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Remarkable Solvent, Porphyrin Ligand, and Substrate Effects on Participation of Multiple Active Oxidants in Manganese(III) Porphyrin Catalyzed Oxidation Reactions

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Abstract: The participation of multiple active oxidants generated from the reactions of two manganese(III) porphyrin complexes containing electron-withdrawing and -donating substituents with peroxyphenylacetic acid (PPAA) as a mechanistic probe was studied by carrying out catalytic oxidations of cyclohexene, 1-octene, and ethylbenzene in various solvent systems, namely, toluene, CH_2Cl_2, CH_3CN, and H_2O/CH_3CN (1:4). With an increase in the concentration of the easy-to-oxidize substrate cyclohexene in the presence of [(TMP)MnCl] (**1a**) with electron-donating substituents, the ratio of heterolysis to homolysis increased gradually in all solvent systems, suggesting that [(TMP)Mn−OOC(O)R] species **2a** is the major active species. When the substrate was changed from the easy-to-oxidize one (cyclohexene) to difficult-to-oxidize ones (1-octene and ethylbenzene), the ratio of heterolysis to homolysis increased a little or did not change. [(F_{20}TPP)Mn−OOC(O)R] species **2b** generated from the reaction of [(F_{20}TPP)MnCl] (**1b**) with electron-withdrawing substituents and PPAA also gradually becomes involved in olefin epoxidation (although to a much lesser degree than with [(TMP)Mn−OOR] **2a**) depending on the concentration of the easy-to-oxidize substrate cyclohexene in all aprotic solvent systems except for CH_3CN, whereas Mn^V=O species is the major active oxidant in the protic solvent system. With difficult-to-oxidize substrates, the ratio of heterolysis to homolysis did not vary except for 1-octene in toluene, indicating that a Mn^V=O intermediate generated from the heterolytic cleavage of **2b** becomes a major reactive species. We also studied the competitive epoxidations of *cis*-2-octene and *trans*-2-octene with two manganese(III) porphyrin complexes by *meta*-chloroperbenzoic acid (MCPBA) in various solvents under catalytic reaction conditions. The ratios of *cis*- to *trans*-2-octene oxide formed in the reactions of MCPBA varied depending on the substrate concentration, further supporting the contention that the reactions of manganese porphyrin complexes with peracids generate multiple reactive oxidizing intermediates.

Keywords: manganese · oxidation · oxido ligands · porphyrinoids · solvent effects

Introduction

Understanding the structures of the reactive intermediates responsible for oxygen atom transfer by heme and nonheme monooxygenase enzymes and their model compounds under catalytic oxygenation conditions has been a major goal of bioinorganic chemistry for the past three decades.[1] In particular, reactions of synthetic manganese porphyrin complexes with various oxidants such as peracids, iodosylbenzene (PhIO), and hydroperoxides have been extensively studied to understand the details of the enzymatic oxidation reaction mechanisms.[2] Although a wide variety of biological oxidation reactions catalyzed by these synthetic manganese porphyrin complexes are mimicked, only recently have the key manganese(V)–oxo porphyrin intermediates been characterized in addition to manganese(IV)–oxo species.[3] They were prepared at low temperature, characterized by a variety of spectroscopic methods, and used directly in reactivity studies of oxygen atom transfer reactions such as olefin epoxidations and alkane hydroxylations.[4] In addition, there is evidence that supports the involvement of Mn−OOR intermediates as the reactive species in the catalytic or stoichiometric oxygenation of hydrocarbons by heme-containing enzymes and manganese-porphyrin complexes.[5] However, it is not completely clear which reactive species are responsible for oxygen atom transfer in the catalytic oxygenation reactions and what factors influence the nature

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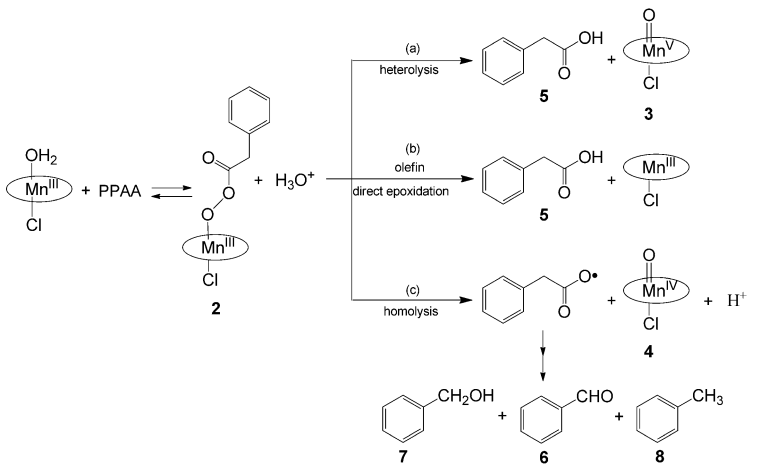


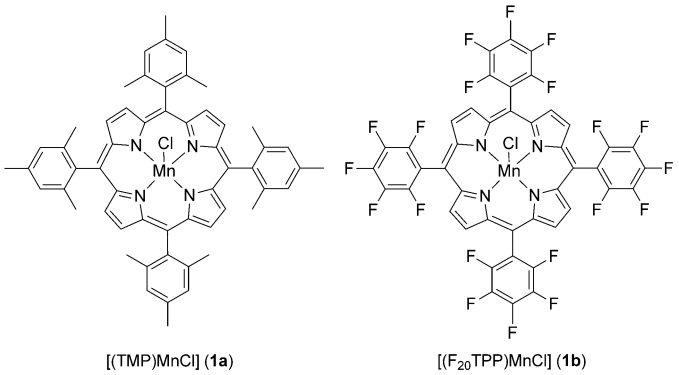
Scheme 1. Possible reactive intermediates from the reaction of PPAA with the manganese complexes.

of the reactive intermediates in synthetic manganese porphyrin systems.

