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Olefin Epoxidation by the Hydrogen Peroxide Adduct of a Novel Non-heme Mangangese(IV) Complex: Demonstration of Oxygen Transfer by Multiple Mechanisms

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Olefin epoxidations are a class of reactions appropriate for the investigation of oxygenation processes in general. Here, we report the catalytic epoxidation of various olefins with a novel, cross-bridged cyclam manganese complex, $Mn(Me_2EBC)Cl_2$ (Me_2EBC is 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane), using hydrogen peroxide as the terminal oxidant, in acetone/water (ratio 4:1) as the solvent medium. Catalytic epoxidation studies with this system have disclosed reactions that proceed by a nonradical pathway other than the expected oxygen-rebound mechanism that is characteristic of high-valent, late-transition-metal catalysts. Direct treatment of olefins with freshly synthesized $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$ ($pK_a = 6.86$) in either neutral or basic solution confirms earlier observations that neither the oxo–Mn^{IV} nor oxo–Mn^{V} species is responsible for olefin epoxidization in this case. Catalytic epoxidation experiments using the ^{18}O labels in an acetone/water ($H_2{}^{18}O$) solvent demonstrate that no ^{18}O from water ($H_2{}^{18}O$) is incorporated into epoxide products even though oxygen exchange was observed between the Mn^{IV} species and $H_2{}^{18}O$, which leads to the conclusion that oxygen transfer does not proceed by the well-known oxygen-rebound mechanism. Experiments using labeled dioxygen, $^{18}O_2$, and hydrogen peroxide, $H_2{}^{18}O_2$, confirm that an oxygen atom is transferred directly from the $H_2{}^{18}O_2$ oxidant to the olefin substrate in the predominant pathway. The hydrogen peroxide adduct of this high-oxidation-state manganese complex, $Mn^{IV}(Me_2EBC)(O)(OOH)^+$, was detected by mass spectra in aqueous solutions prepared from $Mn^{II}(Me_2EBC)Cl_2$ and excess hydrogen peroxide. A Lewis acid pathway, in which oxygen is transferred to the olefin from that adduct, $Mn^{IV}(Me_2EBC)(O)(OOH)^+$, is proposed for epoxidation reactions mediated by this novel, non-heme manganese complex. A minor radical pathway is also apparent in these systems.

Introduction

Understanding the mechanisms of metal-mediated oxygen-transfer processes in nature and in chemical applications is an ongoing challenge.[1] In the preceding two decades, the oxygen-rebound mechanism, which was conceived by Groves,[2] has been accepted as a common mechanism for oxygen-transfer processes in cytochrome P-450 and related biomimetic systems, such as reactions catalyzed by certain coordination compounds of iron, manganese, and chromium. In this mechanism, the critical oxygen atom is first transferred to the metal ion from the oxidant to form a high-oxidation-state metal−oxo species; the same oxygen atom is subsequently transferred to the substrate in alkane oxidation or olefin epoxidation. This perspective has led chemists to expect efficient use of oxidant and high yields in the metal−oxo-mediated epoxidation of olefins.[3,4] Typically, in oxygen-transfer processes catalyzed by manganese complexes, including both heme and non-heme ligands, a pentavalent

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oxo−manganese moiety (e.g., $\mathrm{LMn^{V}{=}O}$[3b,c,5]) has been proposed as the active intermediate for both alkane oxidation and olefin epoxidation. In a few cases, $\mathrm{Mn^{IV}}$−oxo species have also been implicated in oxygen transfer even though the tetravalent manganese species are known to be less reactive than the corresponding $\mathrm{Mn^{V}}$ species.[6] The definitive experiments establishing $\mathrm{Mn^{V}{=}O}$ derivatives as active intermediates in olefin epoxidation included the use of isotopically labeled oxygen, first to confirm oxygen exchange between the manganese−oxo species and labeled aqueous solvent ($\mathrm{H_2{}^{18}O}$) and then to identify the $\mathrm{Mn^{V}{=}O}$ group as the source of the ^{18}O that was subsequently transferred to the olefin, forming the epoxide.[7] Some $\mathrm{Mn^{V}{=}O}$ complexes have been isolated from solution successfully, although those particular compounds are normally not capable of converting olefins to epoxides.[8]

In addition to $\mathrm{LMn^{V}{=}O}$ (where L is a ligand such as a porphyrin or salen) as a common active intermediate for epoxidation, mechanisms requiring other intermediates have been reported under different reaction conditions. In the absence of effective axial ligands, such as imidazoles, the porphyrin complexes of iron and manganese catalyze the homolytic cleavage of the O−O bond in alkyl hydroperoxides to form the alkyoxy radicals and $\mathrm{Fe^{IV}}$ or $\mathrm{Mn^{IV}}$ species. Because of the relative reactivities of these intermediates, a radical process dominates, implicating the radical as the oxidant rather than the high-valent, transition-metal center.[9] It has also been proposed that the alkylperoxy radical, formed in subsequent steps, serves as the active epoxidizing agent in these systems. In another study, the alkylperoxy radical was also proposed as the active intermediate in both hydrogen-abstraction and oxygen-transfer reactions involving radical-chain processes propagated by the combined effects of the metal ion, molecular oxygen, $\mathrm{O_2}$, and an initiator.[10] While the active species are difficult to establish, it has been suggested that, when used as the initiator, an added aldehyde may also serve as a co-oxidant. The complexity is associated with the presence of high-valent metal−oxo or −hydroxo complexes, acyl radicals, acylperoxy radicals, metal−acyl peroxide complexes, and the peracid resulting from hydrogen abstraction by the acylperoxy radical.[11] In the case of *cis*-stilbene epoxidation, the cis/trans ratio of the product, stilbene oxide, was obviously metal ion dependent. *trans*-Stilbene oxide was the main product in each case, supporting the radical mechanism, but the variations in the cis/trans ratio indicated that the roles of various active intermediates differ with the metal ion.

