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Proton-Promoted and Anion-Enhanced Epoxidation of Olefins by Hydrogen Peroxide in the Presence of Nonheme Manganese Catalysts

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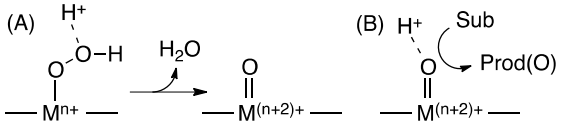
ABSTRACT: We report a remarkable Brønsted acid effect in the epoxidation of olefins by nonheme manganese catalysts and aqueous hydrogen peroxide. More specifically, a mononuclear nonheme manganese complex bearing a tetradentate N4 ligand, Mn^{II}(Dbp-MCP)$(OTf)_2$ (Dbp-MCP = (1*R*,2*R*)-*N*,*N*-dimethyl-*N*,*N*-bis((*R*)-(3,5-di-*tert*-butyl-phenyl)-2-pyridinylmethyl)cyclohexane-1,2-diamine; $OTf^- = CF_3SO_3^-$), is a highly efficient catalyst in the epoxidation of olefins by aqueous H_2O_2 in the presence of H_2SO_4 (1 – 3 mol%). The yields of epoxide products as well as the chemo- and enantioselectivities increase dramatically in the presence of H_2SO_4; no formation of epoxides is observed in the absence of H_2SO_4. In addition, the product yields and enantioselectivities are dependent significantly on the manganese catalysts and Brønsted acids. The catalytic epoxidation of olefins by other oxidants, such as peracids, alkyl hydroperoxides, and iodosylbenzene, is also affected by the presence of H_2SO_4; product yields and enantioselectivities are high and similar irrespective of the oxidants in the presence of H_2SO_4, suggesting that a common epoxidizing intermediate is generated in the reactions of $[Mn^{II}(Dbp\text{-}MCP)]^{2+}$ and the oxidants. Mechanistic studies, performed with ^{18}O-labeled water ($H_2{}^{18}O$) and cumyl hydroperoxide, reveal that a high-valent manganese-oxo species is formed as an epoxidizing intermediate via O-O bond heterolysis of Mn-OOH(R) species. The role of H_2SO_4 is proposed to facilitate the formation of a high-valent Mn-oxo species and to increase the oxidizing power and enantioselectivity of the Mn-oxo oxidant in olefin epoxidation reactions. Density functional theory (DFT) calculations support experimental results such as the formation of a Mn(V)-oxo species as an epoxidizing intermediate.

INTRODUCTION

Development of highly efficient and selective oxidation reactions under mild conditions is of current interest in the communities of synthetic organic, oxidation, and bioinorganic/biomimetic chemistry. In particular, catalytic (asymmetric) epoxidation reactions using earth-abundant transition metals (e.g., Fe and Mn) and environmentally benign oxidants (e.g., H_2O_2) have been attracted much attention recently to develop oxidation methods with low cost and low toxicity considerations, since epoxides are highly useful building blocks for a number of subsequent transformations in organic synthesis.[1,2] In this context, bioinspired catalytic olefin epoxidation reactions utilizing nonheme iron and manganese complexes bearing polydentate *N*-donor ligands as catalysts and aqueous H_2O_2 as a terminal oxidant have been intensively investigated recently.[2] As a result, a number of highly efficient catalytic epoxidation reactions using the biomimetic nonheme iron and manganese catalysts and aqueous H_2O_2 oxidant have been reported;[3-8] a common feature in these reactions is the use of carboxylic acids as additives to improve the catalytic activity and stereo- and enantioselectivities. More recently, Costas and co-workers reported a highly enantioselective epoxidation of α-substituted styrenes by a nonheme iron complex and H_2O_2 in the presence of *N*-protected amino acids.[9] Although the role(s) of the carboxylic acids in the nonheme metal complex-catalyzed epoxidation reactions by H_2O_2 has yet to be understood, it has been proposed that protonation of the hydroperoxide ligand by the coordinated carboxylic acid in metal-hydroperoxo intermediates facilitates the O-O bond cleavage, generating high-valent metal-oxo species as reactive epoxidizing intermediates.[7] Indeed, involvement of the high-valent metal-oxo intermediates in the catalytic epoxidation reactions has been supported experimentally and theoretically.[7c,8h,10]

In biomimetic studies, it has been shown that the O-O bond activation of metal-hydroperoxo species is affected markedly by the protonation of the hydroperoxide ligand (Scheme 1A), resulting in the generation of highly reactive metal-oxo species as active oxidants in oxidation reactions.[11] Further, it has been demonstrated recently that the reactivity of metal-oxo complexes in oxidation reactions increased significantly by binding of Lewis and Brønsted acids (Scheme 1B), resulting from the change of the reduction potentials and oxidizing

power of the metal-oxo complexes.[12,13] The effects of Lewis and Brønsted acids have also been demonstrated in catalytic oxidation reactions.[14] Thus, we have envisioned that protons play important roles *not only* in the formation of metal-oxo species via the O-O bond cleavage of metal-hydroperoxo species *but also* in the increase of the reactivity of the metal-oxo species in the olefin epoxidation reactions by nonheme metal catalysts and H_2O_2 (Scheme 1).



Scheme 1. Proton effects on (A) the hydroperoxide O-O bond cleavage and (B) the reactivity of metal-oxo species.

