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Solvent Effects on Catalytic Epoxidation of Alkenes by Tetra-*n*-butylammonium Periodate and (Tetraarylporphyrinato)manganese(III)

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The epoxidation of cyclooctene and *cis*-stilbene was performed by tetra-*n*-butylammonium periodate ($n\mathrm{Bu_4NIO_4}$) in the presence of (tetraarylporphyrinato)manganese(III) [Mn(por)] and imidazole (im) in various CH_2Cl_2/alcohol solvents (alcohol = CH_3OH, C_2H_5OH, $n\text{-}C_3H_7OH$, $i\text{-}C_3H_7OH$, $t\text{-}C_4H_9OH$). In accord with the coordinating abilities of the alcohols to [Mn(por)], the epoxidation yields increased from CH_2Cl_2/CH_3OH to $CH_2Cl_2/t\text{-}C_4H_9OH$. In the epoxidation of *cis*-stilbene in the presence of (acetato)(tetraphenylporphyrinato)manganese(III) [Mn(tpp)(OAc)], the *cis*- to *trans*-stilbene oxide ratio increased consistently with the bulk of the alcohol in CH_2Cl_2/alcohol solvents. Also, it was found that the interaction of [Mn(tpp)(OAc)] and (acetato)(tetramesitylporphyrinato)manganese(III) [Mn(tmp)(OAc)] with $n\mathrm{Bu_4NIO_4}$ in the presence of imidazole but in the absence of alkenes yields $[\mathrm{Mn(tpp)(O)(im)}]^+$ and $[\mathrm{Mn(tmp)(O)(im)}]^+$ complexes. The formation of the Mn=O species for the small linear alcohols was faster than that for the larger ones, whereas the stability of the Mn=O complex was greater in the presence of the bulkier alcohols. Attempts were made to explain these effects.

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Introduction

Since the pioneering work of Groves and coworkers on the development of synthetic metalloporphyrin models of cytochrome P-450, considerable efforts have been devoted to the understanding of the factors that may control the activity and selectivity of alkene epoxidation by using various metalloporphyrin catalytic systems.[1] Particular attention has been given to the ratios of *cis*/*trans*-stilbene oxide obtained from *cis*-stilbene epoxidation as a probe for the stereoselectivity of P-450 model systems.[1b,2] The exact ratio of the *cis* to *trans* epoxides in these cases, which depends upon the nature of the catalyst and the reaction conditions, has been taken as evidence for the presence of a transient radical species in the general reaction scheme that allows limited rotation about the former alkene bond prior to epoxide ring closure.[1b]

Recent studies have also indicated that the composition of alcohol/acetonitrile and alcohol/CH_2Cl_2 have important effects on the epoxidation reactions by hydrogen peroxide and iron porphyrins.[3] It has been proposed that alcohols function as general acid catalysts and can facilitate O–O bond cleavage.[4] Furthermore, the product ratios for competitive epoxidation of *cis*- and *trans*-stilbene have been correlated with the acidity of the alcohol.[5] In contrast, the generation, characterization, and reactivity studies of (oxido)(porphyrinato)manganese intermediates, under various reaction conditions, have received considerable attention due to their significant roles in the oxygenation of hydrocarbons and as models for P-450 enzymes.[6]

In this report, we demonstrated that the epoxidation yields of cyclooctene and *cis*-stilbene by a mild single-oxygen donor tetra-*n*-butylammonium periodate ($n\mathrm{Bu_4NIO_4}$)[7] in the presence of (tetraarylporphyrinato)manganese(III) [Mn(por)], Figure 1, and imidazole (im) are critically dependent upon the nature of the alcohols in CH_2Cl_2/alcohol solvents. Apparently, the coordinating abilities of the alcohols and their steric and hydrogen-bonding properties can make great differences in terms of the epoxidation yields, *cis*- to *trans*-stilbene oxide ratios, and the formation and stabilization of $[\mathrm{Mn(por)(O)(im)}]^+$ species. The advantage of utilizing neutral $n\mathrm{Bu_4NIO_4}$ rather than H_2O_2 or *m*-chloroperoxybenzoic acid as oxidant in this study is that $n\mathrm{Bu_4NIO_4}$ is a nonhydrogen-bond donor species and would not interfere with the hydrogen bonding of the alcohols. For the case in which the oxidants contain strong hydrogen-bond donor O–H group(s), the hydrogen bonding of the alcohols are apparently disguised by those of the oxidants and consequently no definitive conclusions can be drawn concerning their effects.

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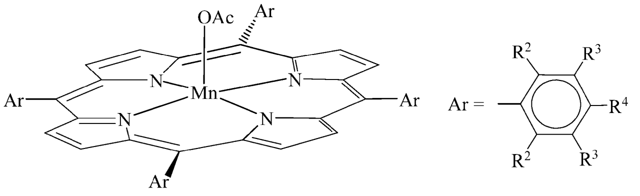

	R^2	R^3	R^4
Mn(tpp)(OAc)	H	H	H
Mn(tmp)(OAc)	CH_3	H	CH_3
Mn(tdcpp)(OAc)	Cl	H	H
Mn(tpfpp)(OAc)	F	F	F

Figure 1. (Tetraarylporphyrinato)manganese(III) complexes used in this study.