Reactions catalyzed by compounds of early-transition-metal ions in their highest oxidation states, such as $\mathrm{Ti^{IV}}$, $\mathrm{V^{V}}$, $\mathrm{W^{VI}}$, $\mathrm{Mo^{VI}}$, and $\mathrm{Re^{VII}}$, display a distinctly different behavior. The high-valent metal ions are relatively stable toward changes in their oxidation states. Consequently, it has long been recognized that their adducts with hydrogen peroxide or alkyl hydroperoxides are the key intermediates in these epoxidation reactions and that the role of the metal ion is that of a Lewis acid.[12] Recent studies have indicated that certain $\mathrm{Fe^{III}}$ adducts of hydrogen peroxide or an alkyl hydroperoxide also serve as the reactive species in oxygen-transfer processes.[13] Further, recent studies have implicated the iodosylbenzene adduct of a manganese−oxo complex as a new active intermediate in epoxidation reactions.[8e,14] Previous to the studies reported in this $\mathrm{Mn(Me_2EBC)Cl_2}$ catalyst system,[15] there has been no known example of an epoxidation reaction in which a high-valent manganese complex, e.g., $\mathrm{Mn^{IV}}$, has been shown to catalyze epoxidation reactions by the Lewis acid mechanism, i.e., via a $\mathrm{Mn^{IV}}$/

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hydrogen peroxide intermediate, even though a Mn^{II}/alkylperoxo complex was isolated in 1998.[16] Our preliminary data using hydrogen peroxide as the terminal oxidant with this $Mn(Me_2EBC)Cl_2$ catalyst revealed that a high-valent manganese compound catalyzes epoxidation reactions, but not by the familiar manganese redox mechanism.[15] Here, we report our continuing study in detail. Compelling evidence supports the proposal that the manganese/hydrogen peroxide complex plays the key role in this epoxidation reaction. Thus, it is demonstrated that all three of the chemical capabilities of high-valent manganese can lead to the epoxidation of olefins: the redox efficacy of high-valent manganese facilitates oxygen atom transfer to olefins accompanied by two-electron reduction of the manganese (the rebound mechanism); in one-electron processes, high-valent manganese can produce radicals (e.g., alkyoxy and/or alkylperoxy radicals) that produce low yields of epoxides and, now, we show that the Lewis acid character of Mn^{IV} can facilitate oxygen atom transfer from hydrogen peroxide to olefins, forming the corresponding epoxides.

Experimental Section

$Mn^{II}(Me_2EBC)Cl_2$ (+99.9%) was generously supplied by the Procter and Gamble Co. $[Mn^{III}(Me_2EBC)Cl_2]PF_6$ and $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$ were synthesized as reported.[17,18] Reagents containing ^{18}O were purchased from Isotope Services. Other reagents were purchased from Aldrich or Lancaster. Elemental analysis was performed by Quantitative Technologies Inc. Mass spectrometry (MS) spectra were measured by the Analytical Service of the University of Kansas on a VG ZAB HS spectrometer equipped with a xenon gun.

Quantitative Epoxidation of Norbornylene with $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2 \cdot H_2O$. In a typical reaction, 0.3255 g (0.5 mmol) of $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2 \cdot H_2O$ was dissolved in 5 mL of an acetone/water (ratio 4:1) solvent mixture. After 1 mmol of norbornylene was added, the reaction mixture was stirred in a controlled atmosphere wetbox at room temperature for at least 2 days in the absence of oxygen. Quantitative analysis of products was performed using gas chromatography (GC).

Catalytic Epoxidation of Olefins. In a typical reaction, a solution of 50 mM (0.005 mmol) $Mn^{II}(Me_2EBC)Cl_2$ was prepared in 5 mL of acetone/water (ratio 4:1). After 0.2 mL of 2.5 M (0.5 mmol) norbornylene in acetone was added to the solvent mixture containing the catalyst, 1 mL of 50% H_2O_2 was added stepwise (0.2 mL per half hour). The reaction mixture was stirred for an additional 1 h at room temperature. The quantitative analysis of the products was performed using chromatography by the internal standard method, and the identities of the products were confirmed by GC−MS. A parallel experiment without a catalyst was run as a control.

Isotopic Labeling: Epoxidation with $H_2{}^{18}O$. In a typical reaction, 0.019 g (0.005 mmol) of $Mn^{II}(Me_2EBC)Cl_2$ and 0.088 g (0.5 mmol) of *cis*-stilbene in 0.2 mL of acetone were added to 2.5 mL of acetone/water (4:1, ^{18}O, 95 atom %). The reaction was initiated by adding 0.5 mL of 50% H_2O_2 stepwise (0.1 mL per half hour). The reaction mixture was stirred for 1 h after the addition was complete. Product analysis was performed by GC−MS. All determinations were repeated to evaluate reproducibility. A parallel experiment with no isotopic labeling was run as a control.

