(2,3-dimethyl-2-butene)	10	51	5	81

were tested as additives to potentially enhance the rate of the epoxidation reaction relative to disproportionation of H_2O_2.[119] It was shown that 6 mol % sodium acetate in the ^tBuOH system and 4 mol % salicylic acid in the DMF system were effective; in the presence of these additives, the reactions required less H_2O_2, decreased reaction times, and the yields of the less reactive alkenes were enhanced, Table 1.

The manganese system described above is similar to $MeReO_3$-mediated epoxidations, but the two methods are complementary in some respects. Less hydrogen peroxide is used in the rhenium system; it is suitable for epoxidation of terminal alkenes, whereas the manganese-based catalyst is not, and $MeReO_3$ does not cause isomerization in the epoxidation of most *cis*-alkenes, whereas the Mn systems do. On the other hand, the manganese catalyst is cheaper, far less toxic, and uses more environmentally compatible solvents (^tBuOH and DMF, as opposed to halogenated hydrocarbons or nitromethane).

5. Coordination Complexes

5.1. Manganese Porphyrins

Porphyrins have been widely investigated as ligands to stabilize metals with respect to undesirable decomposition pathways and tune their reactivities. Manganese and iron porphyrins are the most important catalyst types for epoxidation reactions. Porphyrins of other metals, such as molybdenum, give inferior conversions and selectivities.[120,121] It was Mansuy and co-workers who discovered the effectiveness of Mn–porphyrin complexes for alkene epoxidation in the presence of H_2O_2. Chlorinated porphyrins were required to resist oxidation of the catalyst,
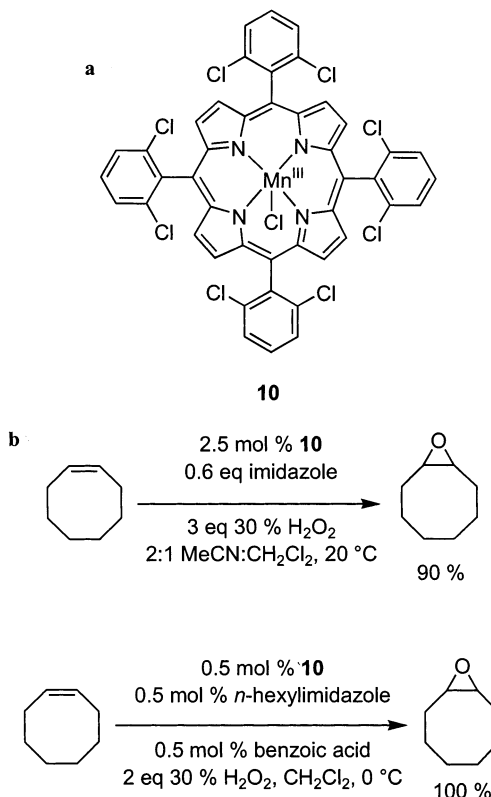
Figure 7. Additives in manganese porphyrin mediated epoxidations: (a) imidazole and (b) an *N*-alkyl imidazole and benzoic acid.

and additives such as imidazole[122–125] or combinations of imidazoles and carboxylic acids[126–129] were used to ensure high reactivities, Figure 7. Cyclooctene oxide was produced in 91% yield in 45 min using only imidazole under the original conditions, and a comparable yield was obtained in only 15 min when *N-n*-hexylimidazole/benzoic acid was added. The improved conditions with benzoic acid also resulted in quantitative formation of terminal aliphatic epoxides, a relatively difficult case, in only 15 min. Epoxidation of *cis*-alkenes was shown to be stereospecific, but *trans*-alkenes are poor substrates for these catalysts, e.g., *trans*-stilbene did not react even after an extended period.

Quici et al. constructed modified porphyrins with pendant ligands to determine the effect of covalently linking units often used as additives.[128,129] A porphyrin with tethered carboxylic acid, and imidazole groups gave enhanced epoxidation rates relative to unmodified porphyrin systems, i.e., cyclooctene was completely epoxidized in 3 min with perfect selectivity and a high initial rate of 500 turnovers min^{-1} (Scheme 5), and similarly high reactivities were observed for other substrates. Scheme 5 shows the possible roles of these additives in the catalytic cycle. Imidazole remains coordinated to the Mn throughout the reaction, whereas carboxylic acid helps cleave the peroxide O–O bond leading to a reactive Mn–oxo intermediate **14**. Oxomanganese species are well-established intermediates in Mn–porphyrin-mediated epoxidations with H_2O_2.[130–133] The oxo–Mn(V) intermediate has been isolated and its formation further studied using spectroscopic techniques.[134]