As alluded above, understanding the effects of protons on the catalytic oxidation reactions by nonheme metal catalysts and H_2O_2 and the reactivity of nonheme metal-oxo complexes in oxidation reactions is of importance in developing efficient catalytic systems.[2,12] We therefore attempted the epoxidation of olefins by aqueous H_2O_2 catalyzed by mononuclear nonheme manganese complexes in the presence of Brønsted acids. Herein, we report for the first time that the epoxidation of olefins by mononuclear nonheme manganese complexes and aqueous H_2O_2 is affected dramatically by the presence of a catalytic amount of sulfuric acid; the yields of epoxide products as well as the chemo- and enantioselectivities are very high in the presence of H_2SO_4, whereas no formation of epoxides is observed in the absence of H_2SO_4. We also show that both the proton and anions of Brønsted acids play key roles in determining the catalytic activity and chemo- and enantioselectivities of the manganese catalysts in the olefin epoxidation reactions. Detailed mechanistic aspects, such as the nature of the epoxidizing intermediate and the O-O bond cleavage mechanism, are discussed as well.

RESULTS AND DISCUSSION

Synthesis and Characterization of Mn^{II}(Dbp-MCP)$(OTf)_2$ (1). A linear tetradentate N4 ligand, (1*R*,2*R*)-*N*,*N*′-dimethyl-*N*,*N*′-bis((*R*)-(3,5-di-*tert*-butyl-phenyl)-2-pyridinylmethyl)cyclohexane-1,2-diamine (Dbp-MCP; see Experimental Section and Figure S1 in Supporting Information (SI) for NMR spectra), was prepared by introducing a 3,5-di-*tert*-butylbenzene group into the 2-pyridinylmethyl positions of (*R*,*R*)-MCP (MCP = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridinylmethyl)cyclohexane-1,2-diamine), and the Mn^{II}(Dbp-MCP)$(OTf)_2$ complex (**1**, see Figure 1A) was synthesized by reacting equimolar amounts of Dbp-MCP and $Mn(OTf)_2$ (OTf^- = $CF_3SO_3^-$) under an Ar atmosphere in CH_3CN (see Experimental Section and Figure S2 in SI for detailed experimental procedures).[5a] The X-ray crystal structure reveals that the Dbp-MCP ligand adopts a *cis*-α topology coordinating a Mn atom (Figure 1A; Tables S1 and S2 in SI for crystallographic data).[15,16]

Catalytic Activities of Manganese(II) Complexes (1 – 4) in the Epoxidation of Olefins. The manganese complex **1** was tested as a catalyst in the epoxidation of cyclooctene by aqueous H_2O_2 in the absence and presence of Brønsted acids. First, when the reaction was

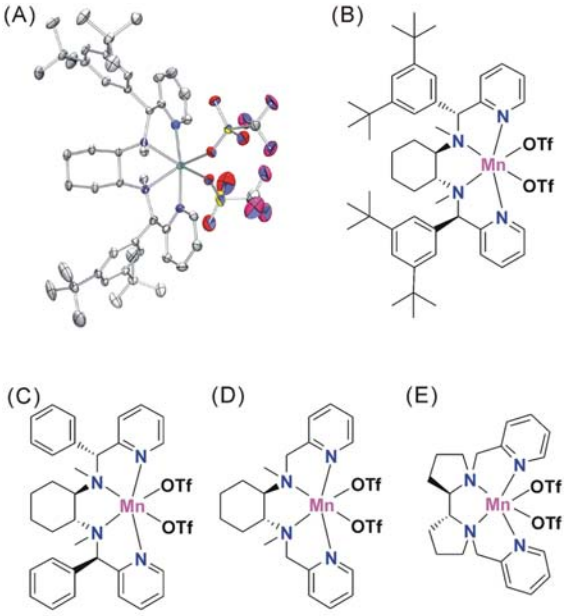
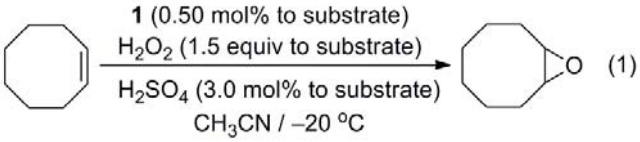


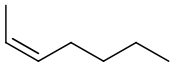
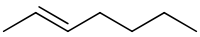
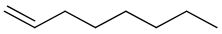
Figure 1. (A) ORTEP-III diagram of **1** (CCDC-917216), showing the 20% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity (see Tables S1 and S2 in SI for crystallographic data). Atom colors are aquamarine for Mn, blue for N, red for O, gray for C, yellow for S, and pink for F. (B – E) Schematic structures of (B) Mn^{II}(Dbp-MCP)$(OTf)_2$ (**1**), (C) Mn^{II}(P-MCP)$(OTf)_2$ (**2**, P-MCP = *N*,*N*′-dimethyl-*N*,*N*′-bis-(phenyl-2-pyridinylmethyl)cyclohexane-1,2-diamine), (D) Mn^{II}(MCP)$(OTf)_2$ (**3**), and (E) Mn^{II}(PDP)$(OTf)_2$ (**4**, PDP = *N*,*N*′-bis(2-pyridinylmethyl)-2,2'-bipyrrolidine)).

carried out in the absence of Brønsted acids, no epoxide formation was observed (Table 1, entry 1). Interestingly, when the identical reaction was carried out in the presence of a small amount of H_2SO_4 (i.e., 6 equiv to **1**) (eq 1), we observed the formation of cyclooctene oxide with a



high yield (Table 1, entry 2). This result indicates that the H_2SO_4 additive plays an important role in generating an efficient epoxidizing species in the reaction of **1** and H_2O_2 (vide infra). We also found that the product yields obtained in the olefin epoxidation were dependent on the Brønsted acids added, such as H_3PO_4, $HClO_4$, CF_3SO_3H, HCl, and acetic acid (Table 1, entries 3 – 7), indicating that the anion of Brønsted acids is an important factor that controls the catalytic activity of **1**. It is noteworthy that the epoxidation reaction using acetic acid (e.g., carboxylic acid) afforded only a small amount of epoxide product (Table 1, entry 7).[3-8] In addition, no epoxidation occurred when an inorganic salt containing SO_4^{2-} (e.g., Na_2SO_4) was used instead of H_2SO_4 (Table 1, entry 8). However, a significant amount of epoxide product (73%) was obtained in the reaction using $NaHSO_4$ as an additive (Table 1, entry 9). The latter results further demonstrate that proton is an essential component for the catalytic epoxidation reaction by **1** and H_2O_2.