Isotopic Labeling: Epoxidation under $^{18}O_2$. In a typical reaction, 3 mL of acetone containing 0.014 g (0.00375 mmol) of $Mn^{II}(Me_2EBC)Cl_2$ and 0.1 g (0.554 mmol) of *cis*-stilbene was injected into a 50-mL flask under atmospheric $^{18}O_2$. The reaction was initiated by injecting 1.5 mL of 2% H_2O_2. The reaction mixture was stirred for 3 h. Product analysis was performed by GC−MS. All determinations were repeated to evaluate reproducibility. A parallel experiment with no isotopic labeling was run as a control.

Isotopic Labeling: Epoxidation with $H_2{}^{18}O_2$. In a typical reaction, 0.00475 g (0.00125 mmol) of $Mn^{II}(Me_2EBC)Cl_2$ and 0.044 g (0.25 mmol) of cis-stilbene in 0.05 mL of acetone were added to 1 mL of acetone. The reaction was initiated by adding 0.5 mL of 2% $H_2{}^{18}O_2$ (90% ^{18}O enrichment, used as received; no further calibration because of the expensive sample). The reaction mixture was stirred for 3 h. Product analysis was performed by GC−MS. All determinations were repeated to evaluate reproducibility. A parallel experiment with no isotopic labeling was run as a control.

Results and Discussion

Product Distributions Suggesting Multiple Mechanisms. The Mn^{II} complex of a cross-bridged cyclam ligand, 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane, $Mn^{II}(Me_2EBC)Cl_2$, has been explored extensively as a potential catalyst for selective oxidation reactions, and its novel behavior in epoxidation reactions constitutes a significant example of selectivity.[17−21] Various olefins were catalytically epoxidized with $Mn(Me_2EBC)Cl_2$ as the catalyst, by incremental addition of 50% H_2O_2 as the terminal oxidant, over a period of 3 h, in an acetone/water (ratio 4:1) solution, at room temperature. Substantial yields of epoxide were obtained in each case (Table 1). Epoxidation of cyclohexene provided an 18% yield of cyclohexene oxide and a 13.3% yield of cyclohexen-1-one. With styrene, the yield of oxide was 45.5%, and 2.8% of benzaldehyde was also obtained. Norbonylene provided a 32% yield of norbornylene oxide. Significantly, epoxidation of *cis*-stilbene provided a 17.5% yield of *cis*-stilbene oxide, accompanied by a 2% yield of *trans*-stilbene oxide and a 2.6% yield of benzaldehyde. This result is very similar to that reported for the iron cyclam/

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Table 1. Epoxidation of Various Olefins by $Mn(Me_2EBC)Cl_2$ and H_2O_2 in Acetone/Water Media[a]

substrate	product	yield (%)
cyclohexene	cyclohexene oxide	18.0
	cyclohexen-1-one	13.3
styrene	styrene oxide	45.5
	benzaldehyde	2.8
norbornylene	norbornylene oxide	32.0
cis-stilbene	*cis*-stilbene oxide	17.5
	trans-stilbene oxide	2.0
	benzaldehyde	2.6

[a] Reaction conditions: solvent, acetone/water (4:1); catalyst, 1 mM; olefin, 0.1 M; 50% H_2O_2 (1 mL) added stepwise by 0.2 mL/0.5 h; room temperature; yield determined by GC with an internal standard.

H_2O_2 system in which the HOO^- adduct was proposed as the intermediate for epoxidation.[13b]

In contrast to the results obtained with hydrogen peroxide as the terminal oxidant, epoxidation of cyclohexene using t-BuOOH provided only a minor yield (1.4%) of cyclohexene oxide and a much greater yield (32.3%) of 2-cyclohexen-1-one. Correspondingly, epoxidation of *cis*-stilbene with t-BuOOH provided only a 0.8% yield of *cis*-stilbene oxide, with a higher 13.5% yield of *trans*-stilbene oxide, and a 6.1% yield of benzaldehyde. These results strongly indicate that multiple mechanisms for olefin epoxidation are operative in these hydrogen peroxide and t-BuOOH oxidant systems. The results obtained with t-BuOOH imply a dominant radical process for oxygen transfer, as described in the literature.[10a]

Failure of $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$ To Epoxidize Olefins. Mn^V−oxo species, and to a lesser extent Mn^{IV}−oxo species, are commonly proposed to be the active intermediates for oxygen-transfer processes in reactions mediated by compounds of manganese. Successful synthesis of $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$ provided the opportunity to determine whether that particular manganese−oxo species can epoxidize olefins directly and provide additional insights into the mechanism of catalytic oxidations using hydrogen peroxide. We specifically ask the question, “does this catalytic reaction proceed by the oxygen-rebound mechanism as described in literature for other manganese systems?”[2] $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$ is conveniently synthesized by oxidation of $Mn^{II}(Me_2EBC)Cl_2$ with hydrogen peroxide in the presence of NH_4PF_6 in an aqueous solution, and the structure has been confirmed by X-ray analysis (Figure 1).[18]

Attempts to produce epoxidation reactions between $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$ and various olefins, including norbornylene, styrene, and *cis*-stilbene, were performed in acetone/H_2O (ratio 4:1) at room temperature. However, no direct reaction occurs between these substrates, e.g., norbornylene, and either the Mn^{III} or Mn^{IV} complex in solution, even upon standing for days. The solution retains the purple color of the Mn^{IV} species, the substrate undergoes no conversion, and no epoxide product was detected by GC. Clearly, the Mn^{IV} complex alone is not capable of epoxidation of olefins even though substantial amounts of the compound would be expected to exist as the oxo complex (pK_{a1} value of $[Mn^{IV}(Me_2EBC)(OH)_2]^{2+}$ is 6.86).