Scheme 5. Possible Catalytic Cycle Showing the Importance of Imidazole and Carboxylates in the Quici Modified Manganese−Porphyrin Epoxidation System
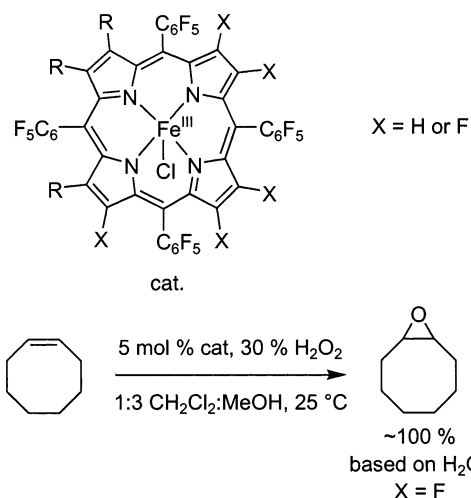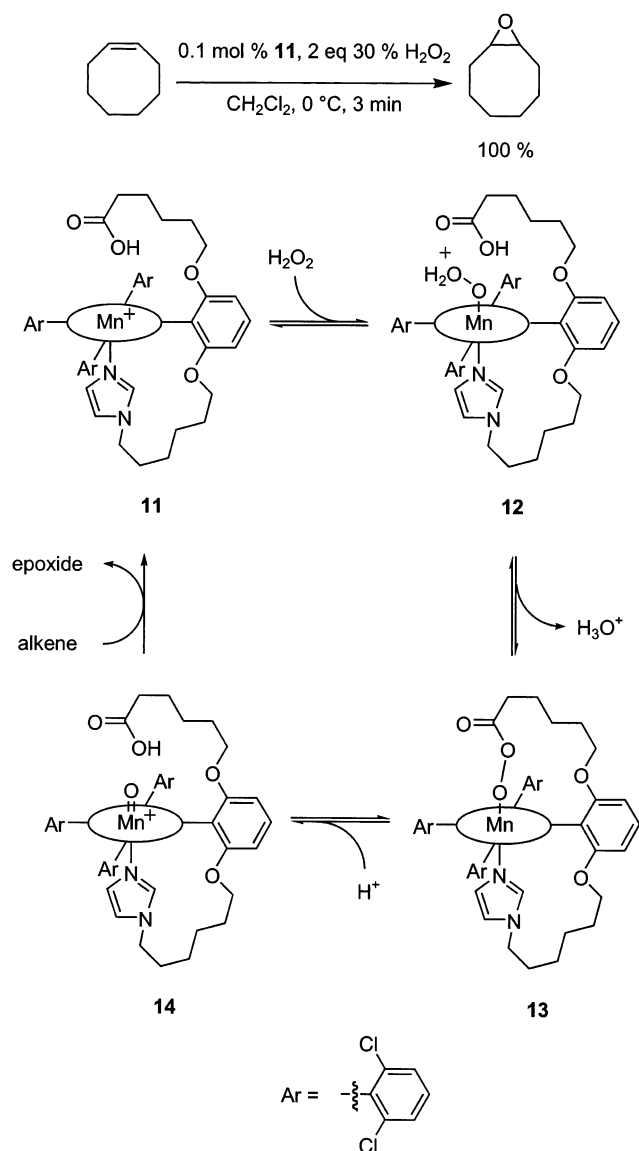

Figure 8. Iron porphyrin mediated epoxidation with electron-poor ligands and protic solvent.

Although other additives including ammonium acetate, amine N-oxides, and sodium bicarbonate were also investigated, their effects were comparable to those of imidazole and/or benzoic acid.[135−137]

Asymmetric Mn−porphyrins have also been synthesized by attaching threitol to the aryl substituents.[138] These catalysts gave up to 88% ee and 85% yields in the epoxidation of 1,2-dihydronaphthalene with iodosylbenzene, but inferior results using H_2O_2 as the oxidant, i.e., 29% ee, 68% yield.

5.2. Iron Porphyrins

Iron porphyrins can be highly active epoxidation catalysts, but the conversions and selectivities obtained from them tend to be inferior to their Mn counterparts unless the reactions are executed under strictly controlled conditions. An appreciation of suitable conditions arose from research to understand why these epoxidations sometimes work only with other oxidants such as iodosylbenzene.[139,140] Traylor made two important discoveries in this area.[141] First, contrary to prior assumptions, peroxides in the presence of Fe−heme systems do not undergo homolytic cleavage to produce radicals and oxoiron intermediates ($>$Fe$=$O; high valent iron^V oxo) but instead give heterolytic cleavage to produce an oxene species (the $>$Fe$=$O•$^+$ iron^{IV} radical cation, from one electron oxidation of the porphyrin ligand). This oxene species is the desired epoxidation catalyst, but unconstructive side reactions (i.e., catalyst decomposition, unselective oxidation) arise when the oxidant and oxene react prior to the epoxidation event. In that case, alkoxy radicals are produced and undesirable side reactions result. Traylor therefore proposed that radical production is minimized by using protic solvents and by keeping the concentration of the oxidant low (e.g., by slow addition), Figure 8. Second, Traylor found that more electron-deficient porphyrins favored epoxidation under the experimental conditions. For instance, highly fluorinated porphyrins and those with other electron-withdrawing groups were shown to catalyze epoxidation of alkenes with H_2O_2 (Figure 8).[142−145] More recently, electron deficient porphyrins were also shown to be catalytically active in ionic liquids.[146]

