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The Kinetics for the Reaction of Hypochlorite with a Manganese(III) Porphyrin and Subsequent Epoxidation of Alkenes in a Homogeneous Solution

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Abstract: The reaction of (5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinato)manganese(II) chloride [(Me$_{12}$TPP)Mn^{III}(Cl)] with hypochlorite has been investigated. The reactions were studied in a wet-dichloromethane solution prepared by mixing, on the stopped-flow bench, solutions (A) containing (Me$_{12}$TPP)Mn^{III}(Cl) + 4′-imidazol-1-ylacetophenone (NAcPhIm) + alkene and those (B) containing ClO$^-$ + benzyldimethyltetradecylammonium chloride (PTC). The time courses of the reactions were followed by conventional stopped-flow and rapid-scan stopped-flow spectrophotometry by monitoring the disappearance of (Me$_{12}$TPP)Mn^{III}(Cl) (λ_{max} = 480 nm, ϵ = 1.05 × 10^5 M^{-1} cm^{-1}) and the appearance of (Me$_{12}$TPP)Mn^{IV}(O) and (Me$_{12}$TPP)Mn^{V}(O). Simulations of the kinetic results were carried out according to the reactions of Scheme I by the fitting of the time course for (Me$_{12}$TPP)Mn^{III}(Cl) disappearance and the yields of epoxide products. The rate constant for ClO$^-$ + (Me$_{12}$TPP)Mn^{III}(Cl) $\rightarrow$ Cl$^-$ + (Me$_{12}$TPP)Mn^{V}(O) was determined as k_1 = (3.8 ± 1.8) × 10^5 M^{-1} s^{-1}. The rate constant for the comproportionation reaction of (Me$_{12}$TPP)Mn^{III}(Cl) + (Me$_{12}$TPP)Mn^{V}(O) $\rightarrow$ 2 (Me$_{12}$TPP)Mn^{IV}(X) is k_2 = 2 × 10^8 M^{-1} s^{-1}. The rate constant for the epoxidation (k_3) of norbornene was determined as (2.3 ± 0.5) × 10^3 M^{-1} s^{-1} while the rate constants for the epoxidation of *cis*-cyclooctene and cyclohexene were determined as (6.2 ± 1.1) × 10^2 M^{-1} s^{-1} and 1.0 × 10^2 M^{-1} s^{-1}, respectively. The N-substituted imidazole (NAcPhIm) does not ligate to (Me$_{12}$TPP)Mn^{III}(Cl) when present in 580-fold excess over manganese(III) porphyrin, and its presence, up to this concentration, does not alter the second-order rate constant for reaction of ClO$^-$ with the latter. The rate constant for epoxidation is also not altered by the presence of NAcPhIm, but the yields of epoxides exhibit a moderate increase. The PTC serves as a counterion to the ClO$^-$ moiety and an increase in its concentration (or an impurity in this reagent) results in it behaving as a substrate for oxidation by (Me$_{12}$TPP)Mn^{V}(O).

The chemical modeling of the peroxide-shunt mechanism for the cytochrome P-450 enzymes has been the impetus of numerous investigations. A major portion of this research has centered on the study of the kinetics and mechanism of oxygen-transfer reactions employing metal(III) porphyrins with appropriate oxygen atom donors.[1] Heme proteins have in common iron(III) protoporphyrin IX as the prosthetic group. Gelb, Toscano, and Sligar[2] have demonstrated that the apoprotein of cytochrome P-450$_{cam}$ can be reconstituted with manganese(III) protoporphyrin IX. Although this substitution results in the loss of competency in the hydroxylation of camphor, it retains the ability to epoxidize 5,6-dehydrocamphor. Manganese porphyrins have been used extensively in model studies of epoxidation reactions.[3]