Results and Discussion

Cyclooctene Epoxidation

The results of cyclooctene epoxidation by $n\mathrm{Bu_4NIO_4}$ in the presence of four [Mn(por)] units in CH_2Cl_2 containing various alcohols with different acidities (pK_a values) and steric properties are presented in Table 1. The epoxidation reactions proceeded with absolute selectivity (100%) and yielded only cyclooctene oxide. A control experiment for the "best" catalytic system indicated that the % of effectively transferred oxygen was 57 % in 5 h and 89% after 24 h (Table 1, Entry 5). In the absence of imidazole the epoxidation yields were very low for both CH_2Cl_2/alcohol solvents (<7%) and neat CH_2Cl_2 (<3%; Table 1, Entries 7, 8). Consideration of the reaction times and the epoxidation yields clearly suggested the following order of catalytic activities for [Mn(por)]: [Mn(tpfpp)(OAc)] < [Mn(tdcpp)(OAc)] < [Mn(tmp)(OAc)] < [Mn(tpp)(OAc)]. Accordingly, the electron-poor and/or bulky [Mn(por)] are less-effective catalysts than the electron-rich ones with less steric hindrance.[8] In contrast, the epoxidation yields for [Mn(por)] were found to be directly related to the steric bulk of the alcohols and increased in the order $CH_3OH < C_2H_5OH < n\text{-}C_3H_7OH < i\text{-}C_3H_7OH < t\text{-}C_4H_9OH$. This seems to be quite consistent with the reversed order of coordinating abilities of the alcohols to [Mn(por)].[9]

In order to see how the presence of coordinating CH_3OH versus noncoordinating $t\text{-}C_4H_9OH$ can affect the epoxidation yields, we performed two different series of epoxidation reactions. In the first series, the only variable was the ratio of im/[Mn(tpp)(OAc)], whereas in the second series, the amounts of the alcohols were changed at a fixed im/[Mn(tpp)(OAc)] ratio.

It was found that the cyclooctene epoxidation yields were quite dependent upon the im/[Mn(tpp)(OAc)] ratio in the various solvents (Table 2). They initially increased to a maximum value by increasing the im/[Mn(tpp)(OAc)] ratio, and they then decreased at higher ratios (Figure 2). The interaction of imidazole with [Mn(tpp)(OAc)] is expected to lead to the formation of both the catalytically active 1:1 [Mn(tpp)(OAc)(im)] and the catalytically inactive 2:1 $[Mn(tpp)(im)_2]OAc$ complexes in equilibrium with [Mn(tpp)(OAc)].[10] Before the maximum yield was reached, the concentration of the 1:1 complex continuously increased by adding imidazole, whereas beyond the maximum yield the further addition of imidazole led to the formation of the inactive 2:1 complex at the expense of the 1:1 complex, which caused a reduction in the epoxidation yields.

Table 2. Cyclooctene epoxidation yields (%) for different im/[Mn(tpp)(OAc)] ratios in various solvents.[a]

Solvent	im/[Mn(tpp)(OAc)] molar ratio							
	0	1	5	10	25	50	100	200
CH_2Cl_2	<3	40	68	78	70	56	37	24
CH_2Cl_2/CH_3OH	7	10	24	45	65	69	61	50
$CH_2Cl_2/t\text{-}C_4H_9OH$	5	49	81	100	98	83	72	67

[a] The molar ratio of [Mn(tpp)(OAc)]/im/cyclooctene/periodate was 1/x/83/167; (x = 0, 1, 5, 10, 25, 50, 100, 200) with a concentration of [Mn(tpp)(OAc)] of 3×10^{-3} M. The reactions were carried out for 5 h at 22 ± 2 °C.

Table 1. Epoxidation of cyclooctene by $n\mathrm{Bu_4NIO_4}$ in the presence of [Mn(por)] catalysts in various solvents.[a,b]

Entry	Solvent	pK_a[c]	[Mn(tpp)(OAc)] Yield / %, 5 h	[Mn(tmp)(OAc)] Yield / %, 5 h	[Mn(tdcpp)(OAc)] Yield / %, 24 h	[Mn(tpfpp)(OAc)] Yield / %, 24 h
1	CH_2Cl_2/CH_3OH[d]	15.3	45	17	41	11
2	CH_2Cl_2/C_2H_5OH[d]	15.9	58	25	45	14
3	$CH_2Cl_2/n\text{-}C_3H_7OH$[d]	16.1	69	34	49	17
4	$CH_2Cl_2/i\text{-}C_3H_7OH$[d]	17.1	86	42	57	28
5	$CH_2Cl_2/t\text{-}C_4H_9OH$[d]	19	100 (57)[e]	60	76	38
6	CH_2Cl_2[f]		78	58	56	16
7	CH_2Cl_2/CH_3OH[g]		7 (<3)[h]	5 (<2)[h]	5 (0)[h]	6 (0)[h]
8	CH_2Cl_2[i]		<3	0	0	0