Recent research suggests that complications in the epoxidation reaction can have several origins,[147,148] and competing mechanisms, especially for electron-rich porphyrins, can complicate mechanistic interpretations. For instance, direct oxidation of the porphyrin ligands by Fe−oxene intermediates can compete with catalytic epoxidation, even if halogenated porphyrins are used. Consequently, reactions of Fe−oxene species with the oxidant to generate free alkoxy radicals may partially explain why Fe−porphyrins in catalytic epoxidations can have poor activities.
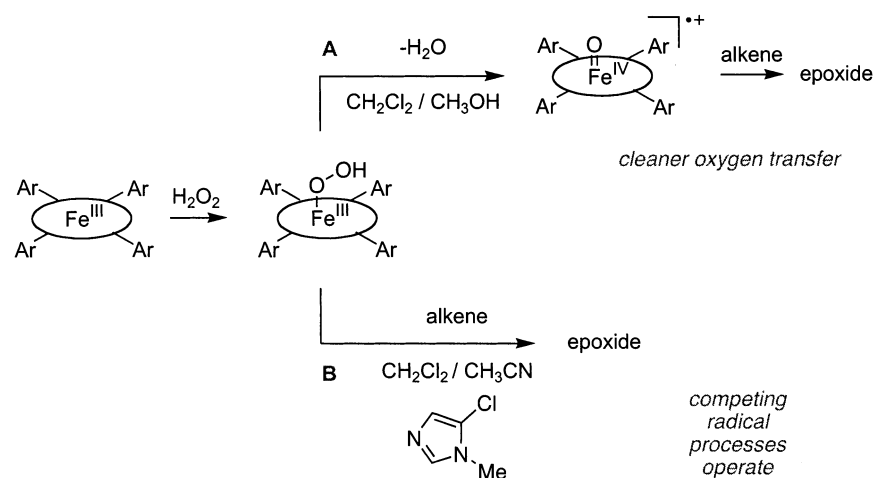
Traylor's observations regarding the advantages of electron-deficient porphyrins, protic solvents, and slow addition of the oxidant spawned further developments in this field. Formation and reactivity of iron intermediates were studied using ^{18}O incorporation experiments.[149,150] When ^{18}O-labeled water was present in the reaction, different levels of incorporation into the epoxide were observed at different

Scheme 6. Two Distinct Pathways for Iron Porphyrin-Mediated Epoxidations Depending on the Conditions Used[a]


[a] Pathway a is favored in polar solvents and low hydrogen peroxide concentrations, whereas pathway b predominates in apolar solvents and high peroxide concentrations.

temperatures; a reaction carried out at -78 °C showed no incorporation, but almost 60% was observed at 40 °C. This, combined with EPR experiments showing that the oxidation state of Fe does not change at low temperatures, suggests that a stable intermediate can epoxidize alkenes at low temperature, and this is distinct from the high-valent Fe−oxene species formed at around 40 °C. Nam concluded that this intermediate is an iron hydroperoxide complex ($>$FeOOH).[149,150]

Experiments involving incorporation of labeled water were used to deduce the role of imidazole in the iron porphyrin mediated epoxidation. If imidazole was added to the reaction (at 25 °C), no incorporation of ^{18}O from water was observed. This suggests that imidazole coordinates the open axial position of the complex that water originally occupied, thus preventing a redox-like tautomerization of coordinated water with the juxtaposed oxo-ligand. This tautomerization would otherwise deliver labeled oxygen into the reactive oxene intermediate, leading to partially ^{18}O-labeled epoxides. Thus, imidazole additives can prevent axial coordination of water and simultaneously attenuate the reactivity of the imidazole containing porphyrin in useful ways. In fact, if the reactions are performed in aprotic solvents with a near-optimal imidazole additive (e.g., 5-chloro-1-methylimidazole), even electron-rich porphyrins could be competent catalysts, Table 2.[151]

Competition experiments using different alkenes have been carried out to explore the effects of using protic or aprotic media (Scheme 6).[152] In this study, reactions using either *cis*- and *trans*-stilbene or cyclooctene and *trans*-stilbene were conducted using different oxidants such as H$_2$O$_2$, *m*-CPBA, or *t*-BuOOH in both protic and aprotic media. The ratios of products formed in each epoxidation reaction were compared. If a common intermediate was formed in two or more reactions, it would be expected that similar ratios of products would be observed. In protic solvents, all the oxidants gave the same ratio of products for a given catalyst. However in aprotic solvents, the product ratios were dependent on the

Table 2. Effects of Catalysts Structure and Additives in Epoxidation Reactions Mediated by Iron Porphyrins
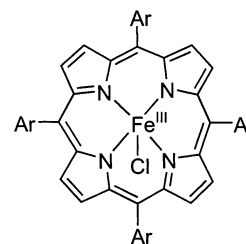
15, 2,4,6-Me$_3$C$_6$H$_3$; **16**, 2,6-Cl$_2$C$_6$H$_3$
17, 2,6-F$_2$C$_6$H$_3$; **18**, C$_6$F$_5$
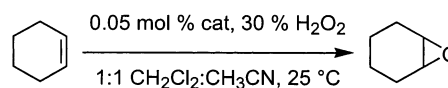
catalyst	yield (%)[a]	yield with additive[b] (%)[a]
15	0	51
16	0	63
17	<2	79
18	<2	65

[a] Yield based on H$_2$O$_2$ used. [b] Additive = 5 mol % 5-chloro-1-methylimidazole.

oxidant. This suggests that the oxidizing species varies in aprotic solvent with the oxidant used. In control experiments, with stoichiometric, preformed high-valent Fe(IV)−porphyrin complexes in aprotic solvents the product ratios were different to any other oxidant used in those aprotic solvents, and similar to ones obtained in protic solvent. It therefore seems that at least two active intermediates are involved, depending on the solvent used. For protic solvents, the reactive intermediate appears to be the high-valent Fe(IV)−porphyrin radical cation complex formed from an iron hydroperoxide precursor (Scheme 6 path **A**), based on the similar product distributions for all the oxidants. In aprotic solvents, Scheme 6

path B, the reactive intermediate is more likely to be the iron hydroperoxide complex itself. Scheme 6 only addresses the case of hydrogen peroxide. Other oxidants in aprotic solvents must give different intermediates, e.g., a *tert*-butyl hydroperoxide iron complex (>Fe-O-O-^{t}Bu, iron^{III}) if t-BuOOH is used as the oxidant. This accounts for the different ratios of products formed under aprotic conditions with different oxidants.

