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Mechanism of Manganese Porphyrin-Catalyzed Oxidation of Alkenes. Role of Manganese(IV)–Oxo Species

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Abstract: The mechanism for the bimolecular reaction of *meso*-tetrakis(2,6-dichlorophenyl)porphinato–oxo–manganese(IV), [$(Cl_8TPP)Mn^{IV}(O)$], with alkenes has been investigated by kinetics and product identification. Kinetic studies were carried out with 11 alkenes (*trans*-4-methoxystilbene, *cis*-4-methoxystilbene, 1,4-diphenyl-1,3-butadiene, 4-methoxystyrene, 1,1-diphenylethylene, 4-methylstyrene, 2,3-dimethyl-2-butene, *trans*-stilbene, *cis*-stilbene, styrene, 4-acetoxystyrene) in methylene chloride solution (30 °C) in air. The reactivities of the alkenes show that the *trans* alkenes are slightly more reactive than their *cis* isomers and that electron releasing substituents slightly favor the reaction. The second-order rate constant values (k_2) correlate well with the potentials for the 1e$^-$ oxidation ($E_{1/2}$) of the alkenes. The slope of the linear plot of log k_2 *vs* $E_{1/2}$ for the series of alkenes (slope = -0.89 V^{-1}) indicate that a mechanism of epoxidation involving rate-determining formation of an alkene derived π-cation-radical is unlikely. For the reaction with substituted styrenes, the linear free-energy relationship of log k_2 *vs* σ^+ ($\rho^+ = -0.99$) supports a transition state with very little charge separation. Product yields determined for the reactions with *cis*-stilbene, *trans*-stilbene, 2,3-dimethyl-2-butene, *cis*-4-methoxystilbene, and *trans*-4-methoxystilbene are in accord with a mechanism involving the formation of a $(porph)Mn^{III}OCC^\bullet$ radical intermediate. Thus, the products of *cis*-stilbene oxidation under aerobic conditions are *cis*-stilbene oxide (7%), *trans*-stilbene oxide (5%), and benzaldehyde (3%). Comparison with the reactions carried out under conditions favoring the transiently stable manganese(V)–oxo species showed more efficient epoxidation with a greater degree of stereospecificity. In a search for radical intermediates the *cis* olefinic substrate (*Z*)-1,2-bis(*trans-2,trans-3*-diphenylcyclopropyl)ethene was used as a radical trap. While no epoxide products were found, a polar oxygen-containing product resulting from the opening of one *trans-2,trans-3*-diphenylcyclopropyl ring by a cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR) was detected supporting the formation of a neutral carbon radical species.

Introduction

Manganese porphyrins have been shown to be very versatile catalysts for the epoxidation of a wide variety of alkenes. The high reactivity of these catalytic systems utilizing oxidants such as iodosylarenes,[1] peracids,[2] hypochlorites,[3] alkylhydroperoxides,[4] hydrogen peroxide,[5] amine *N*-oxides,[6] oxaziridines,[7] monopersulfate,[8] perchlorate, and periodate[9] together with several aerobic systems[10] have been described. In most cases, their behavior is believed to derive from a hypervalent manganese(V)–oxo porphyrin species, which has been suggested as the oxidant in the catalytic systems. Investigations directed toward the elucidation of the mechanisms of oxidation of alkenes by such species have resulted in a number of intermediates being proposed along the reaction path. These include the formation of intermediates such as a metallaoxetane, I,[11] an alkene derived π-radical cation, II,[12] a carbocation, III,[1d,12b–e,13] and a carbon radical, IV,[1b,14] together

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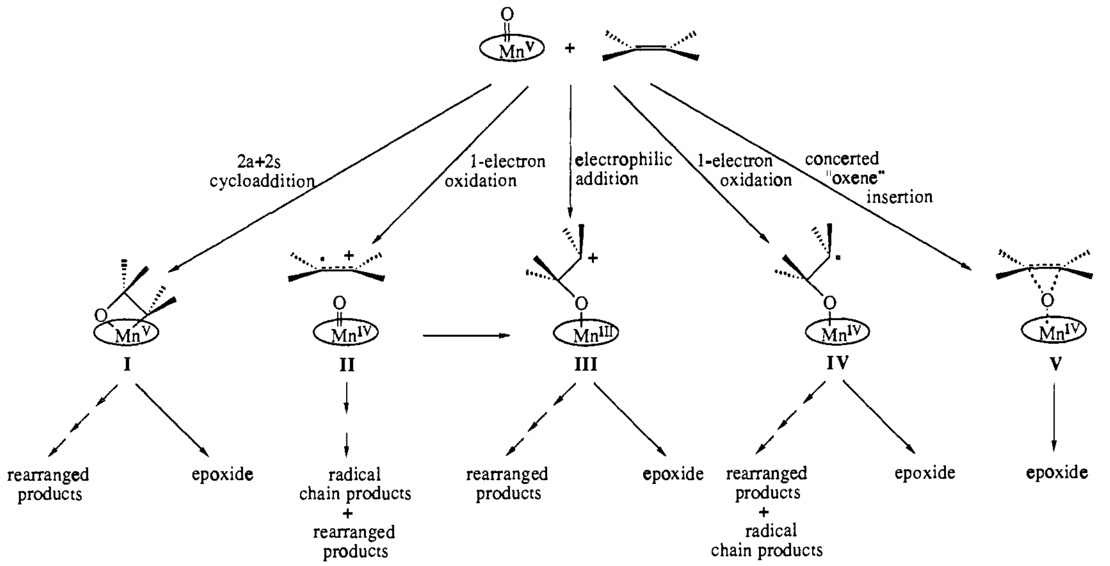
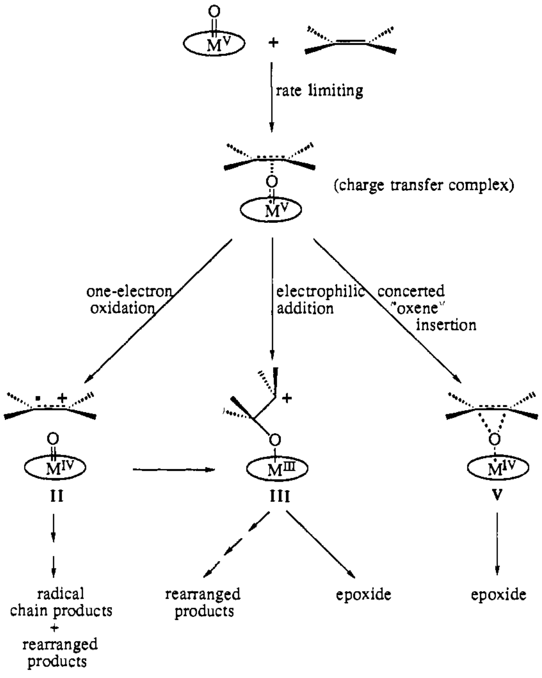
Scheme I