Quite recently, we presented strong evidence that the multiple active oxidants, Mn^{V}=O, Mn^{IV}=O, and Mn^{III}–OO(O)CR, operate simultaneously in olefin epoxidation via manganese complexes such as Mn(salen) (salen = *N*,*N*′-bis-(salicylidene)ethylenediamine anion) and Mn(nonheme), depending on the reaction conditions such as the type of reaction solution and the concentration of the substrate (Scheme 1).[6] In addition, it has been proposed that the nature of solvent might significantly affect partitioning between heterolysis and homolysis of the O–O bond of a Mn–acylperoxo intermediate (Mn–OOC(O)R), and that O–O bond cleavage of the Mn–OOC(O)R complex might proceed predominantly by heterolytic cleavage in protic solvents. Therefore, a discrete Mn^{V}=O intermediate appeared to be the dominant reactive species in protic solvents. Furthermore, we have observed close similarities between these nonheme Mn^{III} complex systems and Mn(saloph) catalysts (saloph = salicylaldehide-o-phenylenediimne), suggesting that this simultaneous operation of the three active oxidants might prevail in all of the manganese catalyzed olefin epoxidations, including Mn(salen), Mn(nonheme), and even Mn(porphyrin) complexes.[6b]

To gain insight into the proposal that the three active oxidants might operate simultaneously in Mn(porphyrin) complex catalyzed olefin epoxidations and to understand the efficient O–O bond activation in which the mechanism of oxidation shares many common features among Mn(salen), Mn(nonheme), and Mn(porphyrin) complexes, we systematically studied the solvent, porphyrin ligand, and substrate effects on two Mn^{III} porphyrin complexes containing electron-withdrawing and -donating substituents, [(TMP)MnCl] (**1a**; TMP = 5,10,15,20-tetramesitylporphyrin) and [(F_{20}TPP)MnCl] (**1b**; F_{20}TPP = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin) (Scheme 2), with peracids.

Herein, we report the results of product distributions of peroxyphenylacetic acid (PPAA) used as a mechanistic probe and competitive epoxidations by *meta*-chloroperbenzoic acid (MCPBA) studied with *cis*- and *trans*-2-octene in manganese(III) porphyrin catalyzed oxidations in various solvents at room temperature. We found from the studies that the three active oxidants might indeed operate simultaneously in Mn(porphyrin) complex catalyzed olefin epoxidations and that the mechanism of oxidation shares many common features among Mn(salen), Mn(nonheme), and Mn(porphyrin) complexes.[6] Moreover, the participation of multiple active oxidants was remarkably influenced by the solvent polarity, the concentration and type of substrate, and porphyrin ligands. Furthermore, we report for the first time that a high-valent manganese(V)–oxo intermediates unexpectedly show a similar preference for *trans*-2-octene over *cis*-2-octene in the competitive epoxidation of *cis*- and *trans*-2-octene, and that the ratios of *cis*- to *trans*-oxide with two manganese(III) porphyrin complexes varied depending on the substrate concentration.



Scheme 2. Structures of manganese(III) porphyrin complexes.

Results and Discussion

In attempts to gain insight into the proposal that the simultaneous operation of the three active oxidants might prevail in all manganese-catalyzed olefin epoxidations, including Mn(salen), Mn(nonheme), and even Mn(porphyrin) complexes,[6b] we used PPAA as a mechanistic probe along with two Mn^{III} porphyrin complexes containing electron-withdrawing and -donating substituents on phenyl groups at the meso position of the porphyrin ring, namely, [(TMP)MnCl] (**1a**) and [(F_{20}TPP)MnCl] (**1b**). As we showed in our previous studies,[7] heterolytic cleavage of the O–O bond of

PPAA affords phenylacetic acid (PAA, **5**; pathway (a) of Scheme 1). In contrast, when the O–O bond of the coordinated anion of PPAA is cleaved homolytically, an acyloxyl radical is generated (pathway (c) of Scheme 1). This acyloxyl radical undergoes rapid β-scission (diffusion-controlled rate ca. $10^9\ s^{-1}$) to give benzaldehyde (**6**), benzyl alcohol (**7**), and toluene (**8**) via the benzyl radical.[7,8] The direct reaction of the acylperoxo intermediate and substrate affords PAA (pathway (b) of Scheme 1), and apparently affects the O–O bond cleavage mode.

Substrate effect on participation of multiple active oxidants: First, we examined the product distribution of PPAA with [(TMP)MnCl] (**1a**) having electron-donating groups in the absence of a substrate in the nonpolar solvent toluene at room temperature. PAA was the dominant degradation product of PPAA (65% based on PPAA; entry 1 in Table S1),[9] with some amounts of benzaldehyde (24%) and benzyl alcohol (4.9%) generated from the homolytic O–O bond cleavage, demonstrating that [(TMP)Mn–OOC(O)R] species **2a** generated from the reaction of **1a** and PPAA underwent partitioning of 69% heterolysis and 31% homolysis (Table 1, entry 1, fourth column).[10] To further examine the interaction between O–O bond cleavage and substrate oxidation, we investigated the concentration effect of an easy-to-oxidize substrate, cyclohexene. If the Mn–OOR species (**2**) was involved in the epoxidation reaction, then the ratio of heterolysis to homolysis would vary with the concentration of cyclohexene employed.[7,8] That is, direct epoxidation of olefin by Mn–OOR species affords PAA, the heterolytic cleavage product of the O–O bond of PPAA, and would result in an increase in the amount of heterolytic cleavage. We increased the concentration of substrate cyclohexene from 0 to 160 mM in the presence of catalyst **1a**. The ratio of heterolysis to homolysis increased gradually within possible experimental error (from 69:31 for 0 mM to 73:27 for 40 mM to 82:18 for 160 mM; Table 1, entries 1—3, fourth column, and Table S1). Under anaerobic conditions, almost identical yields of the products were obtained. These results suggest that [(TMP)Mn–OOC(O)R] species **2a** generated from the reaction of manganese porphyrin complex **1a** and peracid also gradually becomes involved in olefin epoxidation depending on the concentration of cyclohexene in the nonpolar solvent toluene, as shown in Mn(saloph) and Mn(nonheme) complexes.