Overall, the story of epoxidations with iron porphyrin catalysts reflects the delicate balance of steps in this type of catalytic cycle and how easily they are perturbed. The data obtained depend on the electronic structure of the porphyrin, additives, and the solvent used and illustrate the fact that several reactive intermediates are accessible, and they each can deliver oxygen to alkene substrates.

5.3. Manganese Salen Complexes

Manganese salen complexes have been investigated in alkene epoxidations with H_2O_2, largely from the perspective of asymmetric catalysis. Berkessel, the first to report them in epoxidations with H_2O_2, noticed that most Mn coordination complexes required additives such as imidazole to generate the requisite Mn-oxo intermediates via heterolytic cleavage of H_2O_2.[153,154] Consequently, his group constructed catalyst **19** containing a tethered imidazole; it was shown to epoxidize 1,2-dihydronaphthalene in 77% yield and 64% ee, Table 3. Unfortunately, better results were obtained using other oxidants, notably sodium hypochlorite, with these catalysts.[155] Concurrently, Katsuki developed conditions relying on an unfunctionalized Mn-salen complex, **20**, and imidazole in solution,[156] and obtained high enantiomeric excess (96%) but low yields (17%).

Pietikäinen began investigating imidazoles as additives in salen mediated epoxidations with hydrogen peroxide[157] but realized that higher yields and *ee's* could be obtained using carboxylates as additives.[158] High enantioselectivities (92%) and yields (86%) were obtained by adding ammonium acetate to Jacobsen's catalysts **21**. Such conditions are reminiscent of the ammonium acetate/Mn-porphyrin system developed by Mansuy, and there are likely to be mechanistic similarities.[136]

Catalyst deactivation is a problem in salen-mediated epoxidations with aqueous hydrogen peroxide, caused by radical formation via homolytic cleavage of the weak O-O peroxide bond. The additives used in the examples above do elevate this to a certain degree; however, an alternative approach uses anhydrous H_2O_2 adducts, such as $Ph_3P(O)\cdot H_2O_2$ (Ph_3P-$(O)\cdot H_2O_2$ = triphenylphosphine oxide/ H_2O_2 complex) can be used to produce peracids in solution with maleic anhydride, thus avoiding this problem.[159] Urea·H_2O_2 complex (UHP) is also viable for epoxidations with salen complexes.[159] It can be used directly as an oxidant with the dimeric catalyst **22** and ammonium acetate as an additive;[160] cyanochromene was epoxidized in nearly 100% yield and enantioselectivity using this approach. However, this system may not be particularly general for other types of alkenes.

Epoxide *ee's* and yields from salen complexes and anhydrous hydrogen peroxide approach those obtained with other oxidants,[155] but removal of urea or triphenylphosphine oxide side-products is an issue. Moreover, quite large mol percentages of salen catalysts are used, typically in chlorinated solvents with additives. Nonetheless, salen complexes are the best catalysts, to date, for asymmetric epoxidation using (anhydrous or aqueous) H_2O_2 as an oxidant.

There are a few reports of Mn-salen mediated epoxidations of alkenes with hydrogen peroxide that do not feature asymmetric syntheses. For example, polymeric, polynuclear Schiff-base Mn complexes **23**, with repeating salen-like cores, were synthesized and characterized in situ.[161] The goal of this work was to test if the polynuclear characteristics of these materials enhance their reactivities, and/or to eliminate the need for additives. However, they proved to be moderate catalysts for the epoxidation of simple alkenes, and additives such as imidazole were required to achieve catalytic activity with H_2O_2. Other Schiff base ligands have been prepared by template-induced macrocyclization/condensation of diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$) with either pentane-2,4-dione or 1,3-diphenyl-propane-1,3-dione. The binuclear manganese-complexes produced in this way were moderately active in epoxidations, giving yields from 9% to 82% for isoprene and limonene when additives (e.g., ammonium acetate) were included.[162]

5.4. 1,4,7-Triazacyclononane (TACN) Complexes

Interest in TACN-derived catalysts for alkene epoxidation with H_2O_2 originates largely from work at Unilever on potential detergent additives to oxidize away organic staining materials.[163-166] Many Mn-TACN ligands have been used to form epoxidation catalysts with H_2O_2. Interestingly, the same ligand can form various dinuclear complexes depending on the synthesis conditions. For example, dinuclear complexes bearing the Me$_3$TACN ligand **24** have either bridging oxo, peroxo, and/or carboxylate centers as shown in Figure 9.[163] The reactions of complexes **25**-**27** are inefficient with respect to conversion of H_2O_2 to epoxide; complex **27** completely epoxidizes styrene, but 100 equiv of 30% H_2O_2 were used. The efficiency was improved by using oxalate buffer,[167] or adding ascorbic and squaric acid.[168] In retrospect it is evident that additives change the reactivities and selectivities of these reactions in unpredictable ways. For example, 0.1 mol % of the complex formed from ligand **24** and manganese(II) sulfate quantitatively epoxidizes 1-hexene in the presence of 0.3 mol % oxalate buffer and 1.5 eq of 30% H_2O_2, but catalyst **27** even oxidizes hydrocarbons when acetic acid is present.[169] Activated carbonyl additives, such as glyoxylic acid methylester methyl hemiacetal ($CH_3OCHOHCO_2CH_3$) and **27**, can result in production of significant amounts of vicinal *cis*-diols in addition to peroxides.[170]

The modified TACN ligands **28**-**31** have been made, but manganese complexes of these have activities comparable to the ones previously mentioned. Ligand **31** was designed to support the TACN core