with a mechanism involving the concerted insertion of an "oxene" into the alkene double bond, V,[15] (Scheme I).

From studies on the related iron–oxo and chromium–oxo porphyrin species, we recently showed that the *rate-determining formation* of intermediates I–IV are untenable. We described a unified mechanism for the oxygen atom transfer from oxo–metalloporphyrins to alkenes where the rate-determining step of the reaction was the formation of a charge-transfer complex (Scheme II).[16] The reactions following the rate-determining step (epoxidation *vs* rearrangement) were proposed to be dependent on a number of factors that included the oxidation potentials of the alkenes and the active oxidant, the steric and electronic structures of the reactants (steric bulk and geometry of both species and the metal axial ligand of the metalloporphyrin) as well as the propensity of various substrates to undergo rearrangements. While it is most likely that the same conclusions can be reached for epoxidations involving manganese(V)–oxo porphyrin species, in our early studies we found that the manganese porphyrin systems (unlike the iron and chromium porphyrins) also display alkene oxidation products that are attributed to a radical type reaction. For example, the catalytic epoxidation of *cis*-stilbene by (Cl$_8$TPP)Mn^{III}(Cl) [Cl$_8$TPP is the dianion of *meso*-tetrakis(2,6-dichlorophenyl)porphyrin] with C$_6$F$_5$IO,[1d] and (TPP)-Mn^{III}(Cl) [TPP is the dianion of *meso*-tetraphenylporphyrin] with 2-(phenylsulfonyl)-3-(*p*-nitrophenyl)oxaziridine[7] provide *cis*- and *trans*-stilbene oxides. The loss of stereochemistry during the epoxidation was explained by invoking the formation of a carbon-radical intermediate. More recently it has been proposed that the *trans*-epoxide product resulting from a radical-type oxidation most likely arises from contamination of the manganese(V)–oxo porphyrins by manganese(IV)–oxo porphyrin.[16,22b] In contrast, the related oxo–iron(IV) and oxo–chromium(IV) porphyrins are unreactive towards alkenes.[17,18]

Scheme II



M^V=O represents the formal oxidation state of the metalloporphyrin (M = Cr, Mn or Fe) oxidant. No structural inference is to be made from this representation.

We now report details on a kinetic and product study on the reaction of *meso*-tetrakis(2,6-dichlorophenyl)porphinato–oxo–manganese(IV), (Cl$_8$TPP)Mn^{IV}(O), with a variety of reactive alkenes. Unequivocal evidence is presented for the formation of a (porph)Mn^{III}OCC$^\bullet$ radical intermediate in the oxidation of alkenes by (Cl$_8$TPP)Mn^{IV}(O).

Experimental Section

Materials. [*meso*-Tetrakis(2,6-dichlorophenyl)]porphine, (Cl$_8$TPP)-H$_2$, was prepared by a previously reported procedure,[19] and manganese was inserted by the standard route.[20] Anhydrous CH$_2$Cl$_2$ solvent (99+%, Aldrich) and tetramethylammonium hydroxide (25 wt % solution in methanol, Aldrich) were used as received from the supplier. *m*-Chloroperoxybenzoic acid (*m*-CPBA) was available from Aldrich, and its purity (84%) was confirmed by iodometric titration. All alkenes were purchased from commercial vendors, purified as previously described,[21]

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and passed through a short column of neutral alumina immediately prior to use. Commercially available epoxides (Aldrich) used as GC and HPLC standards were purified as previously described.[21] Other epoxides were prepared by *m*-CPBA epoxidation of alkenes[14g] and purified by flash chromatography on silica, followed either by recrystallization or by vacuum transfer. The identity of epoxides was confirmed by ^1H NMR, and purity was verified by ^1H NMR and GC/HPLC. The (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene was from a previous study.[12a]

Instrumentation. Kinetic studies and absorption measurements were conducted using a Cary 14 spectrophotometer interfaced to a Zenith computer by OLIS (On-Line Instrument System Inc.). The cell compartments were thermostated at 30 °C. The GC analyses were performed with a Varian 3700 series gas chromatograph equipped with a flame ionization detector and interfaced to a Hewlett Packard HP3393A integrator. The separation of products was achieved by on-column injection to a SGE, QC3/BP-1 (25 × 0.32 mm i.d.) capillary column at 50 °C (for analysis of 2,3-dimethyl-2-butene oxygenations) or a J&W Scientific, DB-17 (15 × 0.32 mm i.d.) capillary column using a linear temperature gradient from 80 to 240 °C at 3 °C/min (for analysis of *cis*-stilbene and *trans*-stilbene oxygenations). The HPLC analyses for *cis*-4-methoxystilbene, *trans*-4-methoxystilbene, and (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene oxygenations were performed with a Perkin-Elmer Series 10 pump and a Hewlett-Packard variable wavelength detector (Model HP1050) interfaced to a Hewlett-Packard HP3393A integrator. The separations were carried at 245 nm using an Altex RSil-CN (5 μm, 5 × 250 mm i.d.) column and eluted with hexane/CH_2Cl_2 (20/1) at a flow rate of 1 mL min^{-1}. For semipreparative HPLC an ISCO variable wavelength absorbance detector (Model V^4, 254 nm), a fraction collector (Model Retriever II) and an Altex RSil-CN (10 μm, 10 × 250 mm i.d.) column were used, and eluted with hexane/CH_2Cl_2 (9/1) at a flow rate of 2 mL min^{-1}.