Solvent effect on participation of multiple active oxidants: We studied the solvent effects, because it has been demonstrated previously in Mn(saloph) and Mn(nonheme) complexes that the multiple oxidants, Mn^{III}–OOC(O)R (**2**), Mn^{V}=O (**3**), and Mn^{IV}=O (**4**), operate simultaneously as the key active intermediates in aprotic solvents and that Mn^{V}=O species might become the common reactive intermediate in protic solvents.[6] We used a variety of solvents with different polarities for the detailed study, ranging from toluene (dielectric constant: 2.4) to CH_2Cl_2 (dielectric con-

Table 1. Product distributions derived from PPAA and competitive epoxidations mediated by Mn porphyrin complexes in the absence and the presence of substrate in various solvent systems at room temperature.[a]

Entry	Solvent (dielectric constant)	Conc. [mM]	[(TMP)MnCl] (**1a**) cyclohexene	1-octene	ethylbenzene	*cis-/trans*-octene oxide	[(F_{20}TPP)MnCl] (**1b**) cyclohexene	1-octene	ethylbenzene	*cis-/trans*-octene oxide
1	toluene (2.4)	0	2.3 (69:31)	2.3 (69:31)	2.3 (69:31)		2.7 (73:27)	2.7 (73:27)	2.7 (73:27)	
2		40	2.8 (73:27)	2.4 (71:29)	2.5 (72:28)	1.8	4.0 (80:20)	2.8 (74:26)	2.8 (74:26)	2.1
3		160	4.5 (82:18)	2.6 (73:27)	2.6 (72:28)	2.5	5.3 (84:16)	3.8 (79:21)	3.1 (76:24)	2.6
4	CH_2Cl_2 (3.1)	0	2.4 (70:30)	2.4 (70:30)	2.4 (70:30)		2.7 (73:27)	2.7 (73:27)	2.7 (73:27)	
5		40	3.7 (79:21)	2.6 (72:28)	2.6 (72:28)	2.3	3.1 (75:25)	2.5 (71:29)	2.5 (71:29)	1.9
6		160	6.3 (86:14)	3.0 (75:25)	2.4 (71:29)	4.4	5.8 (85:15)	3.0 (75:25)	2.8 (74:26)	2.2
7	CH_3CN (5.8)	0	2.7 (73:27)	2.7 (73:27)	2.7 (73:27)		2.6 (72:28)	2.6 (72:28)	2.6 (72:28)	
8		40	5.9 (86:14)	3.2 (76:24)	3.2 (76:24)	2.5	2.6 (72:28)	2.2 (69:31)	2.1 (68:32)	1.4
9		160	11.3 (92:8)	4.3 (81:19)	3.3 (77:23)	6.4	3.1 (76:24)	2.2 (69:31)	2.6 (72:28)	2.0
10	H_2O/CH_3CN (1:4)	0	4.8 (83:17)	4.8 (83:17)	4.8 (83:17)		45.9 (98:2)	46.1 (98:2)	46.1 (98:2)	
11	H_2O (9.0), CH_3CN (5.8)	20	8.7 (90:10)	5.6 (85:15)	5.0 (83:17)	1.9	41.1 (98:2)	32.1 (97:3)	50.0 (98:2)	1.0
12		40	9.7 (91:9)	5.9 (86:14)	6.7 (87:13)	3.6	35.4 (97:3)	26.4 (96:4)	34.2 (97:3)	1.1
13		160	23.4 (96:4)	7.1 (88:12)	6.6 (87:13)	13.0	29.7 (97:3)	26.5 (96:4)	40.0 (98:2)	1.7

[a] See the Experimental Section for details; numbers in parentheses represent the hetero/homo product ratio.

stant: 3.1) to CH_3CN (dielectric constant: 5.8) to a mixture of H_2O (dielectric constant: 9.0) and CH_3CN (1:4). As shown in Table 1, when a slightly more polar solvent (CH_2Cl_2) was used instead of toluene, the partitioning of [(TMP)Mn−OOC(O)R] species **2a** in the absence of cyclohexene was nearly identical (heterolysis vs. homolysis: 70 vs. 30; Table 1, entry 4, fourth column, and Table S2) to that in toluene.[9] The increase in the concentration of cyclohexene showed a similar pattern for the ratio of heterolysis to homolysis as shown in toluene, but with slightly higher ratios depending on the cyclohexene concentration (Table 1, entries 4–6). In the more polar solvent CH_3CN, the ratio of heterolysis to homolyis in the absence of cyclohexene was slightly higher (73:27 (2.7)) than in toluene and CH_2Cl_2 (Table 1,entry 7).[9] Similarly, increasing the concentrations of cyclohexene increased the ratios of heterolysis to homolysis (Table 1, entries 7–9 and Table S3). In the most polar and protic solvent system of the mixture H_2O/CH_3CN (1:4), the partitioning of [(TMP)Mn−OOC(O)R] species **2a** in the absence of cyclohexene gave the large value of 4.8 (Table 1, entry 10, fourth column, and Table S4),[9] indicating 83% heterolysis and 17% hemolysis. This result indicates that the protic solvent induces the Mn−OOC(O)R species to undergo dominantly heterolytic cleavage. The increase in the concentration of cyclohexene in the mixture H_2O/CH_3CN (1:4) also showed, very surprisingly, a gradual increase in the ratios of heterolysis to homolysis with the highest value of 23.4 with 160 mM cyclohexene (Table 1, entries 10–13), whereas it would be expected that the heterolytic O−O bond cleavage of [(TMP)Mn−OOR] species **2a** occurs by general-acid catalysis prior to the direct interaction between **2a** and olefin in the protic solvent system.[11] Taken together, the concentration dependence of heterolysis versus homolysis in all solvent systems tested in this study suggests that [(TMP)Mn−OOC(O)R] species **2a** is a major active species and gradually becomes involved in olefin epoxidation depending on the concentration of cyclohexene.