In search of an inexpensive epoxidizing system, Meunier and co-workers[1d] introduced the use of ClO$^-$ as the oxygen atom donor (eq 1) in a system consisting of an organic phase containing a

$$\text{(Porph)Mn}^{III}\text{(X)} + \text{ClO}^- \rightarrow \text{(Porph)Mn}^{V}\text{(O)(X)} + \text{Cl}^- \qquad (1a)$$

$$\text{(Porph)Mn}^{V}\text{(O)(X)} + \text{alkene} \rightarrow \text{(Porph)Mn}^{III}\text{(X)} + \text{epoxide} \qquad (1b)$$

manganese(III) porphyrin, a phase-transfer agent, a nitrogen-base ligand, and alkene along with an aqueous phase containing ClO$^-$. A reinvestigation[4] of the kinetics employing this methodology using (5,10,15,20-tetraphenylporphinato)manganese(III) chloride [(TPP)Mn^{III}(Cl)] and (5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinato)manganese(III) chloride [(Me$_{12}$TPP)Mn^{III}(Cl)] resulted in, among others, the following pertinent findings: (i) at the high concentrations of ClO$^-$ usually employed, the reaction is biphasic, with the latter (and major) portions of the reaction involving the slow conversion of a (Me$_{12}$TPP)Mn^{IV}(O) species to the catalytic (Me$_{12}$TPP)Mn^{III}(X) species; (ii) at lower concentrations of ClO$^-$ [equal to or below a 100-fold excess over (Me$_{12}$TPP)Mn^{III}(X)] the appearance of epoxide follows the first-order rate law; and (iii) the phase transfer of ClO$^-$ is rate determining. It was also mentioned that the reactions of eq 1 could be studied in a homogeneous solution by mixing, in a stopped-flow spectrophotometer, a solution of ClO$^-$ and phase-transfer reagent in wet CH$_2$Cl$_2$ with a wet-CH$_2$Cl$_2$ solution of (Porph)Mn^{III}(Cl), alkene, and when desired an imidazole ligating agent. Rates are orders of magnitude greater in the homogeneous as compared to the biphasic system. Although this system is far from ideal for rigorous investigation, it does afford a basic understanding of the reactions involved.

In the present report, we describe the results of a study of the dynamics and products in the epoxidation of norbornene, *cis*-cyclooctene, and cyclohexene by (Me$_{12}$TPP)Mn^{III}(Cl) using ClO$^-$ as the oxygen-transfer agent in the aforementioned monophasic system.

Experimental Section

Materials. (5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)porphinato)manganese(III) chloride [(Me$_{12}$TPP)Mn^{III}(Cl)] was synthesized and purified according to literature procedures.[5,6] (5,10,15,20-Tetraphenylporphinato)manganese(III) chloride [(TPP)Mn^{III}(Cl)] was available from a previous study.[7] *cis*-Cyclooctene (COT) (Aldrich) and

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cyclohexene (CH) (Aldrich) were purified by distillation over LAH under nitrogen, passed though a short column of neutral alumina, and stored under nitrogen prior to use. Norbornene (Nb) (Aldrich) was purified by vacuum sublimation. 4′-Imidazol-1-ylacetophenone (NAcPhIm) (Aldrich) was purified by repeated crystallization from CH_2Cl_2/hexanes. Benzyldimethyltetradecylammonium chloride (PTC, a phase-transfer agent) was obtained from Fluka and used without further purification. Dichloromethane (Fisher) was used as received. The lithium hypochlorite solutions were prepared as previously described.[4]

Instrumentation. Gas chromatographic (GC) analyses were performed on a Varian 3700 gas chromatograph [flame-ionization detector, Varian WCOT capillary column (0.2-mm i.d., 25-m length, Vit. Silica)] interfaced to a Hewlett-Packard 3392A integrator. GC response factors were calibrated with authentic samples and epoxide yields were quantitated on the basis of the inclusion of an internal standard (decane) or by multiple injections in the cases where the internal standard signal was obscured by other peaks. Electronic absorption spectra and spectral changes were recorded with one of the following: (i) a Cary 118 spectrophotometer interfaced to a Zenith computer equipped with OLIS (On-Line Instrument Systems, Inc., Jefferson, GA) data-acquisition and -processing software, (ii) a Cary 14 spectrophotometer with an OLIS computer interface, (iii) a Kontron Uvikon 810 spectrometer, (iv) a rapid-scan stopped-flow spectrophotometer using a Harrick monochromator (Harrick Scientific Corp., Ossining, NY) with an OLIS computer interface, or (v) a Durrum-Gibson D-110 stopped-flow spectrophotometer (Durrum Instrument Corp., Palo Alto, CA) interfaced to an OLIS computer. Pseudo-first-order rate constants were calculated on a Hewlett-Packard 9825A computer equipped with a 9864A digitizer and a 9862A plotter. Kinetic simulations were carried out on a DEC VAX 11-750 employing software based on Gear integrators[8] (John P. Chesick, Haverford College, 1977 and Frank Weigert, DuPont).