Reactions of $(Cl_8TPP)Mn^{IV}(O)$ and $(Cl_8TPP)(B)Mn^{V}(O)$ (B = Imidazole or Pyridine) with Alkenes. General Procedures. $(Cl_8TPP)Mn^{IV}(O)$ was prepared from the reaction of $(Cl_8TPP)Mn^{III}(Cl)$ with *m*-CPBA in CH_2Cl_2 in the presence of tetramethylammonium hydroxide and isolated by chromatography on jacketed basic alumina at −80 °C (eluant, CH_2Cl_2/ethyl acetate, 1:1) by the method described by Groves and Stern for $(TMP)Mn^{III}(Cl)$.[22a] In a typical reaction 31 mg of $(Cl_8TPP)Mn^{III}(Cl)$, 8 mg of *m*-CPBA, and 24 μL of tetramethylammonium hydroxide (25 wt % solution in methanol) were employed. The UV/vis spectrum of $(Cl_8TPP)Mn^{IV}(O)$ was characterized by a broad Soret peak at 422 nm. The FAB mass spectrum of the solid (*m*-nitrobenzyl alcohol matrix) obtained upon evaporation of the solvent gave a parent ion cluster centered at *m/z* 959 consistent with the molecular formula $(Cl_8TPP)Mn^{IV}(O)$. The KBr pellet IR spectrum of the same sample displayed a new band at 728 cm^{-1} attributed to the $Mn^{IV}{=}O$ stretching frequency. In our hands, the $(Cl_8TPP)Mn^{IV}(O)$ fraction collected at −80 °C showed a trace of $(Cl_8TPP)Mn^{III}(Cl)$ due to decomposition. Attempts to obtain the solid $(Cl_8TPP)Mn^{IV}(O)$ by precipitation or evaporation of the solvent provided mixtures of $(Cl_8TPP)Mn^{IV}(O)$ with considerable amounts of $(Cl_8TPP)Mn^{III}(Cl)$. Thus the $(Cl_8TPP)Mn^{IV}(O)$ fraction collected in a receiver flask maintained at −80 °C was used directly for the kinetic and product studies without any further workup.

The kinetic studies were performed under aerobic conditions by mixing a methylene chloride solution of the alkene with an aliquot of the $(Cl_8TPP)Mn^{IV}(O)$ solution (CH_2Cl_2/ethyl acetate, 1:1) and following the course of reaction to completion by UV/vis spectroscopy (*vide infra*). Product analyses carried out by GC were achieved by direct on-column injections. HPLC analyses were carried out as follows. The solvent from the spent reaction solution was removed under reduced pressure. Hexane (~15 mL) was then added to precipitate the manganese–porphyrin, and the mixture was passed through a plug of glass wool. After the hexane was removed under reduced pressure, the residue was dissolved in hexane/CH_2Cl_2 (6/1), made up to 10.0 mL and analyzed by HPLC. Solutions for the reactions carried out under anaerobic conditions were deoxygenated by three freeze–pump–thaw cycles and saturated with oxygen-free argon prior to initiation. The reactions were initiated by addition of alkene *via* a gas-tight syringe or by mixing the alkene placed in the top section of a Thunberg tube attached to the Schlenck flask. All the reactions were carried out in the dark by covering the reaction flasks with aluminum foil.

The reactions of the transiently stable $(Cl_8TPP)(B)Mn^{V}(O)$ (B = imidazole or pyridine) with alkenes were carried by addition of alkene (0.2 mmol) to a CH_2Cl_2 solution (5 mL) of $(Cl_8TPP)Mn^{III}(Cl)$ (0.01 mmol), imidazole/pyridine (0.2 mmol), and *m*-CPBA (0.012 mmol) at −78 °C (acetone/dry-ice bath). After stirring for 1 h at −78 °C, the reaction was quenched with tetrabutylammonium iodide (0.074 g, 0.2 mmol), brought to room temperature, and poured into 30 mL of hexane to precipitate manganese–porphyrin. The precipitate was removed by filtration, and the filtrate evaporated to dryness under reduced pressure. The residue was then dissolved in hexane/CH_2Cl_2 (6/1), made up to 10 mL, and analyzed by HPLC.

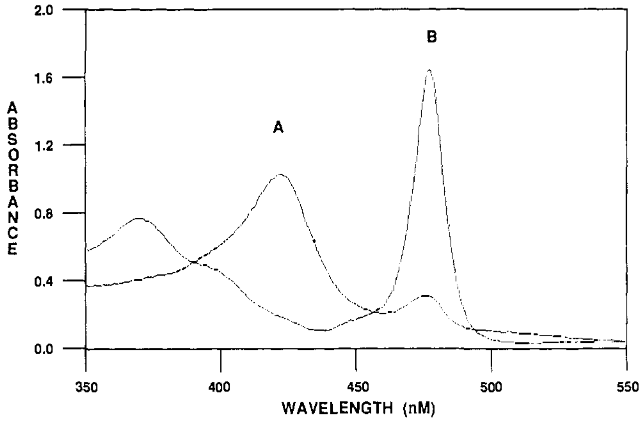


Figure 1. Visible absorption spectra of a methylene chloride solution of (A) $(Cl_8TPP)Mn^{IV}(O)$ (1.7×10^{-5} M) and (B) after its complete conversion to $(Cl_8TPP)Mn^{III}(Cl)$.

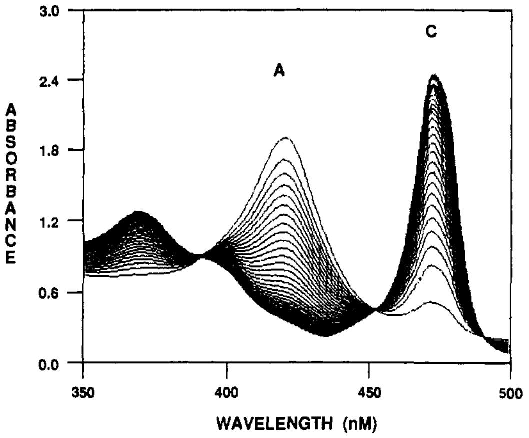


Figure 2. Visible absorption spectral changes observed upon mixing a methylene chloride solution of $(Cl_8TPP)Mn^{IV}(O)$ (1.5×10^{-5} M) with 2,3-dimethyl-2-butene (1.1×10^{-1} M) at 30 °C. Spectral scans were taken at 4-min intervals.