Table 1. Catalytic epoxidation of olefins by **1** and H_2O_2 in the presence of H_2SO_4 or under other reaction conditions[a]

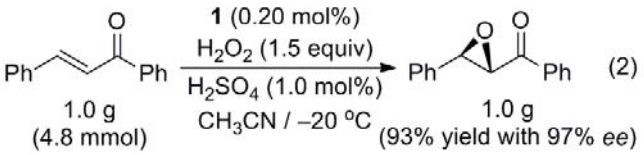
entry	substrate	additive	yield (%)[b,c]
1		none	NR
2		H_2SO_4	91(3)
3		H_3PO_4	Trace
4		$HClO_4$	17(3)
5		CF_3SO_3H	30(4)
6		HCl	NR
7		AcOH	8(2)
8		Na_2SO_4	NR
9		$NaHSO_4$	73(3)
10		H_2SO_4	87(3)
11		H_2SO_4	92(4)
12		H_2SO_4	90(2)
13		H_2SO_4	45(4)
14		H_2SO_4	90(3)

[a] Reaction conditions: olefin (0.25 mmol), catalyst (**1**, 0.50 mol%), and additive (3.0 mol%) in CH_3CN (1.0 mL) were added into a Schlenk tube at –20 °C. Then, 50% H_2O_2 (1.5 equiv) in CH_3CN (0.50 mL) was added to the reaction solution over a period of 1 h using a syringe pump. [b] Yields were obtained by GC analysis using decane or nitrobenzene as an internal standard. NR stands for no reaction. [c] Product yields are based on the amounts of substrate used.

We also examined the catalyst effect in the olefin epoxidation reactions. When the epoxidation of cyclooctene by H_2O_2 was carried out using simple Mn salts (e.g., $MnSO_4$ or $Mn(OTf)_2$) in the absence and presence of H_2SO_4, no formation of epoxide was observed (Table S3 in SI, entries 1 – 4). Then, to investigate the structural effect of manganese catalysts, the epoxidation of cyclooctene by H_2O_2 was carried out using several manganese catalysts in the presence of H_2SO_4 (**2** – **4**; see Figure 1). In these reactions, the yields of cyclooctene oxide were 76% for **2**, 37% for **3**, and 11% for **4** (Table S3 in SI, entries 5 – 7); the product yields are much lower than that obtained in the reaction with **1** as a catalyst. These results indicate that the structure of the manganese catalysts is another important factor that determines the efficiency of the olefin epoxidation by H_2O_2. Taken together, **1** is a highly efficient catalyst in the epoxidation of olefins by aqueous H_2O_2, and the efficiency of the olefin epoxidation by the Mn catalyst and H_2O_2 is determined by the presence of both proton and SO_4^{2-} anion (i.e., H_2SO_4) and the structure of the Mn catalysts.

The catalytic activity of **1** was then examined in the epoxidation of other olefins, such as cyclic olefins (e.g., cyclohexene), *cis*- and *trans*-olefins, and terminal olefin (Table 1, entries 10 – 14). In the epoxidation of cyclohexene, cyclohexene oxide was the sole product with no formation of allylic oxidation products, such as cyclohexenol and cyclohexenone (Table 1, entry 10), suggesting that no autooxidation is involved in the epoxidation of olefins by **1** and H_2O_2 in the presence of H_2SO_4. In the epoxidation of cycloheptene, cycloheptene oxide was yielded as the sole product (Table 1, entry 11). We also found that the olefin epoxidation by **1** and H_2O_2 was highly stereospecific; *cis*- and *trans*-2-heptenes were oxidized to their corresponding *cis*- and *trans*-2-heptene oxides, respectively, and no epimerized products were detected in these reactions (Table 1, entries 12 and 13); it is notable that the product yield in the *trans*-2-heptene epoxidation was lower than that in the *cis*-2-heptene epoxidation. Finally, 1-octene, which is a less reactive terminal olefin,[17] was also oxidized to the corresponding epoxide with a high yield (Table 1, entry 14). The results described above demonstrate that a highly reactive and stereoselective epoxidizing intermediate is generated in the reaction of **1** and H_2O_2 in the presence of H_2SO_4.

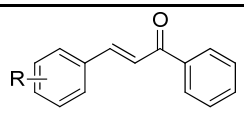
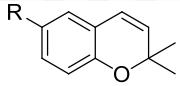
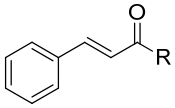
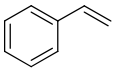
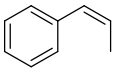
Asymmetric Epoxidation by 1. Since **1** is a chiral complex, this manganese catalyst was examined in the asymmetric epoxidation of olefins by H_2O_2 in the presence of H_2SO_4. As the results are shown in Table 2, the epoxidation of chalcone derivatives by **1** (0.20 mol%) and H_2O_2 (1.5 equiv to substrate) in the presence of H_2SO_4 (5 equiv to **1**) afforded high yields of epoxide products with excellent enantioselectivities (>97% enantiomeric excess (*ee*) values; Table 2, entries 1, 3 and 4; see also Figure S3 in SI). In the case of a chalcone derivative with an electron-donating substituent (e.g., *p*-Me), a moderate yield of epoxide product with an 86% *ee* value was obtained (Table 2, entry 5). Interestingly, in a gram scale reaction (eq 2), we