In contrast, as we and others have proposed, when the substrate is active or the concentration of the substrate is high, the species M−OOC(O)R might gradually become involved in the epoxidation reaction,[12] so we used a difficult-to-oxidize substrate, terminal olefin 1-octene, to investigate the cleavage mode of PPAA with catalyst **1a**. Using the same method as above, we increased the concentration of substrate 1-octene from 0 to 160 mM in the presence of catalyst **1a** in toluene (see Table S5). The ratio of heterolysis to homolysis varied a little within possible experimental error (Table 1, entries 1–3, fifth column). These results indicate that [(TMP)Mn−OOC(O)R] species **2a** might act a little as an active oxidant toward the difficult-to-oxidize substrate 1-octene. Similar product ratios were observed in the other solvent systems (Table 1, fifth column, and Tables S6–S8).

Furthermore, we changed the substrate to one that is more difficult to oxidize, namely, ethylbenzene. The ratios of heterolysis to homolysis varied little with an increase in the concentration of ethylbenzene independent of the solvent polarity, as shown in Table 1 (entries 1–13, sixth column, and Tables S9–S12). These results demonstrate that [(TMP)Mn−OOC(O)R] (**2a**) might not be involved in the oxidation reaction with the difficult-to-oxidize substrate ethylbenzene and the major reactive species is the [(TMP)Mn^V=O] intermediate **3a** generated from the heterolytic cleavage of **2a**. Cook et al. reported a similar type of result, namely that PhIO, PFIB (pentafluoroiodosylbenzene), and MCPBA in a manganese porphyrin complex yielded the same selectivity for a difficult oxidation reaction, alkane hydroxylation, and proposed that metal-based oxidation via a common intermediate, Mn^V=O, occurred.[13]

Porphyrin ligand effect on participation of multiple active oxidants: We explored the porphyrin ligand effect on the participation of the multiple active oxidants in the presence of a manganese(III) porphyrin complex ([(F_{20}TPP)MnCl] (**1b**)) containing electron-withdrawing substituents at the meso position of the porphyrin ring. We first examined the product distribution of PPAA with **1b** in the absence of substrate in the nonpolar solvent toluene at room temperature. The ratio of heterolysis to homolysis was 2.7,[9] similar to that obtained with [(TMP)MnCl] (**1a**) in toluene (Table 1, entry 1, eighth column, and Table S13), demonstrating that the [(F_{20}TPP)Mn−OOC(O)R] species (**2b**) generated from the reaction of **1b** and PPAA underwent partitioning of 73% heterolysis and 27% homolysis. Furthermore, we investigated the concentration effect for the easy-to-oxidize substrate cyclohexene. With increasing concentration of substrate cyclohexene, the ratio of heterolysis to homolysis increased gradually within possible experimental error (Table 1, entries 1–3, eighth column, and Table S13). These results suggest that [(F_{20}TPP)Mn−OOC(O)R] species **2b** generated from the reaction of peracid with [(F_{20}TPP)MnCl] (**1b**) also gradually becomes involved in olefin epoxidation depending on the concentration of cyclohexene in the nonpolar solvent toluene. When toluene was replaced with a slightly more polar solvent CH_2Cl_2, the partitioning of [(F_{20}TPP)Mn−OOC(O)R] species **2b** in the absence of cyclohexene was nearly identical (heterolysis vs. homolysis: 73 vs. 27; Table 1, entry 4, eighth column, and Table S14) to that in toluene.[9] An increase in the concentration of cyclohexene showed a very similar pattern of heterolysis to homolysis to that shown in toluene (Table 1, entries 4–6). In the more polar solvent CH_3CN, the ratio of heterolysis to homolysis in the absence of cyclohexene was also nearly identical (72:28) to those shown in toluene and CH_2Cl_2.[9] However, increasing the concentrations of cyclohexene produced little change in the ratios of heterolysis to homolysis (Table 1, entries 7–9, and Table S15). These unexpected results seem to correlate with the previous report by Collman et al. that the ratios of the competitive epoxidation products of styrene and *cis*-cyclooctene catalyzed by [(F_{20}TPP)MnCl] (**1b**) in CH_3CN are essentially identical, regardless of the oxidants employed.[14] These observations demonstrate that [(F_{20}TPP)Mn−OOC(O)R] species **2b** might have little involvement in olefin epoxidation in the presence of a large amount of substrate in CH_3CN; at present, it is not clear

why **2b** does not act as an active oxidant toward easy-to-oxidize olefins only in CH_3CN. In the most polar and protic solvent system, the mixture H_2O/CH_3CN (1:4), the partitioning of **2b** in the absence of cyclohexene gave the largest value of 45.9,[9] indicating 98% heterolysis and 2% homolysis, which means that the protic solvent pushes Mn−OOC(O)R species exclusively to undergo heterolytic cleavage to produce a discrete Mn^V=O intermediate as the dominant reactive species (Table 1, entry 10, eighth column, and Table S16). In contrast, an increase in the concentration of cyclohexene in the mixture H_2O/CH_3CN (1:4) slightly decreased the ratio of heterolysis to homolysis (Table 1, entries 10–13), indicating that the nonpolar substrate cyclohexene slightly retards the heterolytic cleavage, sensitive to the polar environment.[11]

To investigate the interaction between **2b** and a difficult-to-oxidize substrate, we used 1-octene. Using the same method as above, we increased the concentration of 1-octene in the presence of catalyst **1b** in toluene. The percentage of heterolysis to homolysis varied a little within possible experimental error (Table 1, entries 1–3, ninth column, and Table S17), while almost no change was observed in the other solvent systems (Table 1 and Tables S18–S20). These patterns indicate that there might be a small interaction between O−O bond cleavage and the 1-octene epoxidation reaction in the presence of **1b** only in toluene and no interaction in the other solvent systems.