Spectral Deconvolution of Reaction Mixtures. Assignment of the oxidation state of the manganese porphyrin is based on comparison of its UV/vis spectrum to spectra of manganese porphyrin species of known oxidation state. When the porphyrin is TPP or $Me_{12}TPP$, the positions of the Soret bands for Mn(IV)[3a,9a-c] and Mn(V)[9b,d-g] are 415–426 nm. The spectra of reaction mixtures containing only the two manganese porphyrin species $(Me_{12}TPP)Mn^{IV}(X)$ ($\lambda_{max} \approx 420$ nm, $\epsilon = 8.5 \times 10^4$ M^{-1} cm^{-1}) and $(Me_{12}TPP)Mn^{V}(O)$ ($\lambda_{max} \approx 418$ nm) were manipulated (with OLIS software) in order to approximate the concentration of both species. This was accomplished by subtracting an appropriately scaled reference spectrum of $(Me_{12}TPP)Mn^{IV}(X)$ from the reaction mixture spectrum. From a knowledge of the $[(Me_{12}TPP)Mn^{IV}(X)]$ in the reference spectrum and the scaling factor used in the deconvolution, the concentration of both species was approximated.

Kinetics. For the stopped-flow studies, a water-saturated dichloromethane solution containing $(Me_{12}TPP)Mn^{III}(Cl)$ and any added reagent (NAcPhIm, PTC, alkene) was mixed in the flow cell with a water-saturated dichloromethane solution of PTC and hypochlorite. The hypochlorite solutions were prepared by gentle agitation of a dichloromethane solution, containing 3.0×10^{-2} M PTC, with aqueous lithium hypochlorite (5×10^{-2} M) for 2 min. If these solutions are shaken too vigorously, an emulsion forms which separates extremely slowly. After separation of the phases, the organic layer was passed through a disposable Pasteur pipet containing glass wool followed by filtration through Whatman filter paper (No. 1 Qualitative) to ensure that the solution was homogeneous. The concentration of PTC (3.0×10^{-2} M) in the hypochlorite solution was determined to be optimal for these studies. At a lower [PTC], an insufficient amount of ClO^- was transferred into the organic phase to afford any appreciable reaction. At a higher [PTC], too much ClO^- was transferrred so that reactions were too rapid to monitor by stopped-flow techniques (less than 4 ms) and also emulsion formation became a problem. Immediately prior to the initiation of a kinetic run, the hypochlorite concentration was quantitated by a spectrophotometric iodometric method.[10] Hypochlorite solutions in wet dichloromethane were used within 25 min after their preparation. Kinetic experiments were carried out at 25 ± 1 °C. Due to the basic nature of the hypochlorite solutions and the finding that the hydroxide ion can change the redox state of a manganese porphyrin,[11] test reactions were run to ascertain if the hydroxide ion concentrations employed would change the oxidation state of the manganese(III) catalyst. This was accomplished by preparing dichloromethane solutions from aqueous solutions of KOH (rather than LiOCl) and mixing this with a wet-dichloromethane solution containing the catalyst. The pH of the aqueous KOH solutions was between 10 and 12 whereas the pH of the aqueous solutions of LiOCl was at pH ~10. No change in the spectrum of the catalyst was noted upon mixing with the organic KOH solutions.

Epoxidation Studies. A dichloromethane solution (100 μL) (with and without NAcPhIm) containing $(Me_{12}TPP)Mn^{III}(Cl)$, alkene, and an internal standard was placed in a 1-mL gas-tight vial and sealed with a rubber septum Teflon-lined crimpable cap (Wheaton Scientific, Millville, NJ). The organic hypochlorite solution (100 μL) described previously was injected into the vial immediately after determination of $[ClO^-]$. After allowing the reaction to completion, GC analyses were performed. Yields of epoxides based on initial $[ClO^-]$ are reported.