Because the Mn^{IV} complex is unstable in base, slowly degrading to $Mn^{III}(Me_2EBC)$,[18] a disproportionation mechanism for decomposition was suspected (eq 1). Such a process could produce the corresponding $Mn^V{=}O$ species, which could be effective at epoxidation of olefins.

$$2Mn^{IV} \leftrightarrow Mn^{III} + Mn^{V} \qquad (1)$$

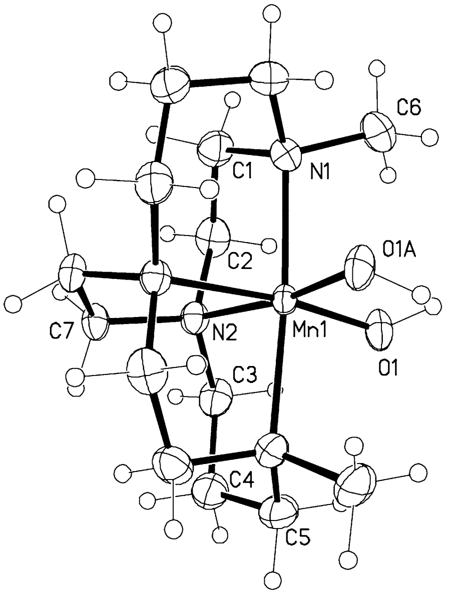

Figure 1. Representation of the crystal structure of the $Mn^{IV}(Me_2EBC)(OH)_2^{2+}$ cation.[18]

As discussed above, Mn^V−oxo[3b,c,5] moieties have frequently been proposed as active intermediates for epoxidation, and while we have shown that $[Mn^{IV}(Me_2EBC)(OH)_2]^{2+}$ does not epoxidize olefins such as norbornylene, the possibility still exists that a Mn^V−oxo derivative, produced by disproportionation in basic media, might reveal its presence by epoxidation of a substrate. One might argue that the presence or absence of Mn^V could be determined by experiments designed to foster epoxidation of, e.g., norbornylene, during disproportionation of Mn^{IV} to a mixture of the trivalent and pentavalent states in basic media. Those experiments were conducted by dissolving the Mn^{IV} complex in base in the presence of norbornylene. In the subsequent analysis of the reactants and products, no epoxide could be detected and no conversion of norbornylene was observed.

Further, when the Mn^{II}, Mn^{III}, or Mn^{IV} complex is treated with various oxidants, such as H_2O_2 and t-BuOOH, in an aqueous solution, no evidence could be found for the existence of Mn^V−oxo species, and $[Mn^{IV}(Me_2EBC)(OH)_2]^{2+}$ has been confirmed to be the dominant species in neutral or acidic solutions by UV−visible spectroscopy. Also, it should be recalled that the synthesis of the Mn^{IV} complex was carried out by oxidation of the Mn^{II} complex using H_2O_2 in an aqueous solution.[18] The presence in the main ligand of π systems that transmit electron density to the Mn^V−oxo moiety, as in the cases of porphyrins and salen ligands, may be necessary to stabilize those Mn^V−oxo species. In that context, it is not surprising that stable Mn^V−oxo derivatives do not exist with these bridged cyclam ligands because their complexes contain only tertiary nitrogen donors and no π-electron systems except those of the two monodentate oxo or hydroxo ligands.

Scheme 1

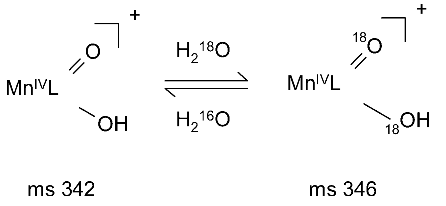

Table 2. Oxygen Source in Epoxide (% ^{18}O) for Epoxdation of *cis*-Stilbene with $Mn^{II}(Me_2EBC)Cl_2$ and Hydrogen Peroxide[a]

run	oxygen source	incorporation of oxygen in *cis*-epoxide (%)	incorporation of oxygen in *trans*-epoxide (%)	note
1[b]	H_2O_2/air/H_2O (blank)	1.7 ± 0.3	2.6 ± 1	^{18}O in epoxide
2[b]	H_2O_2/air/$H_2{}^{18}O$	1.7 ± 0.4	3.8 ± 0.4	^{18}O in epoxide
3[b]	H_2O_2/$^{18}O_2$/H_2O	3.6 ± 0.5	16 ± 3	^{18}O in epoxide
4[c]	$H_2{}^{18}O_2$/air/H_2O	89.9 ± 0.8	72.5 ± 2.4	^{18}O in epoxide

[a] Reaction conditions are described in the Experimental Section. [b] Data for incorporation of oxygen are an average value for three experiments. [c] Data for incorporation of oxygen are an average value of two experiments.