As in the reaction of [(TMP)MnCl] (**1a**) with ethylbenzene, we changed the substrate to ethylbenzene, which is more difficult to oxidize. The ratios of heterolysis to homolysis did not vary with an increase in the concentration of ethylbenzene independent of the solvent polarity, as shown in Table 1 (entries 1–13, tenth column, and Tables S21–S24), suggesting that [(F_{20}TPP)Mn−OOC(O)R] 2**b** might not be involved in the oxidation reaction with the difficult-to-oxidize substrate ethylbenzene.

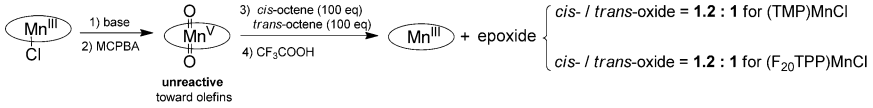
Competitive olefin epoxidation by manganese porphyrin complexes: To examine the selectivity of *cis*- and *trans*-2-octene by multiple oxidants,[15] we studied competitive epoxidations with two manganese(III) porphyrin complexes (**1a** and **1b**) and MCPBA as an oxidant in various solvent systems at room temperature under catalytic reaction conditions. The product ratios are listed in the seventh and eleventh columns of Table 1 and the yields of the epoxide products are shown in Tables S25 and S26.

The competitive epoxidations of *cis*- and *trans*-2-octene, which are considered to be easy-to-oxidize substrates, were first carried out with **1a** in toluene. Surprisingly, the ratios of *cis*- to *trans*-2-octene oxide formed in the reactions of MCPBA varied depending on the substrate concentration (1.8 for 40 mM and 2.5 for 160 mM; Table 1, entries 2 and 3, seventh column). When toluene was replaced with CH_2Cl_2, higher ratios of *cis*- to *trans*-2-octene oxide were obtained (Table 1, entries 5 and 6), relative to those in toluene. In CH_3CN, the ratios were even higher (Table 1, entries 8 and 9). In the most polar and protic solvent system, the mixture H_2O/CH_3CN (1:4), the highest ratio (13.0) was observed at a concentration of 160 mM with a large increase in the ratios (Table 1, entries 11–13). To our knowledge, the change in the ratios of *cis*- and *trans*-oxide depending on a change in the substrate concentration was first observed in metalloporphyrin-catalyzed olefin epoxidation. These results further support the contention that the reactions of the manganese porphyrin complexes with the peracids generate multiple reactive epoxidizing intermediates. If the reactive intermediate generated in the reactions of MCPBA is only one species, then the ratios of the oxide products formed in the competitive epoxidations would be the same independent of the concentration of substrate. In addition, the increase in the ratios of *cis*- and *trans*-2-octene oxide with increasing polarity of the solvent indicates that a greater portion of [(TMP)Mn−OOR] species **2a** among the multiple active oxidants, [(TMP)Mn^V=O] (**3a**), [(TMP)Mn^{IV}=O] (**4a**), and [(TMP)Mn^{III}−OOR] (**2a**), is involved in the olefin epoxidation with increasing polarity of the solvent. This proposal also agrees well with the product distributions of PPAA in the [(TMP)MnCl]-catalyzed epoxidation. On the other hand, the high ratio of *cis*- to *trans*-2-octene oxide observed in the [(TMP)MnCl] (**1a**) reaction might be attributable to the steric effect of the bulky MCPBA ligand bound to the manganese porphyrin, given that the approach of *trans*-olefin to [(TMP)Mn−OOR] **2a** is highly restricted by the steric hindrance between *trans*-olefin and the bulky MCPBA bound to manganese.[15]

When identical competitive epoxidations were carried out with [(F_{20}TPP)MnCl] (**1b**) in the same solvent systems, the ratios of *cis*- to *trans*-2-octene oxide formed in the reactions of MCPBA still varied with the change in the substrate concentration (Table 1, 11th column) but were smaller than those of [(TMP)MnCl] (**1a**). These results again indicate that the reactions of **1b** with peracids generate multiple reactive epoxidizing intermediates, at least to some extent. The decrease in the ratios of *cis*- to *trans*-oxide depending on the solvent polarity under the same concentration of substrate (40 or 160 mM) suggests that a larger portion of [(F_{20}TPP)Mn^V=O] species (**3b**) among the multiple active oxidants, [(F_{20}TPP)Mn^V=O] (**3b**), [(F_{20}TPP)Mn^{IV}=O] (**4b**), and [(F_{20}TPP)Mn−OOR] (**2b**), is involved in the olefin epoxidation upon increasing the polarity of the solvent system. This phenomenon is contrary to that observed with [(TMP)MnCl] (**1a**). In particular, in the protic solvent of the mixture H_2O/CH_3CN (1:4), the ratio of *cis*- to *trans*-2-octene oxide is close to 1 for a low concentration of substrate (20 mM; Table 1, entry 11, 11th column), suggesting that the reactive intermediates formed in the protic solvent might be predominantly the high-valent manganese(V) oxo intermediates. Again, this proposal matches well with the product distributions of PPAA in [(F_{20}TPP)MnCl]-catalyzed epoxidation in the mixture H_2O/CH_3CN (1:4). The slight increase in the ratios of *cis*- to *trans*-2-octene oxide depending on the substrate concentration in the mixture H_2O/CH_3CN (1:4) indicates that [(F_{20}TPP)Mn−OOR] species **2b** is also involved in olefin epoxidation reactions in the protic solvent

system, at least to a small extent, although to a much lower degree than with [(TMP)Mn–OOR] **2a**.