(2)

obtained a similar product yield (93%) with an excellent enantioselectivity (97%), indicating that the present epoxidation protocol can be adapted for large scale applications. **2** (see Figure 1C), which is an analogue of **1**, also provided an excellent *ee* value (95%), but the product yield was lower than that obtained in the reaction with **1** (Table 2, entry 2). Similarly, **3** and **4** afforded low product yields but with high *ee* values (e.g., ~90%) were obtained under the optimized reaction conditions, respectively (Table S4, entries 13 and 14). When H_2SO_4 was omitted or replaced by other Brønsted acids, such as H_3PO_4, $HClO_4$ and CF_3SO_3H, in the epoxidation of chalcone, the product yields and *ee* values were much lower (e.g., <50%) than those obtained with H_2SO_4 (Table S4 in SI), demonstrating again that the SO_4^{2-} anion is a vital component determining the enantioselectivity of the Mn catalyst as well as the catalytic activity.

Table 2. Asymmetric epoxidation of olefins by **1** and H_2O_2 in the presence of H_2SO_4[a]

entry	substrate	yield (%)	*ee* (%)
			
1	R = H	94(3)	97(2)
2[b]	R = H	57(2)	95(2)
3	R = *o*-Cl	89(4)	98(2)
4	R = *m*-Cl	90(3)	98(2)
5	R = *p*-Me	61(3)	86(3)
			
6	R = CN	56(4)	92(2)
7	R = NO_2	45(4)	94(3)
			
8[c]	R = OMe	48(4)	95(3)
9[c]	R = OEt	55(4)	95(2)
10[c]	R = OBn	57(5)	97(2)
11[d]		80(3)	60(2)
12[d]		58(3)	66(3)

[a] Reaction conditions: olefin (0.25 mmol), **1** (0.20 mol%), and H_2SO_4 (1.0 mol%) in CH_3CN (1.0 mL) were added into the Schlenk tube at –20 °C. Then, 50% H_2O_2 (1.5 equiv to substrate) in CH_3CN (0.50 mL) was added to the reaction solution over a period of 1 h using a syringe pump. Total reaction time was 2.0 h. Isolated yields are reported, and the *ee* values were determined by HPLC with a Daicel OD-H, OJ-H or IC column. [b] **2** instead of **1** was used as a catalyst. [c] Reaction was carried out with **1** (1.0 mol%) and H_2SO_4 (3.0 mol%) at 0 °C. [d] **1** (0.50 mol%) and H_2SO_4 (3.0 mol%) were used, and the yields and *ee* values were determined by GC with a CP-Chirasil-Dex CB column.

In the case of chromenes, the product yields were moderate, but the enantioselectivities were high (Table 2, entries 6 and 7; Figure S4 in SI). In the epoxidation of methyl cinnamate, ethyl cinnamate, and benzyl cinnamate, we also obtained high *ee* values with moderate epoxide yields (Table 2, entries 8 – 10; Figure S5 in SI). In contrast, the *ee* values were moderate in the epoxidation of styrene and *cis*-β-methylstyrene (Table 2, entries 11 and 12). Thus, the results described above clearly indicate that **1** is an efficient enantioselective catalyst and both the catalytic activity and the enantioselectivity of **1** in the asymmetric epoxidation reactions by H_2O_2 are determined by the presence of the proton and SO_4^{2-} anion.

Table 3. Asymmetric epoxidation of chalcone by various oxidants catalyzed by **1** in the absence and presence of H_2SO_4[a]

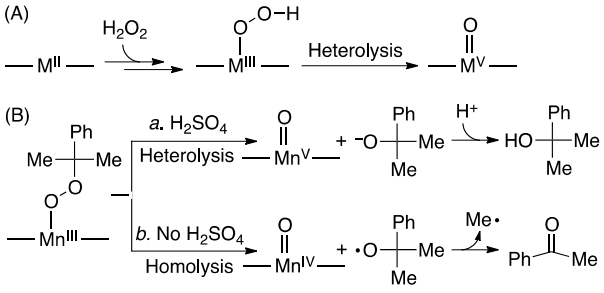
entry	oxidant	H_2SO_4	yield (%)[b]	*ee* (%)[c]
1	*m*-CPBA	no	38(3)	37(3)
2		yes	87(3)	95(2)
3	*t*-BuOOH	no	18(2)	45(3)
4		yes	56(3)	97(2)
5	Cumyl-OOH	no	8(2)	30(3)
6		yes	33(3)	96(2)
7	PhIO	no	25(3)	68(4)
8		yes	78(4)	97(2)

[a] Reaction conditions: oxidant (1.2 equiv) was added into a reaction solution containing chalcone (0.25 mmol) and **1** (0.20 mol%) in the absence and presence of H_2SO_4 (1.0 mol%) in CH_3CN (1.5 mL) at –20 °C. Total reaction time was 2.0 h. [b] Isolated yields are reported. [c] The *ee* values were determined by HPLC equipped with a Daicel OD-H column.