[a] The molar ratio for [Mn(por)]/im/cyclooctene/periodate was 1:10:83:167 with a concentration of [Mn(por)] of 3×10^{-3} M at 22 ± 2 °C. [b] The epoxidation yields (%) were measured relative to starting cyclooctene. All the reactions were run at least in triplicate, and the data represent an average of these reactions with ±8–10%. [c] The pK_a values were obtained from ref.[12] [d] The reactions were carried out in CH_2Cl_2 (1 mL)/alcohol (0.5 mL). [e] The yield for a control experiment at the molar ratio of [Mn(tpp)(OAc)]/im/cyclooctene/periodate, 1:10:83:83. The % yield increased with time to 74% (8 h) and 89% (24 h), and then the reaction was discontinued. [f] The reactions were performed in CH_2Cl_2 (1 mL) with no alcohol present. [g] The reactions were carried out in CH_2Cl_2 (1 mL)/CH_3OH (0.5 mL) with no imidazole. [h] The numbers in the parentheses are for $CH_2Cl_2/t\text{-}C_4H_9OH$, under similar conditions. [i] The reactions were carried out in neat CH_2Cl_2 (1 mL) with no imidazole.

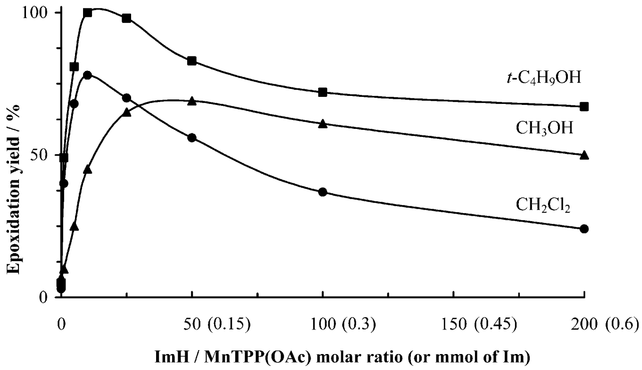

Figure 2. Cyclooctene epoxidation yield (%) vs. im/[Mn(tpp)(OAc)] molar ratio (or vs. number of mmols of imidazole).

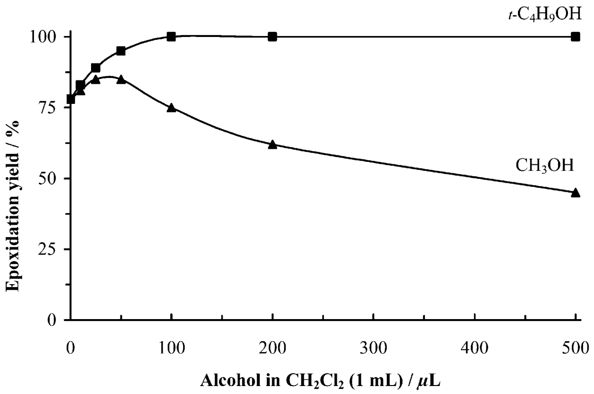

Figure 3. Cyclooctene epoxidation yields (%) vs. number of µL of CH_3OH or t-C_4H_9OH in CH_2Cl_2 (1 mL).

It is notable that the epoxidation curves for both neat CH_2Cl_2 and CH_2Cl_2/t-C_4H_9OH solvents generally displayed sharper increases and decreases than that of CH_2Cl_2/CH_3OH (Figure 2). This is presumably related to the coordination of CH_3OH to [Mn(tpp)(OAc)] to form [Mn(tpp)(OAc)(CH_3OH)] and [Mn(tpp)(CH_3OH)$_2$]OAc;[9] hence, the formation of both catalytically active [Mn(tpp)(OAc)(im)] and inactive [Mn(tpp)(im)$_2$]OAc species was hindered. However, the greater epoxidation yields observed in CH_2Cl_2/t-C_4H_9OH as solvent than that obtained in neat CH_2Cl_2 at all im/[Mn(tpp)(OAc)] ratios must reflect the important solvation effects of t-C_4H_9OH.[9]

In contrast, the cyclooctene epoxidation yields varied very differently by analogous changes in the amounts of CH_3OH and t-C_4H_9OH in CH_2Cl_2 (Table 3). The addition of 10 to 100 µL of t-C_4H_9OH into the reaction solution gradually increased the epoxidation yields to a fixed maximum value, and further addition of the alcohol had no effect (Figure 3). In the case of CH_3OH, the maximum epoxidation yield was achieved at a much smaller amount of the alcohol (≈25 µL) and more addition of CH_3OH (ca. >50 µL) decreased the epoxidation yields.

Table 3. Cyclooctene epoxidation yields (%) in various CH_2Cl_2/CH_3OH and CH_2Cl_2/t-C_4H_9OH solvents.[a]

Solvents	Alcohol (µL)/CH_2Cl_2 (1 mL) ratio						
	0	10	25	50	100	200	500
CH_2Cl_2/CH_3OH	78	80	85	85	75	62	45
CH_2Cl_2/t-C_4H_9OH	78	83	89	95	100	100	100

[a] The molar ratio for [Mn(tpp)(OAc)]/im/cyclooctene/periodate was 1:10:83:167 with a concentration of [Mn(tpp)(OAc)] of 3×10^{-3} M in CH_2Cl_2 at 22 ± 2 °C.