Results

Solution Behavior of $(Cl_8TPP)Mn^{IV}(O)$. Figure 1 shows the optical spectral changes that occur when a CH_2Cl_2 solution of $(Cl_8TPP)Mn^{IV}(O)$ decomposes. Trace A shows the spectrum of $(Cl_8TPP)Mn^{IV}(O)$ (λ_{max} = 422 nm), while trace B shows the spectrum of that sample after decomposition to $(Cl_8TPP)Mn^{III}(Cl)$ (λ_{max} = 478 nm). At 30 °C, the rate constant for the conversion was 5×10^{-5} s^{-1}.

Kinetic Studies on the Reactions of $(Cl_8TPP)Mn^{IV}(O)$ with Alkenes. Addition of an aliquot (0.2 mL) of the $(Cl_8TPP)Mn^{IV}(O)$ eluant to a CH_2Cl_2 solution of 2,3-dimethyl-2-butene (1.1×10^{-1} M, 2.8 mL) produces the optical spectral changes shown in Figure 2. Examination of Figure 2 shows that the Soret absorbance for $(Cl_8TPP)Mn^{IV}(O)$ decreases with a concomitant increase in absorbance at 478 nm. The asymmetric nature of the Soret absorbance at 478 nm indicates that the products are a mixture of manganese(III) porphyrin species containing different axial ligands. The isosbestic points at 392, 453, and 491 nm demonstrate that the conversion of $(Cl_8TPP)Mn^{IV}(O) \rightarrow (Cl_8TPP)Mn^{III}(X)$ does not involve the accumulation of any intermediates.

Table I. Percentage Yields of Products from the Reaction of (Cl$_8$TPP)Mn^{IV}(O) with Alkenes and the Effect of Radical Initiator Additives

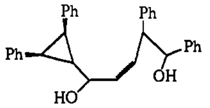
		products, % yield[a]			
alkene	conditions	epoxide	% yield	carbonyl compounds	% yield
cis-stilbene	air	*cis*	7	PhCHO	3
		trans	5		
cis-stilbene	deoxygenated	*cis*	8	PhCHO	<1
		trans	3		
trans-stilbene	air	*trans*	15	PhCHO	13
trans-stilbene	deoxygenated	*trans*	12	PhCHO	5
cis-4-methoxystilbene	air	*trans*	40	(p-MeOPh)$_2$CHCHO	91
trans-4-methoxystilbene	air	*trans*	53	(p-MeOPh)$_2$CHCHO	290
2,3-dimethyl-2-butene	air		10	$(CH_3)_2CO$	*b*
				$CH_3COC(CH_3)_3$	220
cis-stilbene	AIBN, air[c]	*cis*	3	PhCHO	0.2
		trans	0.2	Ph_2CHCHO	0.3
trans-stilbene	AIBN, air[c]	*trans*	0.5	PhCHO	2
				$PhCH_2COPh$	0.1

[a] Yields are based on (Cl$_8$TPP)Mn^{IV}(O). [b] Interference from the 2,3-dimethyl-2-butene peak made GC quantitation difficult. [c] AIBN = azobisisobutyronitrile; yields are based on AIBN.

Rate constants were determined at 30 °C under aerobic conditions in CH_2Cl_2 by following the decrease in the absorbance at 422 nm. Typical pseudo-first-order conditions were used with (Cl$_8$TPP)Mn^{IV}(O) at 1.5×10^{-5} M and alkene concentrations ranging from $\sim 2.0 \times 10^{-2}$ to 2.0×10^{-1} M. Pseudo-first-order rate constants (k_{obsd}) were determined at five values of [alkene]. For all alkenes examined, k_{obsd} was found to be linearly dependent on [alkene]. The second-order rate constants (k_2) for the reaction of alkene with (Cl$_8$TPP)Mn^{IV}(O) were obtained from the slopes of the linear plots of k_{obsd} *vs* [alkene]. The nonzero intercepts equal the first-order rate constants for spontaneous decomposition of (Cl$_8$TPP)Mn^{IV}(O). The values of k_2 that were determined are as follows: 9.2×10^{-3} M^{-1} s^{-1} for *trans*-4-methoxystilbene; 3.6×10^{-3} M^{-1} s^{-1} for *cis*-4-methoxystilbene; 7.9×10^{-3} M^{-1} s^{-1} for 1,4-diphenyl-1,3-butadiene; 1.1×10^{-2} M^{-1} s^{-1} for 4-methoxystyrene; 7.0×10^{-3} M^{-1} s^{-1} for 1,1-diphenylethylene; 3.8×10^{-3} M^{-1} s^{-1} for 4-methylstyrene; 4.0×10^{-3} M^{-1} s^{-1} for 2,3-dimethyl-2-butene; 5.1×10^{-3} M^{-1} s^{-1} for *trans*-stilbene; 3.2×10^{-3} M^{-1} s^{-1} for *cis*-stilbene; 2.3×10^{-3} M^{-1} s^{-1} for styrene; and 1.3×10^{-3} M^{-1} s^{-1} for 4-acetoxystyrene.