The asymmetric olefin epoxidation by **1** was also investigated using various oxidants, such as *m*-chloroperoxybenzoic acid (*m*-CPBA), *tert*-butyl hydroperoxide (*t*-BuOOH), cumyl hydroperoxide (Cumyl-OOH), and iodosylbenzene (PhIO), in the absence and presence of H_2SO_4. As we have observed in the H_2O_2 reactions (vide supra), not only the product yields but also the *ee* values were affected significantly by the presence of H_2SO_4 in the epoxidation of chalcone by **1** and the oxidants (Table 3); both the product yields and the *ee* values were low in the absence of H_2SO_4, even in the reactions of single oxygen atom donors such as *m*-CPBA and PhIO. Most importantly, the *ee* values were virtually the same irrespective of the oxidants in the presence of H_2SO_4 (Table 2, entry 1 and Table 3, entries 2, 4, 6, and 8), suggesting that a common epoxidizing intermediate (e.g., a high-valent Mn-oxo species) was generated in the reactions of H_2O_2, *m*-CPBA, *t*-BuOOH, Cumyl-OOH, and PhIO in the presence of H_2SO_4 (vide infra).

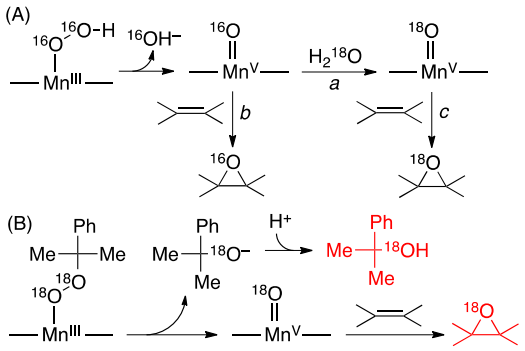
Mechanistic Studies to Elucidate the Role(s) of H_2SO_4. We then investigated the nature of the epoxidizing intermediate formed in the reaction of **1** and H_2O_2 in the presence of H_2SO_4. It has been proposed that the reactions of nonheme iron(II) and manganese(II) complexes bearing N4 ligands, such as TPA[7a] and PDP,[7b] with H_2O_2 in the presence of carboxylic acids generate Fe(V)- and Mn(V)-oxo species, respectively, via O-O bond heterolysis of presumed M(III)-OOH precursors (Scheme 2A).[10] We therefore conducted mechanistic studies to elucidate the nature of the epoxidizing intermediate and the O-O bond cleavage mechanism in the reactions of **1** and ROOH (e.g., R = H and Cumyl). First, we carried out the reaction of **1** with cumyl

hydroperoxide and analyzed product(s) derived from the decomposition of the cumyl hydroperoxide to distinguish homolytic vs heterolytic O-O bond cleavage pathways (Scheme 2B).[18] In this reaction, cumyl alcohol was produced quantitatively in the presence of H_2SO_4 (see Figures S6 and S7 in SI), suggesting that a Mn(III)-alkylperoxo species is converted to a Mn(V)-oxo species via a heterolytic O-O bond cleavage pathway (Scheme 2B, pathway *a*). On the contrary, acetophenone was yielded as a major product when the reaction was performed in the absence of H_2SO_4 (~90% yield based on the amount of Cumyl-OOH), indicating that O-O bond homolysis is a predominant pathway (Scheme 2B, pathway *b*). We therefore conclude that one possible role of H_2SO_4 is to control the O-O bond cleavage pathway to form a Mn-oxo intermediate (vide infra), such as the heterolytic and homolytic O-O bond cleavage of Mn-OOR in the presence and absence of H_2SO_4, respectively (Scheme 2B, pathways *a* and *b*).



Scheme 2. (A) A proposed mechanism for the formation of metal-oxo intermediates in the reaction of a nonheme metal(II) complex and H_2O_2. (B) Heterolytic and homolytic O-O bond cleavage mechanisms in the presence and absence of H_2SO_4, respectively, in the reaction of **1** and ROOH.

To support the intermediacy of a high-valent Mn-oxo species in the catalytic epoxidation reactions, we carried out an ^{18}O-labeled water experiment in the epoxidation of styrene by **1** and H_2O_2 in the presence of H_2SO_4 (Scheme 3A, pathways *a* and *c*).[4c,10b,12a,19] In some cases, although a high-valent metal-oxo species is generated as an epoxidizing intermediate, we would not observe ^{18}O-incorporation from $H_2{}^{18}O$ into the epoxide product due to a slow ^{18}O-exchange between a metal-oxo species and $H_2{}^{18}O$ (Scheme 3A, competition between pathways *a* and *b*).[4c,10b,19] In the present study, a significant amount of ^{18}O-incorporation from $H_2{}^{18}O$ into the styrene oxide was observed in the epoxidation of styrene by **1** and H_2O_2 in the presence of H_2SO_4 (~30% based on 95% ^{18}O-enriched $H_2{}^{18}O$) (Figure S8 in SI), demonstrating unambiguously that a high-valent Mn-oxo species was indeed formed as an epoxidizing intermediate in the reaction of **1** and H_2O_2 in the presence of H_2SO_4. This result is in sharp contrast to the previous reports in the oxidation of organic substrates by H_2O_2 catalyzed by nonheme manganese complexes in the presence of excess amounts of carboxylic acids; no ^{18}O-incorporation from $H_2{}^{18}O$ into the products in the latter reactions was ascribed to the blocking of $H_2{}^{18}O$ coordination to the Mn site by the carboxylic acids.[4c,5c] In a separate study, when ^{18}O-labeled cumyl hydroperoxide (Cumyl-$^{18}O^{18}OH$) was used as a terminal oxidant, the epoxide and cumyl alcohol products contained



Scheme 3. (A) A proposed mechanism for the use of ^{18}O-labeled water experiment to probe the intermediacy of a high-valent Mn-oxo species in the catalytic epoxidation of olefins by **1** and H_2O_2. (B) A reaction scheme showing the source of oxygen found in epoxide product.

the same amount of ^{18}O derived from the Cumyl-$^{18}O^{18}OH$ oxidant (Figures S8 and S9 in SI), demonstrating that the source of oxygen atom in the products was the cumyl hydroperoxide oxidant, not molecular oxygen (Scheme 3B).