Mechanistic Insights from Isotopic Labeling. Isotopically labeled water, $H_2{}^{18}O$, is used in a well-established protocol to implicate a metal−oxo intermediate in the oxygen-transfer process of, e.g., epoxidation.[7,22] For metal−oxo species that equilibrate with solvent, when ^{18}O labeled oxygen is found in the epoxide product, it is generally concluded that a metal−oxo function performed the oxygen-transfer process. The basis of this conclusion is the usual rapid exchange of ^{18}O between $H_2{}^{18}O$ and metal−oxo groups. In the present work, the exchange of ^{18}O was observed between Mn^{IV}−oxo species containing the cross-bridged cyclam and $H_2{}^{18}O$ (Scheme 1). When $[Mn^{IV}(Me_2EBC)(OH)_2]^{2+}$ was dissolved in $H_2{}^{18}O$ (95% ^{18}O), the original MS peak for $[Mn^{IV}(Me_2EBC)(O)(OH)]^+$ at $m/z = 342$, observed for normal aqueous solutions, disappeared and a new MS peak for $[Mn^{IV}(Me_2EBC)(^{18}O)(^{18}OH)]^+$ appeared immediately at $m/z = 346$. This confirmed the ^{18}O exchange between the bridged cyclam manganese−oxo complex and water. Furthermore, this kind of rapid ^{18}O exchange has also been demonstrated by low-frequency resonance Raman.[18]

The ^{18}O-labeling experiment for the oxygen-transfer reaction used 50% H_2O_2 as the terminal oxidant for epoxidation of *cis*-stilbene in the presence of $[Mn^{II}(Me_2EBC)(OH_2)_2]^{2+}$ in 4:1 acetone/$H_2{}^{18}O$ (95% ^{18}O atom). In the control experiments, 4:1 acetone/normal water (H_2O) was used with unlabeled H_2O_2, open to the air. The product analysis by GC−MS shows that the amount of ^{18}O introduced into the epoxide product from $H_2{}^{18}O$ is identical with that obtained in the control experiments, indicating that the deviation from 100% ^{16}O in the epoxide is within experimental error (1.7 ± 0.4% incorporation of ^{18}O from $H_2{}^{18}O$ vs 1.7 ± 0.3% incorporation of ^{18}O from normal water in *cis*-stilbene oxide and 3.8 ± 0.4% incorporation of ^{18}O from $H_2{}^{18}O$ vs 2.6 ± 1% incorporation of ^{18}O from normal water in *trans*-stilbene oxide; see Table 2).[23] The results of these ^{18}O-labeling experiments strongly support the conclusion that manganese−oxo species, such as $Mn^{IV}(O)(OH)^+$, $Mn^{IV}(O)_2$, and $Mn^V(O)_2{}^+$, are not responsible for the oxygen-transfer process in this manganese-complex-catalyzed reaction. This conclusion is consistent with the results in the preceding section where attempts to produce the epoxide of norbornylene by direct reaction with $[Mn^{IV}(Me_2EBC)(OH)_2]^{2+}$ and with its disproportionation products were described.

As shown above, labeling experiments using $H_2{}^{18}O$ have confirmed the elimination of the oxygen-rebound mechanism in which the tetravalent manganese entity would have transferred an oxygen atom to the olefin while undergoing a two-electron reduction at the metal atom. Experiments with pure $[Mn^{IV}(Me_2EBC)(OH)_2]^{2+}$ had already produced the same conclusion. In contrast to those results, catalytic epoxidation of *cis*-stilbene using hydrogen peroxide with $Mn^{II}(Me_2EBC)Cl_2$ provides *cis*-stilbene oxide as the dominant product (17.5% yield of *cis*-stilbene vs 2.0% yield of *trans*-stilbene oxide; see Table 1) and that dominant *cis*-stilbene oxide could not be the product of a radical reaction, i.e., produced by peroxy radical oxidation. Similarly, the high yield of styrene oxide (45.5%), accompanied by the formation of relatively little benzaldehyde, suggests the action of the same nonradical mechanistic process. The epoxidation of olefins by a peroxoy radical has been demonstrated by He and Bruice[10a] in reactions mediated by Fe^{III}(TMP) using t-BuOOH as the terminal oxidant. The epoxides were derived from the reaction with t-BuOO$^•$ rather than $Fe^{IV}{=}O$ species. For example, epoxidation of *cis*-stilbene provided *trans*-stilbene oxide as the dominant product with only a trace amount of *cis*-stilbene oxide. Indeed, experiments using substituted cyclopropylethene to trap the radical intermediate strongly support t-BuOO$^•$ as the active intermediate for epoxidation in this Fe^{III}(TMP)/t-BuOOH system. Similar results when using t-BuOOH as the terminal oxidant with our manganese catalyst (dominant *trans*-stilbene oxide vs minor *cis*-stilbene oxide, dominant cyclohexen-1-one vs minor cyclohexene epoxide, and dominant benzaldehyde vs minor styrene epoxide) indicate a dominant radical process (vide supra).

The results of epoxidation of cyclohexene using H_2O_2 as the terminal oxidant [greater yield of epoxide (18%) vs cyclohexen-1-one (13%)] support at least two active mechanisms for oxygen transfer, one producing the epoxide and the other proceeding by abstraction of a vulnerable allylic hydrogen. Of course, this pair of oxidation products is commonly observed in the course of cyclohexene epoxidation; however, these results summarized here differ from those found when a radical process is dominant. In the latter case, the main products are produced by hydrogen abstraction, with only a low yield or trace of epoxide.[10c,24] In a

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(22) (a) Nam, W.; Valentine, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 1772. (b) Lee, K. A.; Nam, W. *J. Am. Chem. Soc.* **1997**, *119*, 1916. (c) Chen, K.; Que, L., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 6327.

(23) The ^{18}O signal in a control experiment with normal water is a background signal of MS.