Catalyst Integrity. To ascertain the integrity of $(Me_{12}TPP)Mn^{III}(X)$ when subjected to the reaction conditions described in this study, the spent reaction mixture was stirred over 6 M HCl for 12 h to regenerate $(Me_{12}TPP)Mn^{III}(Cl)$. This was subsequently purified by column chromatography on neutral alumina, isolated, and analyzed by mass spectrometry [MS (FAB/*m*-nitrobenzyl alcohol), calcd for $C_{56}H_{52}N_4MnCl$ 871; *m/e* 835 ($M^+ - Cl$)]. UV/vis spectrophotometric analyses of the spent reaction mixtures show a maximum of 5% loss of catalyst.

Results and Discussion

The time course for the oxidation of (5,10,15,20-tetrakis-(2,4,6-trimethylphenyl)porphinato)manganese(III) chloride ($(Me_{12}TPP)Mn^{III}(Cl)$) by hypochlorite in wet dichloromethane in the presence and absence of norbornene, *cis*-cyclooctene, or cyclohexene (25 ± 1 °C) has been studied by stopped-flow and rapid-scan stopped-flow spectrophotometry (between 350 and 650 nm). Dichloromethane saturated with water has been employed as the solvent for all reactions. Reactions were initiated by mixing solutions which we shall refer to as solution A and solution B throughout the text. Solution A contained $(Me_{12}TPP)Mn^{III}(Cl)$ + 4′-imidazol-1-ylacetophenone + alkene while solution B contained benzyldimethyltetradecylammonium chloride + ClO^- (see the Experimental Section). The yields of the corresponding epoxides (eq 1b) were determined by gas chromatographic analyses on completion of the reaction. The $[PTC]_i = 1.5 \times 10^{-2}$ M and the ratio of NAcPhIm to $(Me_{12}TPP)Mn^{III}(Cl)$ (3.1×10^{-6} to 8.3×10^{-6} M) was maintained at (20 ± 1):1 unless otherwise noted. At the concentrations of ClO^- [$(1.1–5.4) \times 10^{-4}$ M] employed, there was little or no decomposition of the manganese porphyrin catalyst. The concentrations of reagents employed in the various experiments are provided either in the tables or in the figure legends.

The product of "oxene" transfer from ClO^- to $(Me_{12}TPP)Mn^{III}(Cl)$ is a manganese oxo porphyrin $2e^-$ oxidized above the manganese(III) state (i.e., compound I state). We shall refer to this species by the abbreviation $(Me_{12}TPP)Mn^{V}(O)$. In the compound I state, it is generally accepted that $1e^-$ oxidation occurs on manganese; however, there is no agreement as to the site of the second $1e^-$ oxidation (manganese vs porphyrin ligand or the oxygen axial ligand[12]). Since there is a large difference (ca. 60 nm) between the positions of the Soret band of $(Me_{12}TPP)Mn^{III}(Cl)$ ($\lambda_{max} = 480$ nm) and $(Me_{12}TPP)Mn^{IV}(X)$ ($\lambda_{max} \approx 420$ nm) or $(Me_{12}TPP)Mn^{V}(O)$ ($\lambda_{max} \approx 418$ nm) (vide infra), one can follow the oxidation of the manganese(III) porphyrin by spectrophotometrically monitoring its disappearance at 480 nm ($\epsilon = 105\,000$ M^{-1} cm^{-1}, H_2O-saturated CH_2Cl_2). At this wavelength the absorbances of the higher valent manganese porphyrin species are minimal ($\epsilon = 11\,000$ M^{-1} cm^{-1}, H_2O-saturated CH_2Cl_2). The concentration of $(Me_{12}TPP)Mn^{III}(Cl)$ used was limited by the ~2.0-cm path length of the observation cell.