Consistent with the experimental results, density functional theory (DFT) calculations on the formation of Mn(V)-oxo complex (**6**) from its precursor, Mn(III)-OOH complex (**5**), revealed that the conversion of **5** to **6** occurs via a heterolytic O-O bond cleavage step (Figures 2 and 3; see also Tables S5 and S6 in SI). The difference between the ground state of Mn(III)-OOH in quintet spin state and the triplet state is 7.0 kcal mol^{-1}, which is consistent with the previous theoretical and experimental results of $[(TMC)Mn(III)\text{-}OOH]^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetra-decane).[20] During the O-O bond elongation, a spin inversion occurs that leads the reaction to occur on a triplet transition state (^{3}**TS**$_{56}$); thus, the O-O bond cleavage shows *two-state reactivity*. The spin of OH group in the

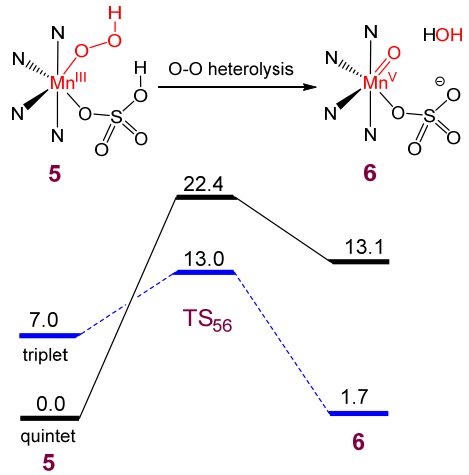


Figure 2. Energy profiles (in kcal mol^{-1}) for the conversion of Mn(III)(OOH) (**5**) to Mn(V)-Oxo (**6**). Energies were calculated at the level of UB3LYP/def2-TZVPP//TZVP(MnOOH, N, HSO_4^-), 6-31G*(C and H in the nonheme ligand). Zero-point energies (ZPE) and solvation were taken into account.

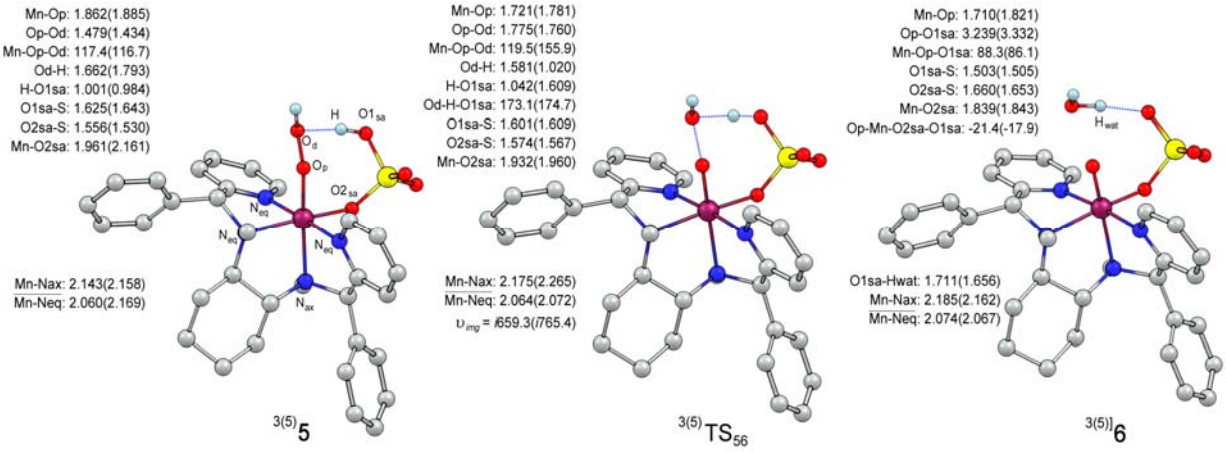


Figure 3. Key geometric information of the transformation **5** to **6**. Values outside of parentheses are the triplet ones and values inside of parenthesis are the quintet ones. Length is in Å unit and imaginary frequency is in cm^{-1} unit. Hydrogen atoms in the ligand are omitted for clarity. Calculations were done at the UB3LYP/B1 level in solvent.

Mn-O-OH moiety is nearly zero (-0.07) (Table S6 in SI) on ^{3}**TS**$_{56}$, and the hydrogen-removed SO_4^- moiety contains no spin on ^{3}**TS**$_{56}$ either, thus, O-O cleavage is heterolytic. The nascent manganese-oxo species ^{3}**6** lies 1.7 kcal mol^{-1} lower than ^{5}**5** and is a Mn(V)-oxo species.

CONCLUSION

A large number of reports have been published using carboxylic acids as additives to improve the catalytic activity and enantioselectivity of metal complexes in the (asymmetric) epoxidation of olefins by aqueous H_2O_2.[3-8] In the present study, we have reported an unexpected novel effect of sulfuric acid in the catalytic (asymmetric) epoxidation of olefins by aqueous H_2O_2 catalyzed by a nonheme manganese complex bearing a tetradentate N4 ligand; the product yields and *ee* values were exceedingly high when both the proton and SO_4^{2-} anion were present in the catalytic reactions. The role(s) of H_2SO_4 was proposed to facilitate the formation of a high-valent Mn-oxo species via heterolytic O-O bond cleavage of a presumed Mn(III)-OOH precursor and to increase the oxidizing power and enantioselectivity of the Mn-oxo oxidant in olefin epoxidation reactions. The involvement of the Mn-oxo species as an epoxidizing intermediate, which was formed via O-O bond heterolysis in the presence of protons, was evidenced experimentally by carrying out isotopically labeled water experiments. In addition, there should be a proton effect on the increase of the reactivity of the Mn-oxo species in the epoxidation of olefins, as we have demonstrated in our previous studies on the effects of Lewis and Brønsted acids on the oxidation of organic substrates by nonheme iron- and manganese-oxo complexes.[12a,13] We have also shown that the enantioselectivity increased dramatically by the presence of SO_4^{2-} anion in the asymmetric epoxidation reactions. Future studies will be focused on understanding the exact role of the SO_4^{2-} anion in increasing the enantioselectivity of the manganese catalyst, by synthesizing a manganese complex coordinating a sulfate anion and using it directly in stoichiometric asymmetric epoxidation reactions.