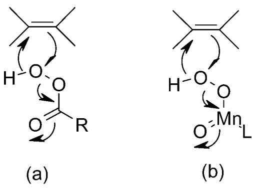
(24) (a) Brill, W. F. *J. Am. Chem. Soc.* **1963**, *85*, 141. (b) Birnbaum, E. R.; Labinger, J. A.; Bercaw, J. E.; Gray, H. B. *Inorg. Chim. Acta* **1998**, *270*, 433. (c) Weiner, H.; Trovarelli, A.; Finke, R. G. *J. Mol. Catal., A* **2003**, *191*, 217.

typical O_2-based reaction dominated by a radical-chain process, cyclohexene oxidation using t-BuOOH as the initiator with a catalyst identified as Mn^{III}_2(2-OHsalphan)$_2$ by Pecoraro et al.,[10c] the cyclohexenylperoxy radical transfers oxygen to cyclohexene to form a low yield of epoxide. Simultaneously, the cyclohexenylperoxy radical, along with other radicals, abstracts hydrogen from cyclohexene to provide the dominant hydrogen-abstraction products. Further, ^{18}O-labeling experiments with $^{18}O_2$ showed that the oxygen source in cyclohexene oxidation products was exclusively $^{18}O_2$, strongly supporting a radical oxidation process.

To further investigate the oxygen source in the present studies, the epoxidation of *cis*-stilbene was performed with 2% H_2O_2 under an atmosphere of $^{18}O_2$ (see Table 2). Table 1 shows that *cis*-stilbene oxide is the dominant product over *trans*-stilbene oxide. The deviation in the ^{16}O content from 100% approximates experimental error (3.6 ± 0.5% vs 1.7 ± 0.3% in the blank), so it is concluded that the cis product derives all of its oxygen from sources other than O_2. This rules out a peroxy radical pathway for the formation of this isomer of the epoxide. The small amount of *trans*-stilbene oxide (∼2%) contained a substantial fraction (16 ± 3%) of oxygen from $^{18}O_2$, implicating the expected radical pathway of the sort described by Pecoraro et al.[10c] The remaining oxygen (84 ± 3%) either may come from a nonradical mechanism or may be the result of the abundance of unlabeled hydrogen peroxide and its involvement in a radical process. The results clearly show that the dominant pathway for epoxidation is not a radical pathway. This conclusion is also consistent with the catalytic results described above.

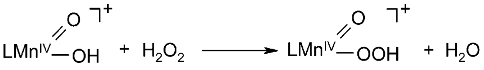
In the complementary experiment in which the label resides on the peroxide, epoxidation of *cis*-stilbene with 2% $H_2{}^{18}O_2$ (90% enrichment of ^{18}O; used as received because of cost) under air provides the corresponding results, in which incorporation of ^{18}O in *cis*-stilbene oxide is 89.9 ± 0.8% while ^{18}O in *trans*-stilbene oxide is 72.5 ± 2.4% (see Table 2). The reproducibility is encouraging, but these experiments use very expensive labeled reactant and were run with small samples so that their accuracy is limited. Even assuming an optimistic ±5%, the observed value would be the same as that using labeled O_2. That is, for labeling experiments with $^{18}O_2$ and $H_2{}^{18}O_2$, the oxygen in *cis*-stilbene oxide comes exclusively from the hydrogen peroxide (95 ± 5%), and that in *trans*-stilbene oxide has two sources, 80 ± 5% from hydrogen peroxide and 20 ± 5% from dioxygen. These results and preceding discussions lead to the conclusion that, in the dominant reaction, *cis*-stilbene is converted to the corresponding epoxide by a nonradical pathway in which the oxygen comes directly from hydrogen peroxide, not via a rebound mechanism involving oxygenation of the manganese atom (recall that the Mn^{IV} complex will not produce the epoxide). However, the manganese atom is a critical element in the mechanism.

Scheme 2



Further, because manganese in this complex is oxidized to the tetravalent state by hydrogen peroxide in media in which that oxidation state is stable (pH < 7), the same species is present whether the manganese is added as Mn^{II}, Mn^{III}, or Mn^{IV}. Unlike certain highly unstable $O{=}Fe^{IV}$ or $O{=}Mn^{V}$ species with very high redox potentials, which can transfer their oxygen atoms directly to olefins by the so-called rebound mechanism, this Mn^{IV} complex is stable in an aqueous solution (pH < 7) with a redox potential too small to transfer oxygen from the $O{=}Mn^{IV}$ moiety directly to olefins.[18] In an example where the $O{=}Mn^{V}$ species is stable in solution and can be isolated, that Mn^{V}−oxo moiety also cannot transfer oxygen to olefin by the oxygen-rebound pathway.[8] It is well-known that high-oxidation-state metal species, such as Re^{VII}, W^{VI}, Mo^{VI}, V^{V}, and even the tetravalent transition-metal species Ti^{IV}, catalyze epoxidations through the formation of complexes that have been called inorganic peracids because they closely resemble the organic peracids in their epoxidation reactions. Consequently, we conclude that a parallel pathway is to be expected for Mn^{IV} and that the reaction we have described here is a prototypical example of such an epoxidation.[25]

Although hydrogen peroxide is a relatively weak electrophile, substitution of hydrogen by an electron-withdrawing carbonyl group (formation of organic peracid) or high valent metal ion (formation of inorganic peracid) polarizes the hydrogen peroxide molecule greatly, making it more electrophilic, and this facilitates its oxygen transfer by a two-electron oxygen-atom-transfer process (heterolysis). Typically, for this Mn^{IV} complex, $LMn^{IV}(O)(OH)^+$ first reacts with H_2O_2 to form a "permanganic acid", $LMn^{IV}(O)(OOH)^+$, by ligand exchange (eq 2). The high charge of Mn^{IV} polarizes



$$\left[LMn^{IV}(=O)-OH\right]^{+} + H_2O_2 \longrightarrow \left[LMn^{IV}(=O)-OOH\right]^{+} + H_2O \qquad (2)$$

the O−O bond, making the protonated distal oxygen susceptible to nucleophilic attack (epoxidation of olefin). Similar mechanisms probably pertain to the epoxidation of olefins by organic and permanganic peracids via transition states a and b, respectively (Scheme 2).