Table 3. Conditions and Catalysts Used in Manganese Salen-Mediated Epoxidations with Hydrogen Peroxide
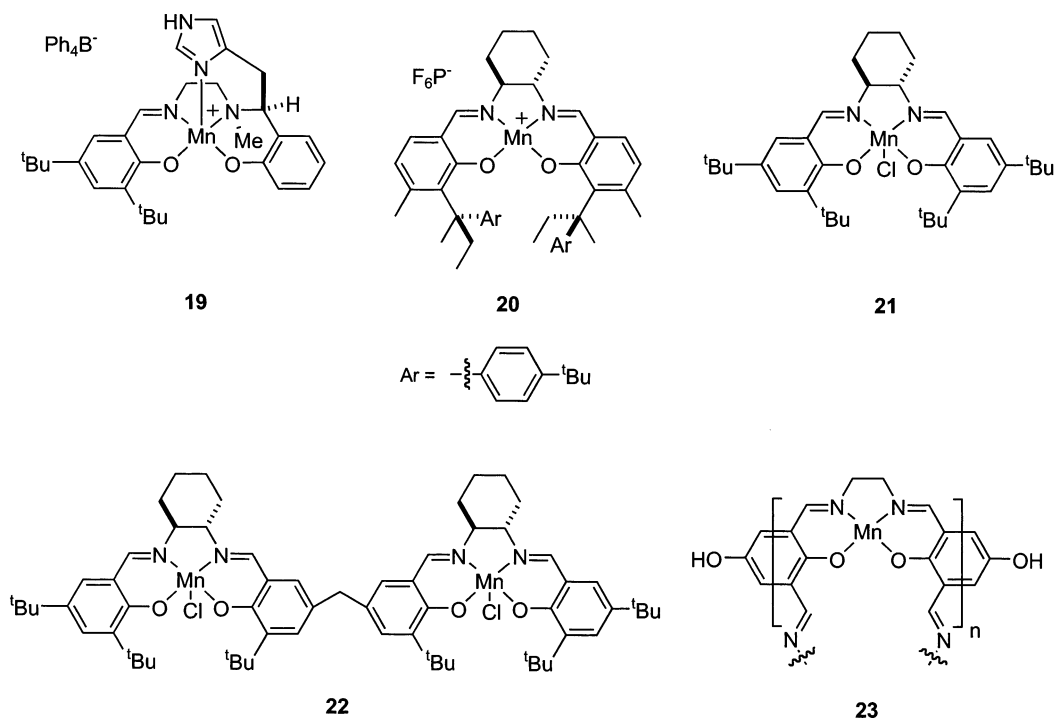
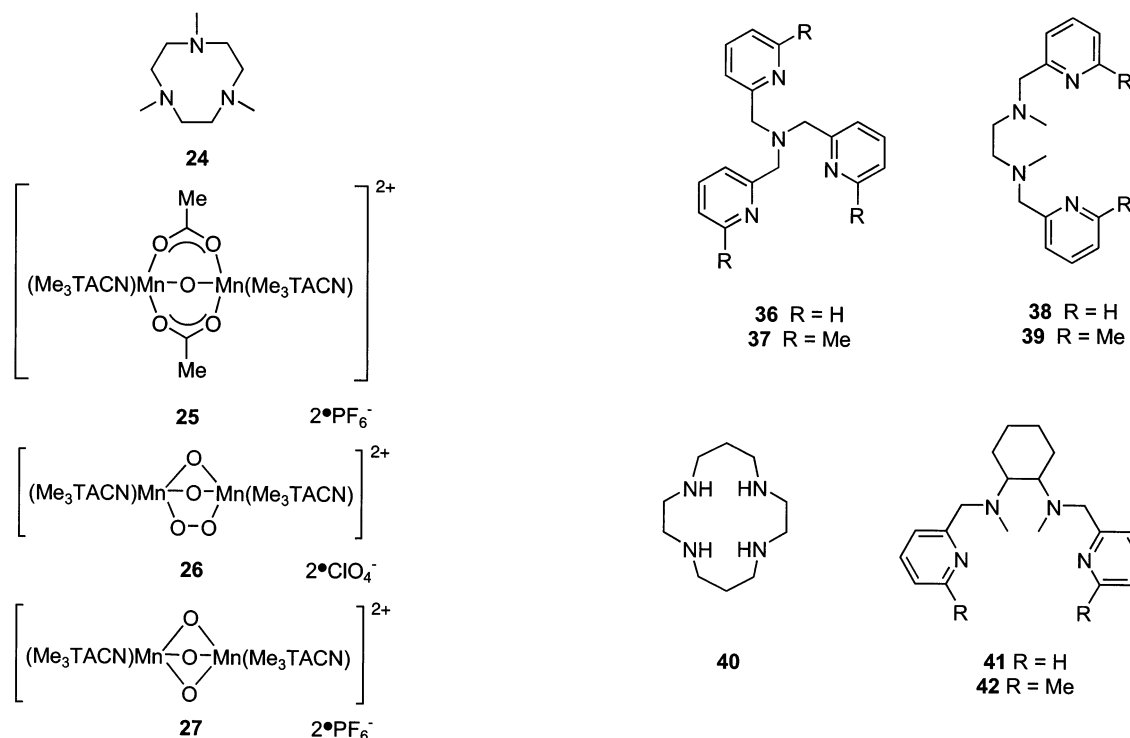| substrate	conditions	yield %	% ee
	10 mol % **19**, 10 eq 30 % H_2O_2 1:1 CH_2Cl_2:H_2O	77	64
	2 mol % **20**, 10 mol % 1-methylimidazole 1 eq 30 % H_2O_2, CH_3CN	17	96
	5 mol % **21**, 20 mol % NH_4OAc 3 eq 30 % H_2O_2, 1:1 CH_2Cl_2:MeOH	86	92
	5 mol % **21**, 2.3 eq NMO 1.5 eq $Ph_3P(O)$•H_2O_2, 2 eq maleic anhydride 4:1 CH_2Cl_2:DMF, -18 °C	73	92
	1 mol % **22**, 8 mol % NH_4OAc 1.2 eq urea•H_2O_2 1:1 CH_2Cl_2:CH_3OH, 2 °C	100	100
	23, imidazole, 30 % H_2O_2 acetone	49	-