For comparison, we prepared dioxo-$Mn^{V}(TMP)^{-}$ and dioxo-$Mn^{V}(F_{20}TPP)^{-}$, under the conditions reported recently by Groves and Nam and co-workers (Figure S1 and S2),[3c,d] and carried out the competitive epoxidations of *cis*- and *trans*-2-octene with them upon the addition of trifluoroacetic acid (Scheme 3).[3d] Neutralization of the excess base with 1 equivalent of trifluoroacetic acid caused an instantaneous reaction with added *cis*- to *trans*-2-octene (1:1 mixture) at room temperature. The ratios of *cis*- to *trans*-2-octene oxide were found to be 1.2:1 for [(TMP)MnCl] and 1.2:1 for [(F_{20}TPP)MnCl] in CH_2Cl_2 (Tables S27 and S28).[16]



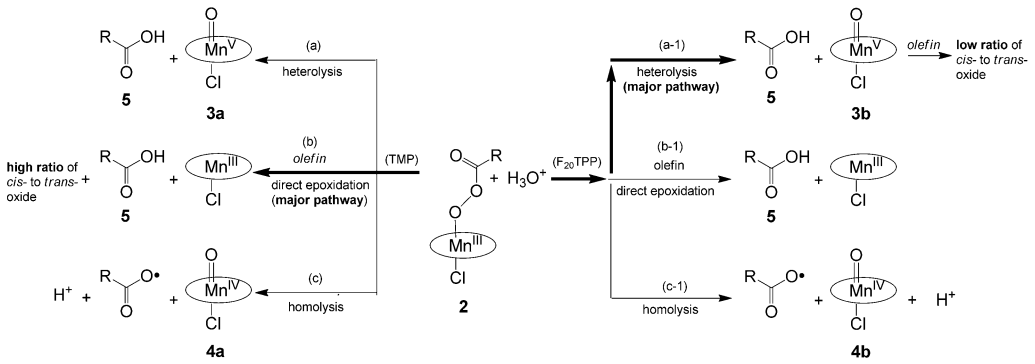
Scheme 3. Competitive epoxidation of *cis*- and *trans*-2-octene by dioxo-$Mn^{V}(TMP)^{-}$ and dioxo-$Mn^{V}(F_{20}TPP)^{-}$ upon the addition of trifluoroacetic acid.

It is worth noting that the intermediate of the high-valent manganese porphyrin complexes show the same preference for *trans*-olefin over *cis*-olefin, and, to the best of our knowledge, this is the first observation of a similar preference for *trans*-oxide over *cis*-oxide in manganese porphyrin catalyzed competitive epoxidations of *cis*- and *trans*-2-octene, although it has been reported in iron porphyrin catalyzed competitive epoxidations.[15a]

Moreover, a striking observation was that the *cis*- to *trans*-epoxide ratios and the patterns of the product distributions of PPAA obtained in the reactions of [(TMP)MnCl] (**1a**) and [(F_{20}TPP)MnCl] (**1b**) in the presence of cyclohexene in the mixture H_2O/CH_3CN (1:4) were very different (Table 1). This difference could possibly be explained by the lifetime of Mn–OOR intermediates **2** generated from the two manganese porphyrin complexes **1a** and **1b** with different electronic properties, assuming that [(F_{20}TPP)Mn–OOR] species **2b** generated from the more electron-deficient manganese porphyrin complex ([(F_{20}TPP)MnCl]; **1b**) might have a shorter lifetime than [(TMP)Mn–OOR] species **2a** generated from the more electron-rich Mn complex ([(TMP)MnCl]; **1a**).

In an effort to prove this assumption, we measured the pH values of **1a** and **1b** in the solvent system H_2O/CH_3CN (1:4). The pH values of **1a** and **1b** were determined to be 8.4 and 6.5, respectively. These values led us to conclude that the heterolytic O–O bond cleavage of [(F_{20}TPP)Mn–OOR] intermediate **2b** generated from **1b** containing the fluorinated electron-deficient porphyrin ligand is accelerated by general-acid catalysis at low pH to produce [(F_{20}TPP)Mn^{V}=O] intermediate **3b** (Scheme 4, pathway (a-1)),[11] whereas the O–O bond cleavage of [(TMP)Mn–OOR] intermediate **2a** generated from **1a** containing a methylated electron-rich porphyrin ligand is relatively retarded at high pH and **2a** has a long lifetime, transferring its oxygen atom to the olefin prior to the formation of [(TMP)Mn^{V}=O] (**3a**; Scheme 4, pathway (b)). This conclusion implies that the pH value of the active site in enzymes might be very important for determining the nature of the reactive intermediates responsible for hydrocarbon oxidations.[11,17]

Proposed mechanism for hydrocarbon oxidation by manganese(III) porphyrin complexes: Based on our results, the most plausible mechanism for the formation of the reactive species responsible for hydrocarbon oxidation by manganese porphyrin complexes could be as shown in Scheme 4. The peracid reacts with a manganese complex to form an initial Mn–acylperoxo intermediate ([Mn^{III}–OOC(O)R] (**2**)), which then undergoes either a heterolytic or hemolytic O–O bond cleavage to afford Mn^{V}=O (**3**) or Mn^{IV}=O (**4**) species, or which transfers its oxygen atom directly to the substrate. In the absence of a substrate, [(TMP)Mn–OOR] (**2a**) intermediate generated from the manganese porphyrin complex **1a** having electron-donating groups in aprotic solvents is cleaved both heterolytically



Scheme 4. Plausible mechanism for the formation of the reactive intermediates responsible for the hydrocarbon oxidations from the reaction of peracids with the manganese porphyrin complexes.