Product Studies on the Reactions of (Cl$_8$TPP)Mn^{IV}(O) with *cis*-Stilbene, *trans*-Stilbene, 2,3-Dimethyl-2-butene, *cis*-4-Methoxystilbene, and *trans*-4-Methoxystilbene. The reactions were carried out using higher concentrations of (Cl$_8$TPP)Mn^{IV}(O) and alkenes than that used for the kinetic studies in order to increase the concentrations of the products. In a typical reaction, a solution of the (Cl$_8$TPP)Mn^{IV}(O) eluant (7.5 μmol, 30 mL) was combined with the alkene (3.0 mmol) and stirred thoroughly for ~24 h before product analysis. Analysis of the spent reaction solutions were carried out by capillary GC (*cis*-stilbene, *trans*-stilbene, and 2,3-dimethyl-2-butene) and HPLC (*cis*-4-methoxystilbene and *trans*-4-methoxystilbene). For reactions carried out under deoxygenated conditions, both (Cl$_8$TPP)Mn^{IV}(O) and alkene solutions were degassed by three freeze–pump–thaw cycles and saturated with oxygen-free argon prior to initiation. The epoxide and carbonyl product yields for the different alkenes under aerobic and deoxygenated conditions are summarized in Table I. Control experiments revealed that the reaction of (Cl$_8$TPP)Mn^{III}(Cl) or (Cl$_8$TPP)Mn^{II} with *cis*-stilbene in the presence of O_2 produced no epoxide or any carbonyl products. By contrast, the radical initiator azobisisobutyronitrile (AIBN) reacts with *cis*- or *trans*-stilbene in the presence of O_2 to produce epoxides and carbonyl products. Reactions carried out under conditions favoring the formation of the transiently stable (Cl$_8$TPP)(B)Mn^{V}(O) (B = imidazole or pyridine) display more efficient epoxidation and greater stereospecificity (Table II).

Reaction of (Cl$_8$TPP)Mn^{IV}(O) with the radical trap (*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene, VI-*Z*. A solution of (Cl$_8$TPP)Mn^{IV}(O) (7.5 μmol, 30 mL, CH_2Cl_2/ethyl acetate, 1:1) was combined with VI-*Z* (3.0 mmol) and stirred thoroughly for ~24 h. The UV/vis spectrum of the spent reaction mixture displayed a blue-shift from the 478-nm Soret band for the chloro ligated (Cl$_8$TPP)Mn^{III} species to 473 nm. This is consistent with empirical correlations for a more basic alkoxyl axial ligand.[23] The spent reaction mixture was stirred with aqueous 0.1 M HCl, washed with H_2O, dried with $MgSO_4$, and analyzed by HPLC. Analytical HPLC analysis revealed a polar product (t_R 8.9 min) and a nonpolar product (t_R 4.0 min). After semipreparative HPLC purification, a sufficient quantity of the polar component was obtained only for mass spectral analysis. The FAB–MS spectrum (*m*-nitrobenzyl alcohol matrix) gave a parent ion (M^+) isotopic cluster centered at *m/z* 447. The relative abundances of the cluster at 447 lacked the characteristic isotopic intensities for chlorine. The highest observed *m/z* in the LRMS spectrum was 412 corresponding to $(M - 35)^+$. Also, the LRMS spectrum displayed peaks centered at 193, 181, and 167, that are diagnostic for diphenylcyclopropyl, diphenylethyl, and diphenylmethyl cations, and peaks centered at 206, 219, 232, and 245 that indicate the presence of four contiguous CH groups. Additionally, the *m/z* peaks at 321, 231, and 205 correspond to a sequential loss of $PhCH_2$, PhCH, and CH_2CH_2 by the fragmentation of *m/z* 412. These observations indicate that one cyclopropyl group in VI-*Z* has undergone a ring opening while the other has remained intact. The mass spectral data is consistent with a compound that contains two -OH groups having the structure of **VII**.



VII

Discussion

The present report describes a study on the kinetics and products of the bimolecular reaction of (Cl$_8$TPP)Mn^{IV}(O) with a number of alkenes in methylene chloride solution. The second-order rate constants (k_2) were determined for 11 alkenes (*trans*-4-methoxystilbene, *cis*-4-methoxystilbene, 1,4-diphenyl-1,3-butadiene, 4-methoxystyrene, 1,1-diphenylethylene, 4-methylstyrene, 2,3-dimethyl-2-butene, *trans*-stilbene, *cis*-stilbene, styrene, 4-acetoxystyrene) under pseudo-first-order conditions of [alkene] $\gg$ [(Cl$_8$TPP)Mn^{IV}(O)] in air at 30 °C. In the course of the reactions, the oxo–manganese(IV) species converts to a manganese(III) species without the formation of any long-lived intermediates (Figure 2). The reactivities of the alkenes show that the *trans* alkenes are slightly more reactive than their *cis* isomers and that electron releasing substituents slightly favor the reaction.

Analysis of the Nature of the Rate-Limiting Step. In order to deduce the nature of the transition state for the rate-determining step of the reaction, the linear free-energy correlation between

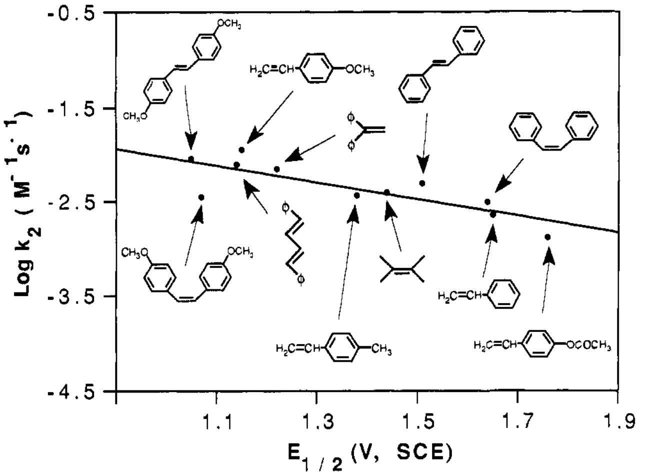


Figure 3. Plot of the log of the second-order rate constants (k_2) for the reaction of $(Cl_8TPP)Mn^{IV}(O)$ with a series of 11 alkenes *vs* the $E_{1/2}$ for $1e^-$ oxidation of the alkenes.