Figure 9. Dinuclear complexes that can form with the same Me₃TACN ligand under different conditions.
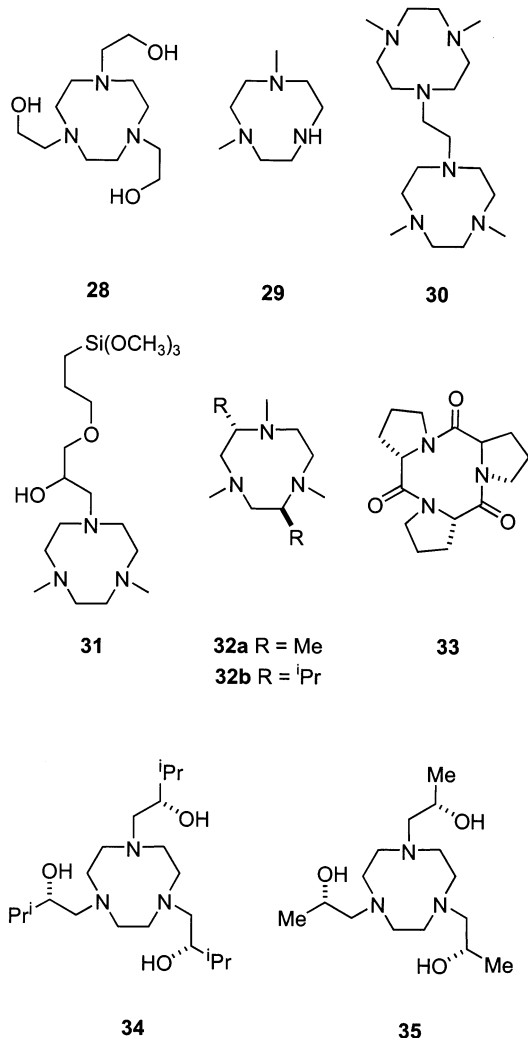

Figure 10. TACN variants used to make epoxidation catalysts that use hydrogen peroxide as a terminal oxidant.
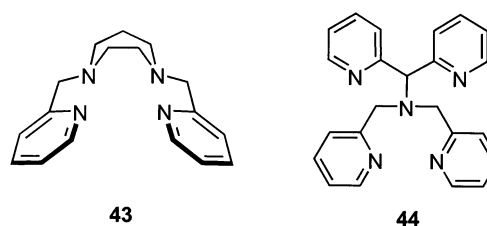

Figure 11. Some ligands used to form nonheme biomimetic catalysts.

on silica for recovery. Attempts to mediate asymmetric epoxidation using the manganese complexes of chiral TACN derivatives, **32**−**35**, and H₂O₂ gave low to moderate enantioselectivities.[171−173]

TACN complexes can be very active for epoxidation, but the ligands are difficult to prepare. Alternative systems that share a similar coordination environment (e.g., polyamine coordinating groups) are therefore very interesting. These are discussed in the next section.

5.5. Iron and Manganese Pyridyl-Amine Complexes

Ligands containing pyridine and amine coordinating groups have been investigated by Que and others, particularly from the perspective of biomimetic, nonheme catalysts, Figure 11.[174−179] Crystallographic studies showed that ligands **36**−**44** with iron form octahedral mono- or dinuclear complexes with bridging carboxylate, oxo, and/or peroxo ligands. Some of these complexes exhibit modest epoxidation and/or dihydroxylation activity with H₂O₂. Mechanistic studies partially explain why some of these catalysts yield epoxides while similar ones produce diols.[180,181] Que and co-workers suggest that the Fe^{III}−OOH intermediate is produced in different spin states according to which ligand is used, and this governs their
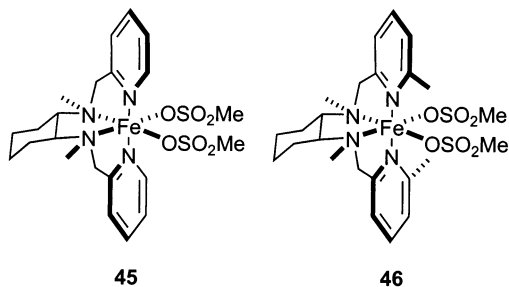
Figure 12. Iron catalysts that give epoxidation and dihydroxylation.

reactivities. They have accumulated evidence that a *cis*-HOFe^V=O is involved in the production of vicinal diols, in contrast to high-valent iron^{IV} oxo radical cation species commonly thought to form with iron porphyrins and H_2O_2, as mentioned previously.