(ca. 70%) and homolytically (ca. 30%) to form high-valent manganese(V)–oxo species **3a** (pathway (a)) and high-valent manganese(IV)–oxo species **4a** (pathway (c)). The O–O bond cleavage of **2a** was shifted more to heterolysis (83%) in the protic solvent. In the presence of an easy-to-oxidize substrate, [(TMP)Mn–OOR] **2a** with a relatively long lifetime reacts directly with the easy-to-oxidize substrate (pathway (b)) as a major pathway to give a high ratio of *cis*- to *trans*-oxide, whereas the partitioning of heterolytic and homolytic O–O bond cleavage prevails in the presence of a difficult-to-oxidize substrate. When the manganese porphyrin complex **1b** having electron-withdrawing groups is used as a catalyst in the absence of substrate, [(F_{20}TPP)Mn–OOR] (**2b**) intermediate generated from **1b** with peracid in aprotic solvents is also cleaved both heterolytically (ca. 73%) and homolytically (ca. 27%), similar to the observation with [(TMP)MnCl] (**1a**), resulting in the formation of high-valent manganese(V)–oxo species **3b** (pathway (a-1)) and high-valent manganese(IV)–oxo species **4b** (pathway (c-1)). In addition, the O–O bond cleavage of **2b** was shifted much more to heterolysis (98%) by the general-acid catalysis in the protic solvent. In the presence of an easy-to-oxidize substrate, somewhat differently, a small portion of [(F_{20}TPP)Mn–OOR] **2b** with a relatively short lifetime reacts directly with the easy-to-oxidize substrate (pathway (b-1)) and a large portion of it undergoes partitioning of heterolytic and homolytic O–O bond cleavage in aprotic solvents, whereas in a protic solvent, the heterolytic O–O bond cleavage of **2b** occurs exclusively to produce high-valent manganese(V)–oxo species **3b** that show a ratio of *cis*- to *trans*-oxide close to 1 (pathway (a-1)). With the difficult-to-oxidize substrate, the partitioning of heterolytic and homolytic O–O bond cleavage of **2b** occurs in the aprotic solvents and its heterolytic O–O bond cleavage occurs exclusively in the protic solvent system.

This proposed mechanism based on our experimental data reminds us that "detection of a particular active oxidant under selected conditions will not necessarily demonstrate the identity of the active oxidant under catalytic turnover conditions", as Newcomb and co-workers stated.[4a]

Conclusion

Our results demonstrate that the participation of the multiple active oxidants Mn^{V}=O, Mn^{IV}=O, and Mn^{III}–OO(O)CR in hydrocarbon oxidation reactions by manganese porphyrin complexes is markedly affected by several factors, such as the solvent polarity, the concentration and type of substrate, and the porphyrin ligands. Moreover, the O–O bond activation mechanism shares many common features among Mn(salen), Mn(nonheme), and Mn(porphyrin) complexes. The results presented in this study not only may provide some useful information for understanding the mechanisms of the O–O bond activation of peracids and hydroperoxides by manganese porphyrin complexes, but also further support the hypothesis of multiple oxidants in enzyme-catalyzed oxidation reactions. More detailed mechanistic studies to elucidate the factors that influence the partitioning of heterolysis versus homolysis and the lifetime of the (porphyrin)Mn–OOR intermediate are currently underway in this laboratory.

Experimental Section

General: Cyclohexene, 1-octene, ethylbenzene, *cis*-2-octene, *trans*-2-octene, cyclohexene oxide, 1-octene oxide, cyclohexenol, cyclohexenone, acetophenone, *sec*-phenethyl alcohol, absolute toluene, mesitylaldehyde, 2,3,4,5,6-pentafluorobenzaldehyde, propionic acid, pyrrole, potassium carbonate, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, triethylamine, hexane, absolute methylene chloride, absolute acetonitrile, DMF, chloroform, trifluoroacetic acid, $Mn(OAc)_2$, $MgSO_4$, Na_2SO_4, and MCPBA (65%) were purchased from Aldrich Chemical Co. and were used without further purification. Peroxyphenylacetic acid (PPAA) was synthesized according to the literature method.[6,7] Manipulations of the porphyrins were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques unless otherwise noted. Solvents used in inert-atmosphere reactions were dried and degassed using standard procedures. Flash column chromatography was carried out with 230–400 mesh silica gel from Sigma–Aldrich using the wet-packing method. All deuterated solvents were purchased from Cambridge Isotope Laboratory.

Instruments: Product analyses for oxidation reactions and partition reactions of PPAA were performed on either a Hewlett–Packard 5890 II Plus gas chromatograph interfaced with Hewlett–Packard Model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with a FID detector using a 30 m capillary column (Hewlett–Packard, DB-5 or HP-FFAP). NMR spectra were recorded on a Varian AS400 (399.937 MHz for ^{1}H and 100.573 MHz for ^{13}C) spectrometer. ^{1}H chemical shifts are referenced to the proton resonance resulting from protic residue in deuterated solvent and ^{13}C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Absorbance and emission spectra were obtained using an Agilent UV/Vis/NIR spectrophotometer using quartz cells. Matrix-assisted laser-desorption-ionization time-of-flight mass spectra (MALDI-TOF) were obtained on a Bruker Daltonics LRF20 MALDI-TOF mass spectrometer at the Industry-Academic Cooperation Foundation.