To capture the inorganic peracid that is the expected main reactive intermediate for the epoxidation reaction described here, $LMn^{IV}(O)(OOH)^+$, the MS spectrum was determined for solutions in which $[Mn^{II}(Me_2EBC)(OH_2)_2]^{2+}$ was added to catalyze the epoxidation reaction by hydrogen peroxide. Indeed, the MS spectra of such solutions show the presence of the HO_2^- complex, $[Mn^{IV}(Me_2EBC)(O)(OOH)]^+$, as a prominent species in these catalytic systems (Figure 2). A moderate MS peak at $m/z = 358$ appears and is attributed to $[Mn^{IV}(Me_2EBC)(O)(OOH)]^+$; furthermore, accurate MS mea-

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(25) (a) Dryuk, V. G. *Tetrahedron* **1976**, *32*, 2855. (b) Kim, C.; Traylor, T. G.; Perrin, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 9513. (c) Sheldon, R. A., Kochi, J. K., Eds. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; p 48. (d) Deubel, D. V.; Frenking, G.; Gisdakis, P.; Herrmann, W. A.; Rösch, N.; Sundermeyer, J. *Acc. Chem. Res.* **2004**, *37*, 645.

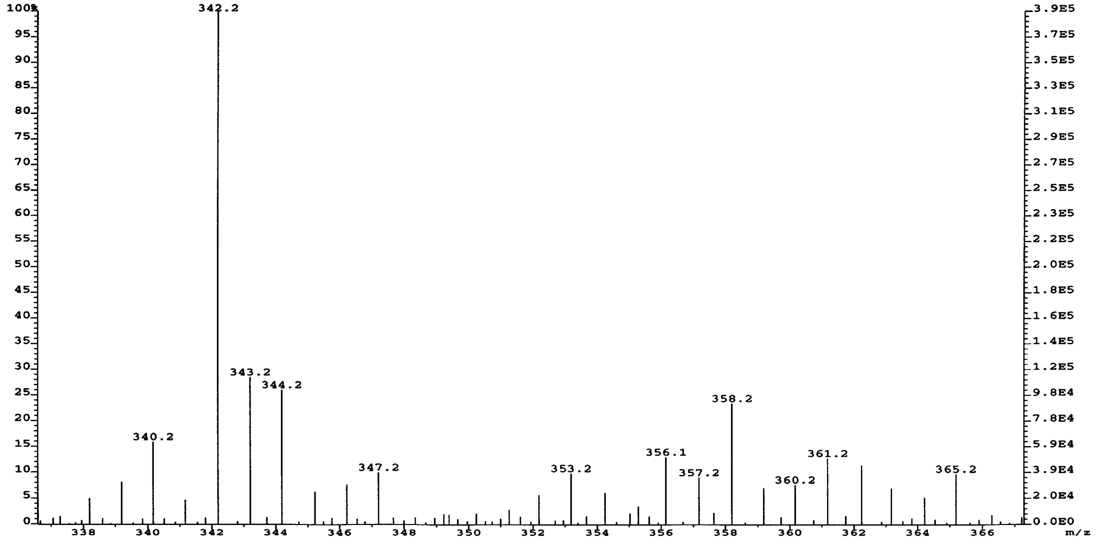
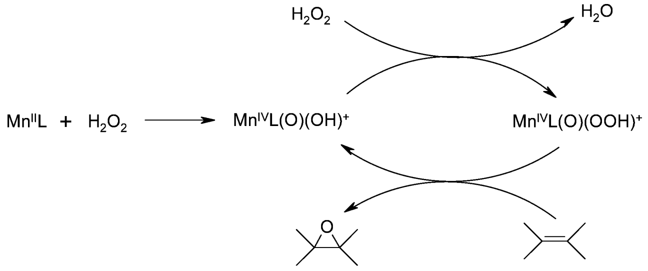


Figure 2. Electrospray ionization MS spectrum identifying $Mn^{IV}(Me_2EBC)(O)(OOH)^+$ at *m/z* = 358 (acetone solution containing aqueous H_2O_2).

Scheme 3. Summarizes This Rational Mechanism for Olefin Epoxidation by Solutions Prepared from $Mn^{II}(Me_2EBC)Cl_2$ and H_2O_2



surement proves that this MS peak corresponds precisely to $[Mn^{IV}(Me_2EBC)(O)(OOH)]^+$ (M^+ calcd, 358.1777; found, 358.1761). It follows that the only viable model to explain the dominant catalytic process in these systems is the inorganic peracid pathway (or the Lewis acid pathway) in which an oxygen atom is transferred directly from the hydroperoxide complex of Mn^{IV} to the olefinic double bond (Scheme 3). To our knowledge, prior to the studies on this catalyst system, there has been no experimentally detectable hydroperoxide adduct of the manganese complex reported even though it has been generally proposed to be the transient intermediate in the oxygen evolution process and other chemical and biological processes.[26] Recently, a series of publications have provided evidence to support the proposed presence of hydroperoxide or alkyl peroxide adducts of iron complexes as the active intermediates for hydroxylation of alkanes and epoxidation of olefins.[13] In retrospect, one should expect the hydroperoxide adduct of Mn^{IV} to exist in the reaction solution and serve as an active intermediate for epoxidation in this and other manganese systems in which the Mn^{IV}/Mn^{III} couple has a modest potential, because the Mn^{IV} ion is reminiscent of Ti^{IV} from among the early transition metals, Ti, V, W, Mo, and Re, which are well-known to form Lewis acid catalysts.