the second-order rate constants (k_2) and the potentials for the $1e^-$ oxidation ($E_{1/2}$) of the alkenes was examined. For reactions that involve an initial outer-sphere electron transfer, the relationship between the rate constants and the potentials for $1e^-$ oxidation of the alkenes can take three possible scenarios: (i) at one extreme, the diffusion of reactants toward each other can be rate-limiting such that log k_2 is independent of $\Delta E_{1/2}$ (slope = 0); (ii) while at the other extreme, $1e^-$ transfer can be so endothermic that log k_2 is directly proportional to $\Delta E_{1/2}$ for the overall $1e^-$ electron transfer (slope = -16.6 V^{-1}); (iii) or an intermediate region, where log k_2 for rate-limiting $1e^-$ transfer can be dependent on $\Delta E_{1/2}$, with the slope depending on the degree of electron transfer in the transition state, changing from 0 to -16.6 V^{-1}.[24,25] As shown in Figure 3, the values of log k_2 correlate well with the $E_{1/2}$ values for the alkenes. The values of k_2 range from 1.3×10^{-3} to 1.1×10^{-2} M^{-1} s^{-1}, while the alkene $E_{1/2}$ values range from 1.05 to 1.76 V. The linear correlation of Figure 3 is given by eq 1 and

$$\log k_2 = -0.89E_{1/2} - 1.14 \qquad (1)$$

the slope of -0.89 V^{-1} corresponds to a Brønsted α of 0.05 in a conventional Brønsted plot of log k_2 *vs* log K_{eq}. Thus, in the reaction of $(Cl_8TPP)Mn^{IV}(O)$ with alkenes, there is very little electron transfer. Hence, it is concluded that a mechanism involving rate-limiting formation of an alkene-derived π-cation radical (eq 2) cannot be correct. The behavior maybe compared

$$(Cl_8TPP)Mn^{IV}(O) + \text{alkene} \rightarrow (Cl_8TPP)Mn^{III}(O) + \text{alkene}^{\bullet+} \qquad (2)$$

to that of the related and much more intensively studied hypervalent $(Br_8TPP)Cr^{V}(O)(ClO_4^-)$ which undergoes rate limiting formation of a charge-transfer complex (slope = -2.99 V^{-1}; Brønsted α = 0.18).[21]

Additionally, Figure 4 shows that there is a linear free-energy correlation of log k_2 and σ^+ for the epoxidation of substituted styrenes by $(Cl_8TPP)Mn^{IV}(O)$. The correlation line of Figure 4 is given by eq 3 where the ρ^+ value is -0.99. The low ρ^+ value

$$\log k_2 = -0.99\sigma^+ - 2.68 \qquad (3)$$

precludes rate-limiting carbocation formation *via* electrophilic addition. Reported ρ^+ values for known electrophilic additions to substituted styrenes are much greater (-3.58 for hydration and -4.8 for bromination).[26,27] In the oxidation of substituted styrenes by $(Br_8TPP)Cr^{V}(O)(ClO_4^-)$, ρ^+ equals -1.9.[21]

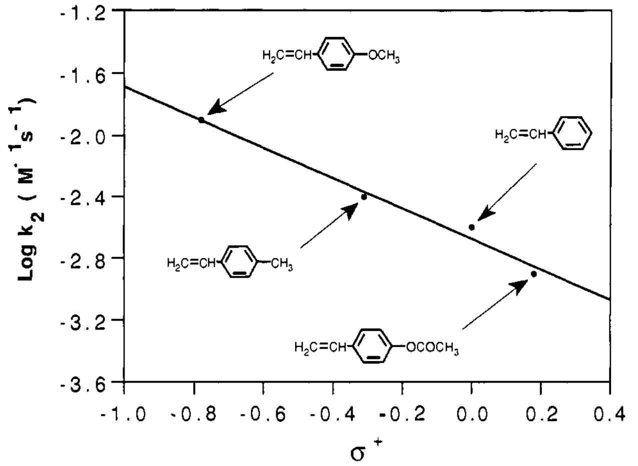


Figure 4. Plot of the log of the second-order rate constants (k_2) for the reaction of $(Cl_8TPP)Mn^{IV}(O)$ with a series of four substituted styrenes *vs* the substituent constants σ^+ at 30 °C.

These observations indicate transition states for rate-limiting steps which involve very little charge separation. If $1e^-$ transfer were involved in the reaction of $(Cl_8TPP)Mn^{IV}(O)$ with alkenes, then the transition state is very early. Such a case can be described by the rate-determining formation of a charge-transfer complex. Formation of a neutral carbon-radical would also show slight sensitivity to polar effects. For example, the radical decomposition of the substituted peresters of $PhCH_2C(O)OOC(CH_3)_3$ yield ρ^+ in the neighborhood of -1.[28]

Analysis of Products. The aerobic reaction of $(Cl_8TPP)Mn^{IV}(O)$ with *cis*-stilbene produced *cis*-stilbene oxide (7%), *trans*-stilbene oxide (5%), and benzaldehyde (3%), while the reaction with *trans*-stilbene produced *trans*-stilbene oxide (15%) and benzaldehyde (13%) (Table I). The production of *trans*-epoxide from *cis*-stilbene requires that the intermediate leading to its direct formation must undergo a *cis*/*trans* inversion. This may be accounted for by a mechanism involving radical intermediates as described by the series of reactions shown in Scheme III. The *cis* carbon radical intermediate **2** has a sufficiently long lifetime to allow partial isomerization by rotation around the alkene C–C bond to provide the more stable *trans*-**2** and *trans*-epoxide. With *trans*-stilbene, the reaction yields the most stable *trans*-**2** and, hence, only *trans*-stilbene oxide. In the presence of molecular dioxygen, however, the carbon radical intermediate can react with O_2 to generate the peroxy radical species **3** which could ring-close to form a dioxetane and regenerate $(Cl_8TPP)Mn^{IV}(O)$. Cleavage of the dioxetane provides PhCHO.[29] Additionally, it has been proposed that peroxy radicals could act as radical-chain initiators to generate more alkylperoxyl radicals with O_2, which could oxidize the alkene to the *cis*- and *trans*-epoxides and PhCHO.[22a] When the reactions were carried out in deoxygenated solutions, both *cis*-stilbene oxide (8%) and *trans*-stilbene oxide (3%) were obtained. However, detection of <1% PhCHO in these samples indicate that our septum-capped flasks are not completely impervious to adventitious dioxygen. The aerobic