Synthesis of tetramesitylporphyrin (TMP): Tetramesitylporphyrin was synthesized by modified literature procedures.[18] Under a nitrogen atmosphere, mesitylaldehyde (4 mL, 27.1 mmol) and freshly distilled pyrrole (1.9 mL, 27.1 mmol) were dissolved in chloroform (500 mL) in a 1 L round-bottomed flask equipped with a magnetic stirbar. The mixture was degassed for 10 min followed by an injection of boron trifluoride diethyl etherate (0.24 mL, 1.98 mmol) into the reaction solution by syringe. The reaction mixture was stirred at room temperature for 3 h under N_2. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1 g) was introduced to the reaction mixture and the resulting mixture was heated at reflux for a further 1 h. After cooling, triethylamine (0.33 mL) was injected by syringe and stirred for 10 min. The crude reaction mixture was evaporated to dryness using a rotary evaporator and the residue was purified by silica-gel column chromatography (methylene chloride/hexane 1:2 v/v) to afford pure TMP as a purple solid (635 mg, 11.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 8H), 7.3 (s, 8H), 2.61 (s, 12H), 1.85 (s, 24H), −2.50 ppm (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 134.4, 134.1, 133.1, 131.9, 121.1, 32.0, 21.9 ppm. MS (MALDI-TOF): m/z = 781.87 for [M^+]; calcd 783.05.

Synthesis of tetrakis(pentafluorophenyl)porphyrin (F_{20}TPP): Tetrakis-(pentafluorophenyl)porphyrin was synthesized by modified literature procedures.[18] 2,3,4,5,6-Pentafluorobenzaldehyde (1 g, 5.1 mmol) and pyrrole (0.342 g, 5.1 mmol) were dissolved in propionic acid (25 mL) in a 100 mL round-bottomed flask equipped with a magnetic stirbar and a water-cooled reflux condenser. The mixture was then allowed to reflux for 2.5 h under air. After cooling, the reaction mixture was evaporated to

dryness using a rotary evaporator to yield a dark residue, which was dissolved in methylene chloride. The resulting solution was washed with aqueous potassium carbonate (0.1 M) and water (50 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated to dryness using a rotary evaporator. The resulting residue was purified by silica-gel column chromatography (methylene chloride/hexane 1:3 v/v) to afford pure F_{20}TPP as a purple solid (200 mg, 16.0%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.92$ (s, 8H), -1.53 ppm (s, 2H). HRMS (MALDI-TOF): m/z calcd: 974.55 $[M^+]$; found: 973.14.

Synthesis of (tetramesitylporphyrinato)manganese(III) chloride (1a): A solution of TMP (235 mg, 0.3 mmol) and $Mn(OAc)_2$ (1.47 g, 6 mmol) in DMF (120 mL) was heated to reflux for 6 h. The reaction mixture was evaporated to dryness using a rotary evaporator. The resulting mixture was dissolved in methylene chloride and treated with 10% aqueous HCl at room temperature for 10 min. The organic layer was separated, dried over Na_2SO_4, filtered and concentrated to dryness using a rotary evaporator. The resulting solid was purified by alumina column chromatography (methylene chloride/hexane 1:1 v/v) to afford pure **1a** as a dark brown solid (214 mg, 82.0%). HRMS (MALDI-TOF): m/z calcd: 1009.00 $[M-Cl]^+$; found: 1009.31.

Synthesis of {tetrakis(pentafluorophenyl)porphyrinato}manganese(III) chloride (1b): A solution of F_{20}TPP (300 mg, 0.308 mmol) and $Mn(OAc)_2$ (230 mg, 0.924 mmol) in DMF (120 mL) was heated to reflux for 4 h under air. The reaction mixture was evaporated to dryness using a rotary evaporator. The resulting mixture was dissolved in methylene chloride and treated with 10% aqueous HCl at room temperature for 10 min. The solution was washed with water and organic layer was collected. The solution was dried over $MgSO_4$. After evaporation of solvent, the solid was purified by silica-gel column chromatography (methylene chloride/MeOH 9:1 v/v) to afford pure **1b** as a dark brown solid. HRMS (MALDI-TOF): m/z calcd: 1024.47 $[M-Cl]^+$; found: 1023.31.

Analysis of the O–O bond cleavage products from the oxidation reactions of substrates by Mn^{III} porphyrin complexes with PPAA: To a mixture of substrate (0–0.16 mmol), the Mn^{III} porphyrin complex (1.0×10^{-3} mmol), and solvent (1 mL) was added PPAA (0.04 mmol). The mixture was stirred for 10 min at room temperature. Each reaction was monitored by GC/MS analysis of 20 μL aliquots withdrawn from the reaction mixture. All reactions were run at least in triplicate and the average product yields are presented. Product yields were based on substrate or PPAA.

Competitive reactions of *cis*-2-octene and *trans*-2-octene by manganese(III) porphyrin complexes with MCPBA: To a mixture of *cis*-2-octene (0.01–0.08 mmol) and *trans*-2-octene (0.01–0.08 mmol), the Mn^{III} porphyrin complex (1.0×10^{-3} mmol), and solvent (1 mL) was added MCPBA (0.04 mmol). The mixture was stirred for 10 min at room temperature. Each reaction was analyzed by GC/MS analysis of 20 μL aliquots withdrawn from the reaction mixture. All reactions were run at least in triplicate and the average product yields are presented. Product yields were based on substrate or MCPBA.

Competitive reactions of *cis*-2-octene and *trans*-2-octene by dioxo-Mn^V(TMP)$^-$ and dioxo-$Mn^V(F_{20}TPP)^-$ upon the addition of trifluoroacetic acid: A solution of (TMP)$Mn^V(O)_2^-$ (3.0×10^{-3} mmol) was prepared by reacting (TMP)$Mn^{III}Cl$ (3.0×10^{-3} mmol) with 1 equiv MCPBA in the presence of 20 equiv TBAH in CH_2Cl_2 (1 mL) at room temperature. After *cis*-2-octene (0.3 mmol) and *trans*-2-octene (0.3 mmol) were added to the reaction solution, it was stirred for 5 min at room temperature. Then, trifluoroacetic acid (6.0×10^{-2} mmol) was added to the mixture. The same method was used to make dioxo-$Mn^V(F_{20}TPP)^-$. All reactions were run at least in triplicate and the average product yields are presented. Product yields were based on manganese(III) porphyrin.

Acknowledgements

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