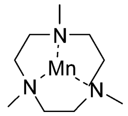


Figure 3. Structure of the Mn(TMTACN) moiety.

As discussed above, the dominant pathway for epoxidation using H_2O_2 as the terminal oxidant proceeds via the hydrogen peroxide adduct of Mn^{IV}, whereas a radical process predominates in the epoxidation reaction using t-BuOOH as the terminal oxidant. This mechanistic contrast can be rationalized on the basis of the physical chemistry parameters of the O−O bonds in these two oxidants. The bond dissociation energy of the O−O bond in H_2O_2 is 213.8 kJ/mol, which is 21.8 kJ/mol higher than that of the O−O bond in t-BuOOH (192 kJ/mol).[27] Further, the activation energy for thermal cleavage of the O−O bond in H_2O_2 is also higher than that in t-BuOOH (48 vs 42 kcal/mol).[28] This difference in proclivity to undergo O−O bond cleavage appears to carry over to the metal complexes of t-BuOOH and H_2O_2.

Mn(TMTACN) (Figure 3) catalysts containing three tertiary nitrogen donors and no π-electron system bear a substantial similarity to our catalyst, which contains four tertiary nitrogen donors and no π-electron system. It has been reported that only oxygen from the terminal oxidant is incorporated in the epoxide when using $H_2{}^{18}O_2$ with this catalyst.[29] We suspect an epoxidation mechanism similar to that reported here in which a manganese(IV) hydroperoxide species serves as the active intermediate. Because $[O{=}Mn^V(TMTACN)(biphenol)]^+$ has been detected by MS, an $O{=}Mn^V(TMTACN)^+$ species was proposed as the active

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(26) (a) Dubé, C. E.; Wright, D. W.; Armstrong, W. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2169. (b) Riley, D. P.; Lennon, P. J.; Neumann, W. L.; Weiss, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 6522. (c) Shul'pin, G. B.; Nizova, G. V.; Kozlov, Y. N.; Pechenkina, I. G. *New J. Chem.* **2002**, *26*, 1238. (d) Ashur, I.; Brandis, A.; Greenwald, M.; Vakrat-Haglili, Y.; Rosenbach-Belkin, V.; Scheer, H.; Scherz, A. *J. Am. Chem. Soc.* **2003**, *125*, 8852. (e) Jackson, T. A.; Karapetian, A.; Miller, A.; Brunold, T. C. *Biochemistry* **2005**, *44*, 1504.

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(28) Sheldon, R. A.; Kochi, J. K. *Metal-catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981; p 20.

(29) Hage, R.; Iburg, J. E.; Kerschner, J.; Koek, J. H.; Lempers, E. L. M.; Martens, R. J.; Racherla, U. S.; Russell, S. W.; Swarthoff, T.; van Tliet, M. R. P.; Warnaar, J. B.; van der Wolf, L.; Krijnen, B. *Nature* **1994**, *369*, 637. (b) Gilbert, B. C.; Smith, J. R. L.; Payeras, A. M.; Oakes, J.; Prats, R. P. *J. Mol. Catal., A* **2004**, *219*, 265.

intermediate for epoxidation even though [O═Mn^{V}(TMTACN)]$^{+}$ could not be detected by MS.[29b] The occurrence of pentavalent manganese in O═Mn^{V}(TMTACN)(biphenol)$^{+}$ can be rationalized because the biphenolic ligand is a strong electron donor, which makes the electron density in the combined ligand system resemble the well-known salen ligand whose Mn^{V} complex O═Mn^{V}(salen) has often been proposed as the active intermediate for epoxidation.[4c,30]

In summary, compelling evidence from experiments using $H_2{}^{18}O$, $^{18}O_2$, and $H_2{}^{18}O_2$ establishes a hydrogen peroxide adduct of the Mn^{IV} complex as the dominant active intermediates for oxygen transfer to olefins, using H_2O_2 as the terminal oxidant with Mn(Me$_2$EBC)Cl$_2$ as the catalyst. The high charge of Mn^{IV} polarizes the O−O bond greatly, facilitating oxygen transfer directly to the olefin by heterolysis of the O−O bond. This stands in contrast to the usual expectation that such epoxidations occur by an oxygen-rebound process, in which the oxidation state of the manganese changes by two units. Further, this example clearly shows that high-valent manganese complexes can oxygenate by two mechanisms because a radical process is also supported by this catalyst. These results provide a new insight into the roles manganese can play in oxygenation processes in the laboratory, industry, and nature.

Acknowledgment. Support by the Procter and Gamble Co. is deeply appreciated, and we also thank the National Science Foundation Engineering Research Center (Grant EEC-0310689) for partial support. At The University of Kansas, MS measurements were performed by R. C. Drake.

Supporting Information Available: Properties of H_2O_2 in acetone and GC−MS graphs for the epoxidation of olefins under various reaction conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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