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Scheme III

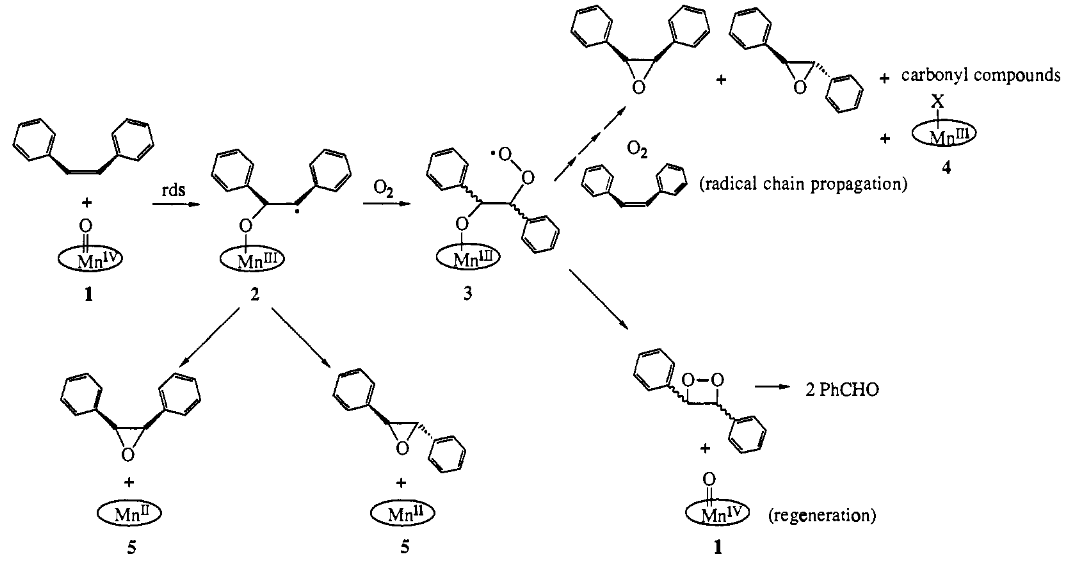

Table II. Percentage Yields of Products from the Reaction of $(Cl_8TPP)(B)Mn^{V}(O)$ with Alkenes (B = Imidazole or Pyridine)

		products, % yield^a			
alkene	conditions^b	epoxide	% yield	carbonyl compounds	% yield
cis-stilbene	air, −70 °C,	*cis*	79	PhCHO	2.9
	imidazole	*trans*	5.2	Ph_2CHCHO	13
cis-stilbene	air, −70 °C,	*cis*	61	PhCHO	6.9
	pyridine	*trans*	3.7	Ph_2CHCHO	19
				$PhCH_2COPh$	1

^{a} Yields are based on *m*-CPBA. ^{b} The transiently stable $(Cl_8TPP)(B)Mn^{V}(O)$ was generated *in situ* by the reaction of $(Cl_8TPP)Mn^{III}(Cl)$ with *m*-CPBA at −70 °C in the presence of imidazole or pyridine and allowed to react with *cis*-stilbene.

reaction of $(Cl_8TPP)Mn^{IV}(O)$ with *cis*-4-methoxystilbene, *trans*-4-methoxystilbene, and 2,3-dimethyl-2-butene shows yields of epoxides and carbonyl products (Table I) that are consistent with Scheme III. For *cis*-4-methoxystilbene, the only epoxide product was *trans*-4-methoxystilbene oxide in accord with the stability of the radical intermediate allowing greater time for *cis* → *trans* isomerization prior to epoxide formation.

Also, examination of products obtained from the aerobic reaction of *cis*- and *trans*-stilbenes with $(Cl_8TPP)Mn^{IV}(O)$ and radical initiators such as azobisisobutyronitrile (AIBN) suggests that similar propagation steps may be involved in both systems. Control experiments on the reaction of $(Cl_8TPP)Mn^{III}(Cl)$ or $(Cl_8TPP)Mn^{II}$ with *cis*-stilbene in the presence of O_2 produced no epoxide or any rearranged products suggesting that these species are not involved in the propagation sequence. Thus aerobic oxidation of $(Cl_8TPP)Mn^{II}$ is not an accessible route for manganese(IV).

For comparison, when the oxidation reactions were carried out under conditions favoring the predominant formation of the transient $(Cl_8TPP)(B)Mn^{V}(O)$ (B = imidazole or pyridine) more efficient epoxidation was observed with a greater degree of stereospecificity (Table II). Solutions of $(Cl_8TPP)(B)Mn^{V}(O)$ were prepared by the oxidation of $(Cl_8TPP)Mn^{III}(Cl)$ with *m*-CPBA in the presence of imidazole or pyridine at −78 °C. The addition of pyridine or imidazole has been shown to favor the formation of the manganese(V)–oxo species.[4,5]

Analysis of Products Formed from the Reaction with the Radical Trap (*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene, VI-*Z*. Formation of radical intermediates were confirmed by employing the *cis* olefinic substrate **VI-*Z*** incorporating the hypersensitive radical trapping group, *trans*-2,*trans*-3-diphenylcyclopropyl in the epoxidation reaction. The ring openings of *trans*-2,*trans*-3-diphenylcarbinyl radicals by a cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR) is very fast with rate constants $\geq 2 \times 10^{10}\ s^{-1}$ at room temperature.[14e,f]

The reaction of **VI-*Z*** with $(Cl_8TPP)Mn^{IV}(O)$ provided a polar oxygen-containing product and a very nonpolar product. No epoxide products could be detected to 0.1% detection limit. Mass spectral analysis showed that the polar product contained one intact *trans*-2,*trans*-3-diphenylcyclopropyl group (*vide supra*). The structure of the polar product was identified as **VII** after examining the fragmentation patterns from the mass spectra. A pathway that could explain the formation of **VII** from **VI-*Z*** is given in Scheme IV. CPCRR of **6** gives **7**, which then adds dioxygen and abstracts a H• to form the hydroperoxide **9**. Hydrolysis of **9** provides **VIII**, which under MS analysis is detected as **VII**.