Small changes in the ligand-structure can have startling effects on the reactivity of the complexes in these reactions. For instance, alkenes react with hydrogen peroxide in the presence of Fe complex **45** to produce mostly epoxides, while a similar complex **46** produces vicinal *cis*-diols. These catalysts are easily prepared in optically active form, and the epoxide and diol are produced with high diastereomeric excesses (100%), but low to moderate enantiomeric excess (9−82%).[182,183] These iron catalysts are not synthetically useful because they give very few turnovers. For example, catalyst **45** only gave about seven turnovers, while **46** gave 17. Furthermore, these catalysts are not highly selective for one product; the best selectivity obtained was 1:6 in favor of the epoxide with catalyst **45**. However, they are interesting since they are the first iron complexes to mediate asymmetric dihydroxylation.

Activities of these iron catalysts in epoxidation reactions are also influenced by additives. Jacobsen found addition of acetic acid gave rapid, H_2O_2-efficient epoxidation using complex **47** and the conditions listed in Scheme 7.[184] This methodology works

**Scheme 7. Jacobsen Iron Catalyst System for Epoxidation of Terminal Aliphatic Alkenes with 50 % Hydrogen Peroxide**
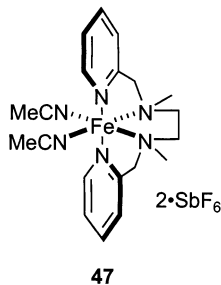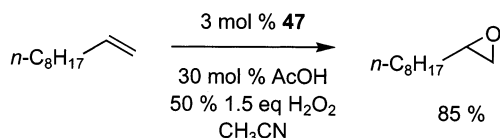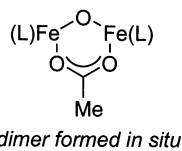
best for aliphatic alkenes, generally considered more difficult substrates. The dinuclear complex **48** shown in Scheme 7 has been implicated as a possible intermediate through crystallographic studies.

Scheme 8. Feringa's Dinuclear Manganese Complex for Epoxidation of Alkenes with 30 % Hydrogen Peroxide
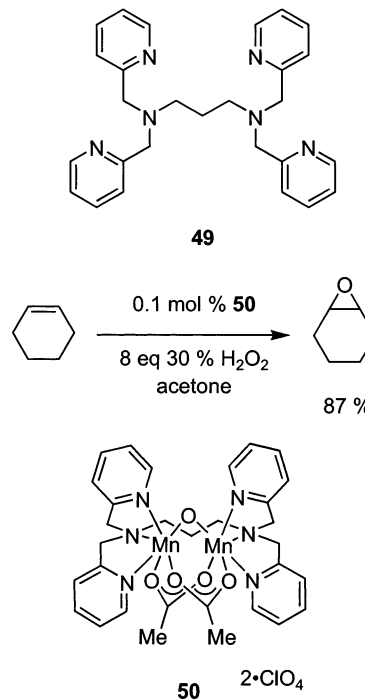
Derivatives of the supported iron complexes mentioned in section 2.2 also have the potential to be developed into asymmetric catalysts, though the enantioselectivites obtained so far have been modest.[43]

Manganese catalysts of pyridyl-amine ligands can also be active in epoxidation. Ligand **49** can be complexed to form a dinuclear complex with oxo and acetate ligands, **50**.[185] This complex is similar to the in situ formed dinuclear-iron complex **48** in structure, but it epoxidizes alkenes with good yields and low catalyst-loadings, Scheme 8.

5.6. Other Coordination Complexes

Some other coordination complexes mediate epoxidation of alkenes by H_2O_2, but not very well. Ruthenium coordination compounds,[186,187] diphosphine platinum(II) complexes,[188] and manganese oxazoline complexes[189] give poor conversions and/or selectivities.

6. Conclusions

Good epoxidation catalysts must activate H_2O_2 without radical production. The key to clean activation seems to be that the O−O bond must be cleaved heterolytically; homolytic cleavage generates free radicals in solution (Fenton-type chemistry), leading to spurious reactions that can degrade the catalyst, and unproductive consumption of the substrate and product (Scheme 9). Traylor's important contributions to the development of iron porphyrin epoxidation catalysts, for instance, stem from his realization that heterolytic cleavage was operative and desirable and should therefore be optimized. Various nonobvious strategies have emerged to facilitate clean

Scheme 9. Cleavage Pathways for the O−O Bond in Hydrogen Peroxide: (a) Homolytic Cleavage Mechanism of Hydrogen Peroxide O−O Bond; (b) Heterolytic Cleavage Mechanism of Hydrogen Peroxide O−O Bond
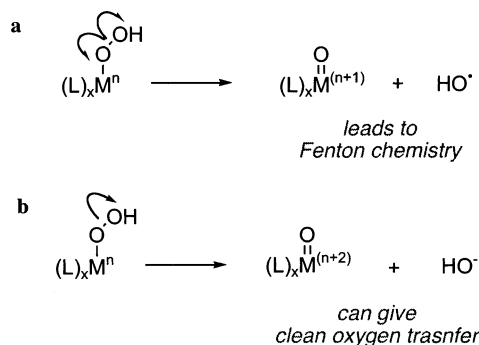
heterolytic activation of hydrogen peroxide. For example, the $MnSO_4$/bicarbonate oxidation system relies on equilibrium between hydrogen carbonate and peroxide to form peroxymonocarbonate, which appears to transfer oxygen to the metal, Scheme 4. Other systems use fluorinated solvents to polarize H_2O_2 through a network of hydrogen bonding, thus activating the O−O bond toward heterolytic cleavage, Figure 5.