The initial increases observed in the epoxidation yields by adding small amounts of CH_3OH (<25 µL) and t-C_4H_9OH (<100 µL) presumably reflect the solvation effects of the alcohols. At the low concentrations of CH_3OH where its coordination to [Mn(tpp)(OAc)] is not so significant, apparently the solvation effect is the predominant factor, and hence, the epoxidation yield is enhanced by increasing the amount of CH_3OH. However, the solvation process would reach its saturation level at some concentration of CH_3OH (≈50 µL) and t-C_4H_9OH (≈100 µL). Beyond these limits, further addition of the coordinating CH_3OH should cause a reduction in the catalytic activity of [Mn(tpp)(OAc)], whereas for the noncoordinating t-C_4H_9OH no particular effect is expected and observed.

cis-Stilbene Epoxidation

The results of epoxidation of *cis*-stilbene in the presence of varied [Mn(por)] in various CH_2Cl_2/alcohol solvents are given in Table 4. Although the oxidation of *cis*-stilbene by the [Mn(tpp)(OAc)] catalyst led to various mixtures of *cis*- and *trans*-stilbene oxides, its reactions with other [Mn(por)] catalysts proceeded with absolute stereoselectivity and pure *cis*-stilbene oxide was the sole product. Again, the epoxidation yields were very sensitive to the nature of the alcohols and increased in the order CH_3OH < C_2H_5OH < n-C_3H_7OH < i-C_3H_7OH < t-C_4H_9OH for every [Mn(por)].

A novel finding was that the *cis*/*trans*-stilbene oxide ratio in the epoxidation of *cis*-stilbene by [Mn(tpp)(OAc)] was dependent upon the molecular size of the alcohol and increased as the steric bulk of the alcohol increased. For the linear alcohols, the ratios were rather close (≈14 ± 2; Table 4, Entries 1–3), whereas for the bulky alcohols they were quite different and much higher than those for the linear ones (Table 4, Entries 4, 5). These results suggest that the steric properties of the alcohols can have an important role in determining the ratio of *cis*/*trans*-stilbene oxide.

Formation of hydrogen bonds between the alcohols and the expected active oxidant(s)[8b] can cause significant steric hindrance at the oxygenation site (Figure 4). In the course of epoxidation of *cis*-stilbene, the formation of *trans*-stilbene oxide requires free rotation about the alkene C=C bond. Such a rotation is expected to be hindered by the steric interactions of the hydrogen-bonded alcohols. It is apparent that the bulkier alcohols can generate a greater hindrance than the linear ones, and consequently a larger *cis*/*trans*-stilbene oxide ratio would result. Observation of the same *cis*/*trans*-stilbene oxide ratio of 12 for both neat

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Table 4. Epoxidation of *cis*-stilbene by $n\mathrm{Bu_4NIO_4}$ in the presence of [Mn(por)] catalysts in various solvents.[a,b]

Entry	Solvent	[Mn(tpp)(OAc)]				[Mn(tmp)(OAc)]	[Mn(tdcpp)(OAc)]	[Mn(tpfpp)(OAc)]
		Conv. / % 5 h	*cis* oxide	*trans* oxide	*cis*/*trans* ratio	*cis* oxide, 5 h	*cis* oxide, 24 h	*cis* oxide, 24 h
1	CH_2Cl_2/CH_3OH[c]	70.5	65	5.5	12	25	23	14
2	CH_2Cl_2/C_2H_5OH[c]	85.5	80	5.5	14.5	27	28	17
3	$CH_2Cl_2/n\text{-}C_3H_7OH$[c]	88	83	5	16.5	31	31	18
4	$CH_2Cl_2/i\text{-}C_3H_7OH$[c]	92	88	4	22	36	42	31
5	$CH_2Cl_2/t\text{-}C_4H_9OH$[c]	95	92	3	≈31	39	55	37
6	CH_2Cl_2[d]	80	74	6	12	48	35	26
7	CH_2Cl_2/CH_3OH[e]	5(<3)[f]				2 (0)[f]	3 (0)[f]	3 (0)[f]
8	CH_2Cl_2[g]	<2				0	0	0

[a] The molar ratio for [Mn(por)]/im/*cis*-stilbene/periodate was 1:10:83:167 with a concentration of [Mn(por)] of 3×10^{-3} M, at 22 ± 2 °C. [b] The epoxidation yields (%) were measured relative to the starting *cis*-stilbene. All the reactions were run at least in triplicate, and the data represent an average of these reactions with ±5–7%. [c] The reactions were carried out in CH_2Cl_2 (1 mL)/alcohol (0.5 mL). [d] The reactions were performed in neat CH_2Cl_2 (1 mL) with no alcohol present. [e] The reactions were carried out in CH_2Cl_2 (1 mL)/CH_3OH (0.5 mL) with no imidazole. [f] The numbers in the parentheses are for $CH_2Cl_2/t\text{-}C_4H_9OH$ under similar conditions. [g] The reactions were carried out in neat CH_2Cl_2 (1 mL) with no imidazole or alcohol.