EXPERIMENTAL SECTION

Materials. All chemicals were purchased from Aldrich, Alfa Aesar, and TCI with the maximum purity available, and used as received unless otherwise indicated. Solvents were dried according to published procedures and distilled under argon prior to use.[21] All reactions were performed under an Ar atmosphere using dried solvent and standard Schlenk techniques unless otherwise noted. $H_2{}^{18}O$ (95% ^{18}O-enriched) and $^{18}O_2$ (98% ^{18}O-enriched) were purchased from ICON Services Inc. (Summit, NJ, USA). Cumyl-$^{18}O^{18}OH$ (90% ^{18}O-enriched) was synthesized by reacting cumene and $^{18}O_2$ in hexane at 85 °C according to literature methods.[22] *m*-CPBA (77%) was obtained from Aldrich and purified by washing with phosphate buffer (pH 7.2) and recrystallized from *n*-hexane/ether to remove the free carboxylic acid. Final purity was >98%. Ligands, (*R,R*)-MCP, (*R,R*)-P-MCP, and (*R,R*)-PDP, and their manganese complexes, Mn^{II}(MCP)$(OTf)_2$, Mn^{II}(P-MCP)$(OTf)_2$, and Mn^{II}(PDP)$(OTf)_2$ were prepared according to the known methods.[5a,17]

Synthesis of Dbp-MCP Ligand and Its Mn(II) Complex. Dbp-MCP ligand was prepared by introducing a 3,5-di-*tert*-butylbenzene group into the 2-pyridinylmethyl positions of (*R,R*)-MCP (Figure S2 in SI).[5a] A solution of ligand (1.46 g, 5.0 mmol; Figure S2 in SI, ligand **a**) in Et_2O was added dropwise to a vigorously stirred Grignard reagent (50 mmol) in Et_2O (20 mL) at room temperature and the reaction mixture was stirred for 24 h. Then, saturated NH_4Cl was added to quench the reaction, and the organic phase was dried over anhydrous Na_2SO_4 and purified by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) to afford the corresponding ligand (Figure S2 in SI, ligand **b**) with 70% isolated yield. To a solution of ligand **b** (0.50 mmol) in THF (15 mL) was added NaH (ca. 60% in oil, 60 mg, 2.5 mmol) at 0 °C. After stirring for 1 h, CH_3I (2.1 mmol) was added to the resulting solution, and the reaction solution was stirred for 4 h. The reaction mixture was quenched by distilled water and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4. The crude product was purified by chromatography on silica gel

(petroleum ether/EtOAc = 3:1) to afford the ligand Dbp-MCP with 84% isolated yield (0.29 g) (see Figure S2 in SI).

$Mn^{II}(Dbp\text{-}MCP)(OTf)_2$ (**1**) was prepared by adding $Mn(CF_3SO_3)_2$ (0.10 mmol) to a solution of Dbp-MCP (0.10 mmol) under an Ar atmosphere in CH_3CN (1.0 mL). The reaction mixture was stirred for 1 day and diethyl ether was carefully layered on the solution over 2 days. The off-white crystals was isolated and washed with cold ether.

Dbp-MCP: $[\alpha]_D^{20} = -78.1$ (c = 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) in ppm: δ = 8.48 (d, *J* = 4.2 Hz, 2H), 8.06 (d, *J* = 7.9 Hz, 2H), 7.79 (t, *J* = 7.6 Hz, 2H), 7.28 (s, 4H), 7.23 (s, 2H), 7.16-7.10 (m, 2H), 4.86 (s, 2H), 2.29 (d, *J* = 7.9 Hz, 2H), 2.18 (s, 6H), 1.86 (d, *J* = 11.6 Hz, 2H), 1.46 (s, 2H), 1.23 (s, 36H), 1.00 (d, *J* = 8.0 Hz, 2H), 0.65 (t, *J* = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) in ppm: δ = 164.7, 150.3, 148.9, 139.5, 136.5, 123.6, 121.8, 121.7, 121.0, 77.2, 76.0, 59.2, 34.8, 31.4, 25.3, 24.2. Dbp-MCP ligand: HRMS calcd. for $[Dbp\text{-}MCP+H]^+$: 701.5517, found: 701.5514. $Mn^{II}(Dbp\text{-}MCP)(OTf)_2$ (**1**): HRMS calcd. for $[Mn^{II}(Dbp\text{-}MCP)(OTf)]^+$: 904.4332, found: 904.4325. Anal. Calcd. for $C_{50}H_{68}F_6MnN_4O_6S_2{\cdot}H_2O$: C 56.01, H 6.58, N 5.23. found C 55.93, H 6.65, N 5.18.