Once the activated catalyst−peroxide adduct has been formed, efficient transfer of oxygen to the alkene substrate is important. Oxygen-transfer from a metal can be achieved directly, or in two steps. A good example of a two-step oxygen transfer is in the chemistry of basic hydrotalcite catalysts that first delivers peroxide anion to a nitrile or amide, giving an intermediate that reacts with alkene. Clearly, direct transfer is better with respect to minimization of reaction byproducts. Direct transfer of oxygen from M=O systems to alkenes is further complicated by the fact that more than one mechanism must be operative because some systems are stereospecific for *cis*-epoxide formation while others are not (cf. the $MeReO_3$ and $MnSO_4$/bicarbonate systems).

Often, the physical properties of catalysts are critical for developing epoxidation conditions. Partition coefficients between two solvents, or the solubilities in homogeneous media, can differentiate good from poor epoxidation systems. For example, many ammonium cations had to be tested to find suitable peroxotungstate catalyst in the Venturello systems (Figures 2 and 3). However, solubility effects are not always simply obstacles to be surmounted in catalyst development, they can also be exploited. For instance, Zuwei used insolubility of the reduced catalyst for recovery in his system (Scheme 2).
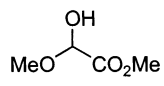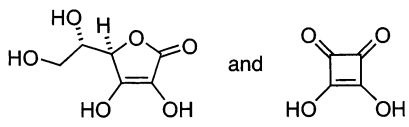
There are other important, but subtle properties of catalysts that must often be optimized to obtain useful reactivities in epoxidation reactions. This is particularly true for coordination complexes where electronic and steric effects of a ligand can have dramatic and unpredictable effects on reactivities. One of the most striking examples of this is for the iron catalysts **42** and **43** where a methyl in the 6-position of the pyridine ring causes a shift from epoxidation to dihydroxylation activity.

Most homogeneous epoxidation systems are greatly enhanced by adding molecules that can coordinate to the reaction mixture. These additives are often tertiary heterocyclic amines (i.e., pyridines, pyrazoles, and imidazoles) or carboxylates (i.e., acetates, benzoates, or glyoxylates). Useful additives favorably change catalytic efficiencies, selectivities, and reactivities and do not complicate isolation of the epoxide products. Epoxidation catalysis by Mn−TACN derivatives illustrates the importance of these extras coordinating groups. Efficiency of epoxidation in that system increases when oxalate buffer is used, and in other cases, the product distributions are additive dependent; Mn−TACNs/acetic acid allows oxidation of hydrocarbons and Mn−TACNs/activated carbonyls favors dihydroxylation in conjunction with epoxidation. Without imidazole derivatives, electron-rich Fe−porphyrins do not produce epoxides at all with H_2O_2. Addition of heterocyclic amines facilitates MTO mediated epoxidation under basic conditions. In general, the most useful epoxidation catalysts based on coordination complexes or soluble metal oxides are always used in conjunction with an additive; Table 4 summarizes some examples of this. Additives facilitate catalyst tuning without re-designing the ligand, and their value may be underappreciated in the field. The process of discovering which additive to use, however, clearly requires trial and error and cannot be predicted reliably; modern high-throughput screening techniques are therefore valuable in this regard.

There is no single method for epoxidations using hydrogen peroxide that is uniformly better than the rest. The best method available depends on desired substrate and reaction scale. Zeolites can be superior for large-scale production of small, stable epoxides; these catalysts are cheap, robust, and easily removed from the products. Methyltrioxorhenium or manganese sulfate systems allow convenient production of racemic, acid-sensitive epoxides using commercially available reagents. Phosphate/tungstic acid systems are more Lewis acidic and require elevated temperatures. Each of these systems has attributes and limitations that are to some extent complementary. The rhenium system gives clean selective reactions, manganese is less toxic and should be less problematic with respect to trace heavy metal contamination in the product, and the tungsten-based epoxidations are older and have therefore been more widely applied. Porphyrin catalysts can be successfully applied to specific cases but are less likely to be used because the catalysts must be prepared first.

There are no satisfactory conditions for certain catalytic epoxidations with hydrogen peroxide. For instance, large-scale epoxidation of a high molecular mass, *cis*-alkene at the late stages of a pharmaceutical synthesis might be very challenging. Heterogeneous catalysts are inappropriate for nonvolatile, high molecular mass alkenes that do not fit in molecular pores, the requirement for stereospecific formation of *cis*-epoxide would rule out several possibilities, and environmental/toxicity issues might well rule out all the remaining alternatives. Such challenging cases are rare, but they can arise.

Table 4. Additives Used for Different Catalysts in Epoxidations with Hydrogen Peroxide

catalyst	additive
Na$_2$WO$_4$·2H$_2$O	NH$_2$CH$_2$PO$_3$H$_2$
	PO$_4$$^{3-}$
	(n-BuO)$_3$P(O)
MeReO$_3$	3-cyanopyridine, pyridine, or pyrazole
HReO$_4$	MePh$_2$As
MnSO$_4$	2-hydroxybenzoic acid
Mn-porphyrin	imidazole, NH$_4$OAc or imidazole and benzoic acid
Fe-porphyrin	
Mn-Salen	imidazole or acetic acid
	oxalic acid, acetic acid
Mn-TACN	
Fe and Mn pyridine based complexes	acetic acid

Nontoxic catalysts that stereospecifically mediate epoxidation of a broad range of alkenes under mild conditions with very efficient use of hydrogen peroxide have yet to be developed. Moreover, there is no good method for asymmetric epoxidation of alkenes using hydrogen peroxide. Manganese−salen catalysts are the best available at this time, but the enantiomeric excesses are never excellent, and they are poor for terminal or *trans*-epoxides. Overall, much work has been done to overcome many of the problems in catalytic epoxidations with hydrogen peroxide, but more needs to be done to solve them all.

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