Summation of Findings. The major findings of this investigation on the reaction of $(Cl_8TPP)Mn^{IV}(O)$ with alkenes may be summarized as follows.

(i) *trans*-Alkenes are slightly more reactive than their *cis* isomers. The greater reactivity of the *trans* isomers is in strong contrast to the epoxidation reactions catalyzed by $(porph^{\bullet+})Fe^{IV}(O)$ and $(porph)Cr^{V}(O)(X)$ which display high reactivity of *cis* olefins compared to the *trans* isomers.[30,31] The kinetic selectivity of the *cis* olefins is attributed to steric effects due to the greater accessibility of the *cis* isomers to the active oxidant on the porphyrin. However, reactions of alkenes with simple free radicals such as hydroxyl,[32] peroxyacetyl,[33] and methyl radicals[34] show a preference for the *trans* isomer.

(ii) Electron donating substituents slightly enhance the rate of epoxidation. A Hammett treatment of the data gives a ρ^+ of −0.99 for substituted styrenes (Figure 4) which is in agreement with the development of very little charge in the transition state for epoxidation. This may be explained by the rate-determining formation of a charge-transfer complex or a neutral carbon-radical intermediate.

(iii) Epoxide products display a large loss in stereoselectivity.

(iv) The reaction produces a polar, oxygen-containing ring-opened product with the radical trapping probe **VI-*Z*** leading to the conclusion that radical intermediates had been formed.

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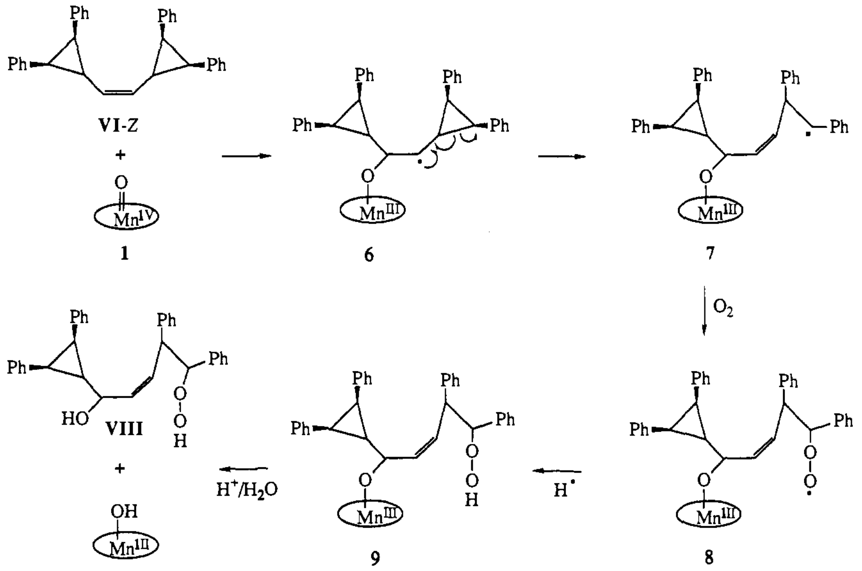
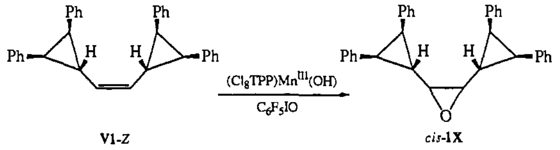
Scheme IV



(v) The mechanism for epoxidation cannot involve rate-limiting formation of an alkene-derived π-radical cation intermediate or a carbocation intermediate.

These findings are consistent with a mechanism involving the formation of $(Cl_8TPP)Mn^{III}OCC^•$ (Scheme III). A radical type mechanism has been suggested by Groves and Stern, who studied the reaction of $(TMP)Mn^{IV}(O)$ [TMP is the dianion of *meso*-tetrakis(mesityl)porphyrin] with *cis*-β-methylstyrene.[22] Their studies revealed that the product distribution and the ratio between *cis*-epoxide/*trans*-epoxide were different in the presence and absence of molecular dioxygen, a result interpreted to involve carbon radical intermediates.

The reactions of $(Cl_8TPP)Mn^{IV}{=}O$ contrasts markedly to those of $(Cl_8TPP)Mn^{V}{=}O$. With $(Cl_8TPP)Mn^{V}{=}O$, a high degree of stereospecificity is observed showing very little *cis*/*trans* isomerization. The small amounts of *trans*-epoxides from *cis*-alkenes in epoxidations with $(Cl_8TPP)Mn^{V}{=}O$ is attributed to the contamination of the manganese(V)–oxo species by manganese(IV)–oxo species. This assertion is supported by mechanistic studies on the reactions of **VI-*Z*** with $(Cl_8TPP)Mn^{V}(O)(X)$ [formed by the reaction of $(Cl_8TPP)Mn^{III}(OH)$ with C_6F_5IO], which provides the *cis*-epoxide, **IX**, (eq 4) (84% yield) as the major product.[14f] In contrast, $(Cl_8TPP)Mn^{IV}{=}O$ does not give an epoxide with **VI-*Z***.



(4)

The alkene nucleophile likely interacts with the π*-orbital of the Mn=O group of $(porph)Mn^{IV}{=}O$ (d^3, $S = {}^3/_2$) and $(porph)Mn^{V}{=}O$ (d^2, $S = 1$) before collapsing to product. Metal–oxo species have been described as a resonance hybrid of covalent, radical, and ionic structures (eq 5), with the importance of a

$$(porph)M^{2+}O^{2-} \leftrightarrow (porph)M^{+}O^{-} \leftrightarrow (porph)M{=}O \leftrightarrow (porph)\dot{M}\text{-}\dot{O} \leftrightarrow (porph)M^{-}O^{+} \quad (5)$$

given resonance form subject to influence by metal oxidation state, ancillary ligands, solvents, and other unspecified reaction conditions.[35] The formation of a radical intermediate in the reaction between the $(porph)Mn^{IV}{=}O$ and alkenes may suggest the importance of the radical form of $Mn^{IV}{=}O$ in the transition state of the reaction.

Acknowledgment. This work was supported by a grant from the National Institutes of Health.

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