Instrumentation. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer. All NMR spectra were recorded at room temperature and were indirectly referenced to TMS using residual solvent signals as internal standards. High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics micrOTOF-Q II™ mass spectrometer with an ESI source. Elemental analyses were conducted with a Vario EL cube Elemental analyzer. Product analysis was performed with Agilent Technologies 6890N gas chromatograph (HP-5 column, 30 m × 0.32 mm × 0.25 μm film thickness) with a flame ionization detector and Thermo Finnigan (Austin, Texas, USA) FOCUS DSQ (dual stage quadrupole) mass spectrometer interfaced with Finnigan FOCUS gas chromatograph (GC-MS). High Performance Liquid Chromatography (HPLC) analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump) or DIOMEX Pump Series P580 equipped with a variable wavelength UV-200 detector. Chiralpak OD-H, OJ-H and IC were purchased from Daicel Chemical Industries, LTD. HPLC equipped with SunFire C18 5μm (4.6 mm × 25 mm column) was also used. Column chromatography was generally performed on silica gel (200 – 300 mesh) and TLC inspections were on silica gel GF254 plates.

Catalytic Epoxidation of Olefins by 1. Reaction conditions for the catalytic epoxidation of simple olefins are as follows: substrate (0.25 mmol), $Mn^{II}(Dbp\text{-}MCP)(OTf)_2$ (**1**) (1.5 mL, 1.3×10^{-3} mmol, 0.87 mg/mL in CH_3CN), and H_2SO_4 (0.30 mL, 7.5×10^{-3} mmol, 2.45 mg/mL in CH_3CN) were added to a Schlenk tube in CH_3CN (1.0 mL). Then, 1.5 equiv of 50% H_2O_2 (diluted in 0.50 mL of CH_3CN) was added dropwise via a syringe pump over 1 h. After the reaction mixture was stirred for the given time at –20 °C, the reaction solution was subjected to GC analysis to determine the product yield.

Asymmetric Epoxidation of Olefins by 1. Reaction conditions for the asymmetric epoxidation of olefins are as follows: substrate (0.25 mmol), $Mn^{II}(Dbp\text{-}MCP)(OTf)_2$ (**1**) (0.60 mL, 5.0×10^{-4} mmol, 0.87 mg/mL in CH_3CN), and H_2SO_4 (0.10 mL, 2.5×10^{-3} mmol, 2.45 mg/mL in CH_3CN) were added to a Schlenk tube in CH_3CN (1.0 mL). Then, 1.5 equiv of 50% H_2O_2 (diluted in 0.50 mL of CH_3CN) was added dropwise via a syringe pump over 1 h. After the reaction mixture was stirred for the given time at –20 °C, the reaction solution was subjected to silicon column or GC to determine the product yield. The *ee* values were determined by GC or HPLC equipped with chiral columns.

Gram-scale Reaction for the Asymmetric Epoxidation of Chalcone by 1. Chalcone (1.0 g, 4.8 mmol), **1** (0.20 mol%), and H_2SO_4 (1.0 mol%) were added into a Schlenk tube containing 20 mL CH_3CN, and the resulting mixture was cooled to –20 °C. Then, 50% H_2O_2 (1.5 equiv to substrate) was added dropwise over a period of 1 h via a syringe pump. The isolated yield was 93% and the *ee* value, which was determined by HPLC equipped with a Daicel OD-H, was 97%.

Decayed Products of Cumyl Hydroperoxide in Catalytic Reactions. The products obtained in the catalytic oxidation of chalcone (0.20 M) by **1** (2.0 mM) and cumyl hydroperoxide (20 mM) in the absence and presence of H_2SO_4 (10 mM) at room temperature were analyzed by HPLC equipped with SunFire C18 5μm (4.6 mm × 25 mm column). Water and methanol were used as mobile phase. In the presence of H_2SO_4 (10 mM), cumyl alcohol (2-phenylpropan-2-ol) was formed as a sole product with >99% yield based on the amount of cumyl hydroperoxide used (see Figure S7 in SI), whereas, in the absence of H_2SO_4, acetophenone (~90% yield based on the amount of the cumyl hydroperoxide used) was formed as a major product with a small amount of cumyl alcohol (~10%).

^{18}O-Labeled Experiments. An acetonitrile solution of H_2O_2 (40 mM) was added to a solution containing **1** (2.0 mM), H_2SO_4 (12 mM), styrene (2.0×10^2 mM), and $H_2{}^{18}O$ (20 μL) under inert atmosphere in CH_3CN at room temperature. The reaction solution was stirred for 1 min at room temperature and then analyzed by GC-MS. The ^{16}O and ^{18}O compositions in styrene oxide were analyzed by comparing the relative abundances at m/z = 119 for styrene oxide-^{16}O and at m/z = 121 for styrene oxide-^{18}O (Figure S8 in SI).

DFT Calculations. The spin-unrestricted B3LYP functional[23] was employed with two basis sets: (i) The TZVP basis set[24a] for MnOOH, N and atoms of sulfuric acid (H_2SO_4), and 6-31G* basis set for the rest atoms of the supporting ligand of **2**, which was used instead of **1** for more efficient calculations. This basis set is denoted as B1 and is used to optimize the transition states and minima; (ii) The Def2-TZVPP basis set[24b] for all atoms, denoted as B2, used for single point energy corrections. Transition states were ascertained by vibrational frequency analysis to possess only one imaginary frequency. All optimizations and single point calculations were performed with solvation included using the self-consistent reaction field (SCRF) calculations in the conductor-like polarizable continuum model (CPCM); the dielectric constant corresponding to acetonitrile solvent (ε = 35.688) was used. DFT calculations were performed with the Gaussian 09 suite of quantum chemical packages.[25]

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11579.

Full crystallographic data are also available from the Cambridge Crystallographic Data Centre (CCDC-917216).

Figures S1 – S9, Tables S1 – S6 and the coordinates of DFT calculated structures (PDF). Crystallographic data for Mn^{II}(Dbp-MCP)$(OTf)_2$, compound **1** (CIF).

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Notes

The authors declare no competing financial interest.

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