CH_2Cl_2 (Table 4, Entry 6) and CH_2Cl_2/CH_3OH (Table 4, Entry 1) suggests analogous overall steric effects for the solvation of the active oxidant(s) by CH_3OH and CH_2Cl_2. Absence of any *trans*-stilbene oxide for the epoxidation of *cis*-stilbene by the other [Mn(por)] catalysts indicates that the steric hindrance at their oxygenation site is so great that no rotation about the alkene bond is possible.

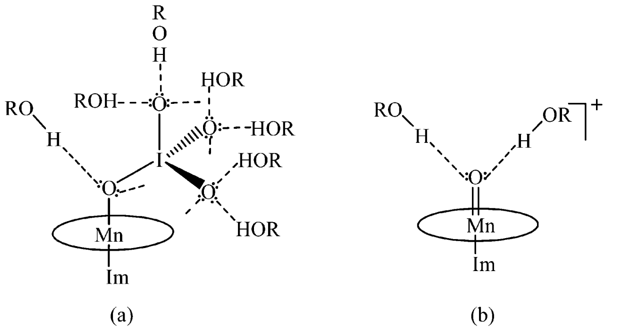

Figure 4. Possible hydrogen bonding of ROH to the oxygen donor sites of the presumed active oxidants: (a) $[\mathrm{Mn(por)(IO_4)(im)}]$ and (b) $[\mathrm{Mn(por)(O)(im)}]^+$. Some hydrogen-bonded ROH groups are omitted for clarity and their likely positions are indicated by dashed lines.

The epoxidation yields for alkenes are expected to be related to the stereoelectronic properties of the species involved. *cis*-Stilbene is bulkier than cyclooctene, but it contains a more electron-rich C=C bond because of π resonance with the phenyl rings. The higher epoxidation yields for *cis*-stilbene than cyclooctene in the presence of the least hindered [Mn(tpp)(OAc)] catalyst in all the solvents, except $CH_2Cl_2/t\text{-}C_4H_9OH$, clearly suggests that the electron-rich C=C bond is more reactive than the electron-poor one. However, the steric effects become the dominating factor when bulky [Mn(por)] catalysts and/or bulky alcohols are employed.

Active Oxidant

[Mn(tpp)(OAc)]

The UV/Vis spectra for the interaction of [Mn(tpp)(OAc)] with $n\mathrm{Bu_4NIO_4}$ in CH_2Cl_2 in the absence or presence of imidazole, and also in CH_2Cl_2/alcohol solvents containing imidazole, are shown in Figure 5. The Soret band for [Mn(tpp)(OAc)] in CH_2Cl_2 (λ_{max} = 478 nm) displayed no changes upon the addition of an excess amount of $n\mathrm{Bu_4NIO_4}$ {$n\mathrm{Bu_4NIO_4}$/[Mn(tpp)(OAc)], 200; solution **a**; Figure 5a}. This suggests that the replacement of OAc^- by IO_4^- and the formation of $[\mathrm{Mn(tpp)(IO_4)}]$ has no effect on the UV/Vis spectrum. In contrast, addition of imidazole into solution **a** {im/[Mn(tpp)(OAc)], 100; solution **b**} caused some broadening and intensity loss of the corresponding Soret band (λ_{max} = 474 nm) and also broadening and intensification of the band ≈404 nm (Figure 5b). However, contrary to solution **a**, the [Mn(por)] species was unstable in solution **b** and degraded in ca. 30 min. This indicates that coordination of imidazole to $[\mathrm{Mn(tpp)(IO_4)}]$ yields a highly active oxidant.[8b] When 50 μL of $t\text{-}C_4H_9OH$ was added into solution **b** (2 mL) to give solution **c**, the UV/Vis spectrum reduced in intensity and broadened (Figure 5c). However, the presence of $t\text{-}C_4H_9OH$ in solution **c** greatly increased the lifetime of the [Mn(por)] species, and the UV/Vis spectrum did not change much over a period of 2 h. For CH_3OH (50 μL) in solution **b** (yielding solution **d**), the UV/Vis spectrum dramatically changed and a new broad band appeared rapidly (λ_{max} = 416 nm; Figure 5d). The other alcohols also gave similar UV/Vis spectra and produced new broad bands (λ_{max} = 414 ± 2 nm). This band, which is presumably due to $[\mathrm{Mn(tpp)(O)(im)}]^+$,[11] disappeared rapidly in the presence of cyclooctene.

The UV/Vis spectra for a 30 min interaction of [Mn(tpp)(OAc)] (10^{-5} M) with $n\mathrm{Bu_4NIO_4}$ in the presence of imidazole in various CH_2Cl_2/alcohol solvents are presented

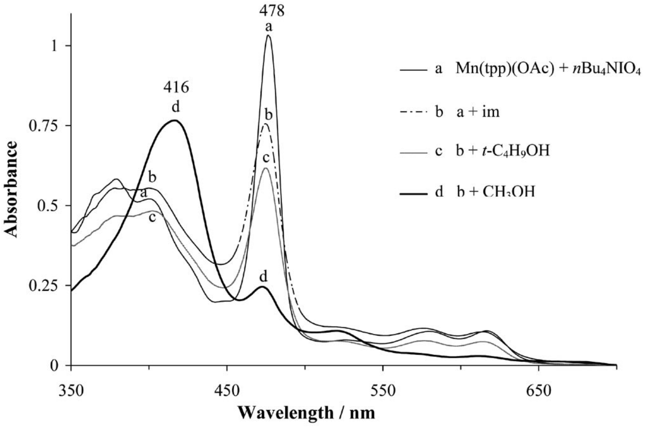

Figure 5. UV/Vis spectra for the interaction of [Mn(tpp)(OAc)] (10^{-5} M) with an excess amount of $n\mathrm{Bu_4NIO_4}$: (a) in neat CH_2Cl_2; (b) in CH_2Cl_2 containing imidazole; (c) in CH_2Cl_2 (2 mL)/t-C_4H_9OH (50 µL) containing imidazole; (d) in CH_2Cl_2 (2 mL)/CH_3OH (50 µL) containing imidazole. All the spectra were recorded 5 min after adding $n\mathrm{Bu_4NIO_4}$, as the last component, at room temperature.

in Figure 6. It is shown that the conversion of the [Mn(tpp)(IO_4)(im)] complex ($\lambda_{\max}$ = 478 nm) into $[\mathrm{Mn(tpp)(O)(im)}]^+$ ($\lambda_{\max}$ = 414 nm) is virtually complete in CH_2Cl_2/CH_3OH and the relative intensities of the Mn=O bands for different alcohols increases in accord with their acid strengths, that is, $CH_3OH > C_2H_5OH > n\text{-}C_3H_7OH > i\text{-}C_3H_7OH > t\text{-}C_4H_9OH$. In the case of bulky i-C_3H_7OH and t-C_4H_9OH, the formation of Mn=O species is far from completion and their corresponding UV/Vis spectra did not display many changes over a period of several hours. In fact, $[\mathrm{Mn(tpp)(O)(im)}]^+$ showed unusually high stability in all CH_2Cl_2/alcohol solvents, particularly in the presence of the bulkier alcohols.

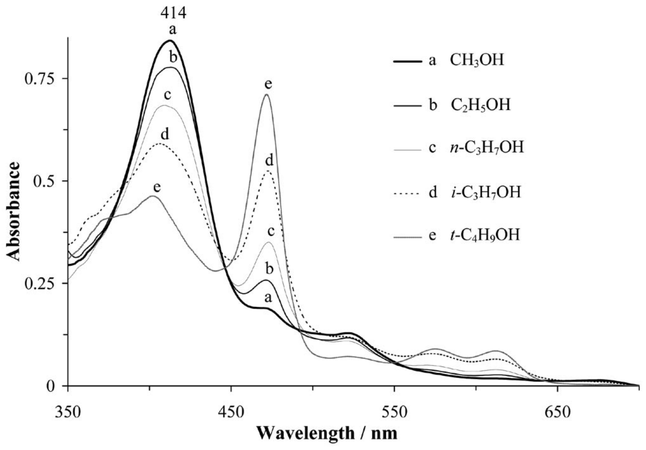

Figure 6. The UV/Vis spectra of [Mn(tpp)(OAc)] (2×10^{-5} mmol)/im (2×10^{-3} mmol)/$n\mathrm{Bu_4NIO_4}$ (5×10^{-3} mmol) in CH_2Cl_2 (2 mL)/alcohol (50 µL) solvents [alcohol = CH_3OH (a); C_2H_5OH (b); nC_3H_7OH (c); i-C_3H_7OH (d); t-C_4H_9OH (e)]. All the spectra were recorded 30 min after the final addition of $n\mathrm{Bu_4NIO_4}$, at room temperature.

It is noteworthy that the steric strains at the oxygenation sites of the two possible active oxidants (Figure 4) must be different. Thus, it is expected that the oxygenation of *cis*-stilbene by bulky [Mn(tpp)(IO_4)(im)] would result in a higher *cis*/*trans*-stilbene oxide ratio than by the less-hindered $[\mathrm{Mn(tpp)(O)(im)}]^+$.[8b] In contrast, on the basis of the UV/Vis spectra, different ratios of these active oxidants might be available in the epoxidation of *cis*-stilbene by $n\mathrm{Bu_4NIO_4}$ and [Mn(tpp)(OAc)] in the presence of imidazole in various CH_2Cl_2/alcohols solvents. Indeed, the lower *cis*/*trans*-stilbene oxide ratios obtained for the smaller alcohols relative to those of the bulkier ones (Table 4) might be partly due to the higher $[\mathrm{Mn(tpp)(O)(im)}]^+$/[Mn(tpp)($IO_4$)(im)] ratios in the presence of the smaller alcohols.

[Mn(tmp)(OAc)]

The UV/Vis spectra for various solutions of [Mn(tmp)(OAc)] in CH_2Cl_2 containing only $n\mathrm{Bu_4NIO_4}$ {$n\mathrm{Bu_4NIO_4}$/[Mn(tmp)(OAc)], 200; solution **a**} or imidazole {im/[Mn(tmp)(OAc)], 50; solution **b**} in the presence of t-C_4H_9OH (solution **c**) or CH_3OH (solution **d**) are given in Figure 7. Similar to [Mn(tpp)(OAc)], the UV/Vis spectra for [Mn(tmp)(OAc)] in neat CH_2Cl_2 ($\lambda_{\max}$ = 478 nm), with or without an excess amount of $n\mathrm{Bu_4NIO_4}$, were exactly the same (Figure 7a). However, in contrast to [Mn(tpp)(OAc)], addition of imidazole into solution **a** generated a new distinct band ($\lambda_{\max}$ = 414 nm), which was presumably related to the $[\mathrm{Mn(tmp)(O)(im)}]^+$ species (Figure 7b).[11c] When t-C_4H_9OH (50 µL) was added into solution **b** (2 mL), the solution **c** obtained also displayed a similar band ($\lambda_{\max}$ = 410 nm; Figure 7c). For CH_3OH in solution **b** (producing solution **d**), the spectral changes due to the formation of the $[\mathrm{Mn(tmp)(O)(im)}]^+$ complex were very dramatic (Figure 7d).

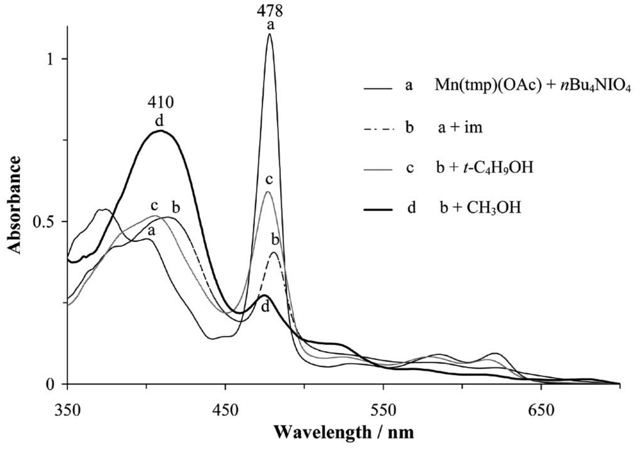

Figure 7. UV/Vis spectra for the interaction of [Mn(tmp)(OAc)] (10^{-5} M) with an excess amount of $n\mathrm{Bu_4NIO_4}$: (a) in neat CH_2Cl_2; (b) in CH_2Cl_2 containing imidazole; (c) in CH_2Cl_2 (2 mL)/t-C_4H_9OH (50 µL) containing imidazole; (d) in CH_2Cl_2 (2 mL)/CH_3OH (50 µL) containing imidazole. All the spectra were recorded 2 h after adding $n\mathrm{Bu_4NIO_4}$, as the last component, at room temperature.

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Similar to [Mn(tpp)(OAc)], the formation of Mn=O species in the presence of alcohols of smaller molecular size was faster than that for the larger ones (Figure S1). Also, the stability of the Mn=O species was considerably greater in the presence of the bulkier alcohols. However, in every case the lifetime of $[Mn(tmp)(O)(im)]^+$ was much longer than that of $[Mn(tpp)(O)(im)]^+$.

These results clearly indicate that the formation rates of Mn=O species and their relative stabilities strongly depend upon the nature of the alcohols. Apparently, hydrogen bonding between the alcohols and the coordinated periodate (Figure 4) can facilitate the heterolytic cleavage of $MnO–IO_3$ bond[3,4] and the formation of a $[Mn(por)(O)(im)]^+$ species. Furthermore, the obtained IO_3^- and $[Mn(por)(O)(im)]^+$ will be stabilized by hydrogen bonding to the alcohols. Accordingly, small alcohols with stronger acidities and hydrogen-bonding capabilities than those of the larger ones can yield Mn=O species more efficiently, as observed. In contrast, the resulting Mn=O species are stabilized more effectively by the larger alcohols than the smaller ones, as the former can cause greater hindrance and shielding of the active oxidant(s) through hydrogen bonding.

The UV/Vis spectra for the interaction of the electron-poor [Mn(tpfpp)(OAc)] (Figure S2) and [Mn(tdcpp)(OAc)] (not shown) with $n\mathrm{Bu_4NIO_4}$ in various CH_2Cl_2/alcohol solvents showed no sign of formation of Mn=O species, which indicates that the occurrence of the Mn=O complex requires an electron-rich porphyrin. Accordingly, the primary active oxidizing species for the electron-poor [Mn(por)] is presumably the $[Mn(por)(IO_4)(im)]$ complex. However, $[Mn(por)(O)(im)]^+$ may occur transiently.

Conclusions

The effects of alcohols in CH_2Cl_2/alcohol solvents upon the epoxidation of alkenes by $n\mathrm{Bu_4NIO_4}$ and [Mn(por)] in the presence of imidazole are apparently related to their steric bulk and/or acidities. Coordination of the alcohols to [Mn(por)], which is more efficient for smaller alcohols than for larger ones, would lead to reduction of the epoxidation yields. In contrast, solvation of the active oxidants by the bulkier alcohols causes a longer lifetime of the active oxidant(s) and greater steric hindrance at the oxygenation site(s) than that achieved by the smaller ones. Finally, the smaller alcohols with stronger acidities and hydrogen-bonding capabilities than those of the larger ones produce Mn=O complexes more rapidly.

Experimental Section

General: All the solvents were distilled under an atmosphere of nitrogen prior to use. Dichloromethane was purified by distillation over P_2O_5 or CaH_2 before use and stored over molecular sieves (Linde 4A). Reagent-grade carbon tetrachloride was dried by passing it through activity I neutral alumina and stored over molecular sieves (Linde 4A). *n*-Pentane, methanol (99.8%), ethanol (99.6%), *n*-propanol (99.8%), and isopropyl alcohol (99.5%) were obtained from Merck or Fluka, and *tert*-butyl alcohol (99.4%) was purchased from Aldrich. Deionized, double-glass distilled water was used for all experiments. Alkenes were obtained from Fluka and Merck. The purity of the starting alkenes was checked by gas chromatography or NMR spectroscopy to ensure that no oxidation products were present before the reactions. A constant temperature bath was used to maintain the temperature at 22 ± 2 °C.

Materials: Porphyrin ligands were prepared by previously reported procedures,[13] and manganese was inserted by standard route.[14] Tetra-*n*-butylammonium periodate was synthesized by the method of Santaniello[15] with some modifications. A solution of $NaIO_4$ (2.14 g, 100 mmol) in water (10 mL) was added with stirring to a solution of tetra-*n*-butylammonium hydrogen sulfate ($n\mathrm{Bu_4NHSO_4}$; 3.4 g, 100 mmol) in water (20 mL). The precipitated $n\mathrm{Bu_4NIO_4}$ was dissolved in CH_2Cl_2 (50 mL), and the organic phase was dried with magnesium sulfate ($MgSO_4$) or sodium sulfate (Na_2SO_4) and then filtered. After evaporation of the solvent, the remaining paste was washed with hexane (10 mL) and dried under vacuum.

Instrumentation: Electronic absorption spectra were recorded with a MultiSpect-1501 Shimadzu spectrophotometer. ^{1}H NMR spectra were recorded with a Bruker Avance DPX 250 MHz spectrometer. GC analyses were performed with a Shimadzu 14A series gas chromatograph capillary column and a flame-ionization detector. The separation of products was achieved by on-column injection on a glass column (length 1.5 m, internal diameter 3 mm) packed with silicon DC-200; mesh 60–80. Nitrogen was used as the carrier gas.

Epoxidation of Cyclooctene: Stock CH_2Cl_2 solutions of [Mn(por)] (3 mmol), imidazole (30 mmol), neat cyclooctene (34 µL, 250 mmol), and neat dodecane (2 µL) as an internal standard, were put into a 5-mL round-bottomed flask containing CH_2Cl_2 (1 mL) and alcohol (0.5 mL) and then tetra-*n*-butylammonium periodate (0.217 g, 500 mmol) was added to initiate the reaction. The reaction solution was stirred for the required time, and aliquots (2 µL) were then removed from the reaction solution and injected into the GC column to monitor the formation of cyclooctene epoxide. The concentration of the epoxide was determined by comparison of its peak area with that of the internal standard. Both peak heights and peak areas were used to measure the concentration of various species; averaging of the two methods usually gave the most consistent results. The temperature program for the analysis was 1 min at 80 °C, and the rate program was set at 20 °C min^{-1} up to 175 °C and 1.5 min at 175 °C. Data were obtained in triplicate to ensure precision, and the repeatability of the data was within ±10%.

Epoxidation of *cis*-Stilbene: Stock CH_2Cl_2 solutions of [Mn(por)] (3 mmol), imidazole (30 mmol), and *cis*-stilbene (45 mg, 250 mmol) were introduced into a 5-mL round-bottomed flask containing CH_2Cl_2 (1 mL), with or without alcohol (0.5 mL), and then $n\mathrm{Bu_4NIO_4}$ (0.217 g, 500 mmol) was added to initiate the reaction. The reaction solution was stirred for the required time, and then the solvent was removed under reduced pressure. *n*-Pentane (5 mL) was added to precipitate [Mn(por)] and $n\mathrm{Bu_4NX}$ ($X=OAc^-, IO_4^-, IO_3^-$). The resulting mixture was filtered, and *n*-pentane was removed under vacuum. The composition of the products was determined by ^{1}H NMR spectroscopy (CCl_4, TMS). *cis*-Stilbene epoxide was characterized by a singlet at δ = 4.35–4.45 ppm for the epoxidic proton and the *trans* isomer by a singlet at δ 3.80–3.90 ppm.[1b]

UV/Vis Spectra: Stock CH_2Cl_2 solutions of [Mn(por)] (10^{-5} M, 2 mL), imidazole (0.5 M, 10–25 µL), and $n\mathrm{Bu_4NIO_4}$ (0.25 M, 50 µL) were added into a 1-cm UV cell containing CH_2Cl_2 (2 mL) and alcohol (50 µL), if needed. The spectral changes were monitored at different times.

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Supporting Information (see footnote on the first page of this article): UV/Vis spectra of [Mn(tmp)(OAc)]/im/$n\mathrm{Bu_4NIO_4}$ in various $\mathrm{CH_2Cl_2}$/alcohol solvents; UV/Vis spectra for interaction of [Mn(tpfpp)(OAc)] with $n\mathrm{Bu_4NIO_4}$ in various solvents.

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