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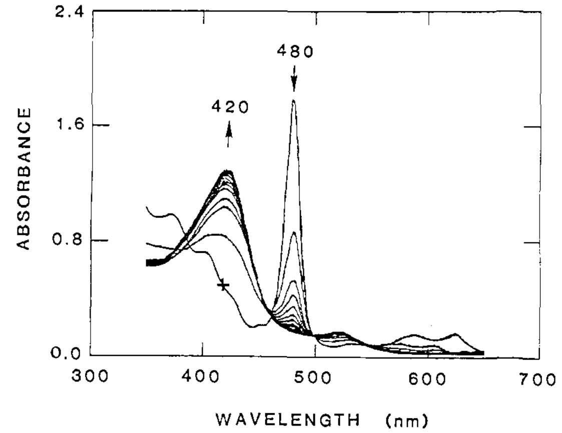

Figure 1. A typical example of a rapid-scan stopped-flow experiment showing the conversion of $(Me_{12}TPP)Mn^{III}(Cl)$ (λ_{max} = 480 nm) to a mixture of $(Me_{12}TPP)Mn^{IV}(X)$ (λ_{max} = 420 nm) and $(Me_{12}TPP)Mn^{V}(O)$ ($\lambda_{max} \approx 418$ nm). The experimental conditions were as follows: $[(Me_{12}TPP)Mn^{III}(Cl)]_i = 8.5 \times 10^{-6}$ M, $[ClO^-]_i = 3.4 \times 10^{-4}$ M, and $[NAcPhIm]_i = 1.7 \times 10^{-4}$ M; 20 scans were acquired in 200 ms and the initial wait time was 5 ms. A reference spectrum of $(Me_{12}TPP)Mn^{III}(Cl)$ is marked with a cursor.

In the absence of alkene in solution A, mixing solution A and solution B results in a decrease in A_{480}, which follows the first-order rate law. As shown in Figure 1, the disappearance of $(Me_{12}TPP)Mn^{III}(Cl)$ (λ_{max} = 480 nm) is accompanied by an increase in the absorbance at ~420 nm, attributable to some $(Me_{12}TPP)Mn^{V}(O)$ plus $(Me_{12}TPP)Mn^{IV}(X)$. Formation of a manganese(IV) product occurs by comproportionation of unreacted manganese(III) porphyrin with manganese(V)-oxo porphyrin (eq 2). Rapid-scan stopped-flow experiments conducted

$$(Me_{12}TPP)Mn^{III}(X) + (Me_{12}TPP)Mn^{V}(O) \rightarrow 2(Me_{12}TPP)Mn^{IV}(X) \quad (2)$$

in the presence of alkene showed a sharper Soret band (Figure 2) for the higher valent manganese porphyrin species. This is due to the decreased $[(Me_{12}TPP)Mn^{V}(O)]$ (λ_{max} ~ 418 nm), which is consumed in reaction with alkene.

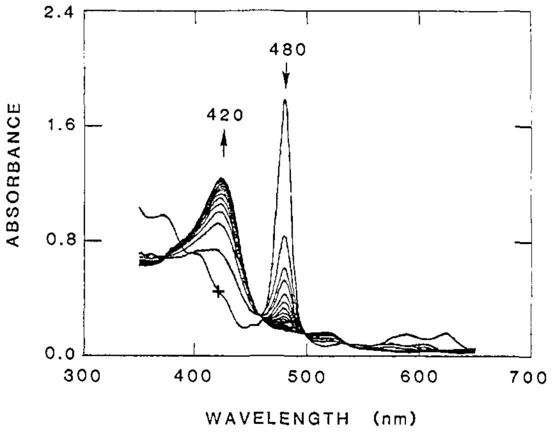

Figure 2. A typical example of a rapid-scan stopped-flow experiment showing the conversion of $(Me_{12}TPP)Mn^{III}(Cl)$ (λ_{max} = 480 nm) to $(Me_{12}TPP)Mn^{IV}(X)$ (λ_{max} = 420 nm). The experimental conditions were as follows: $[(Me_{12}TPP)Mn^{III}(Cl)]_i = 8.5 \times 10^{-6}$ M, $[ClO^-]_i = 1.3 \times 10^{-4}$ M, $[COT]_i = 8.5 \times 10^{-2}$ M, and $[NAcPhIm]_i = 1.7 \times 10^{-4}$ M; 20 scans were acquired in 200 ms and the initial wait time was 5 ms. A reference spectrum of $(Me_{12}TPP)Mn^{III}(Cl)$ is marked with a cursor.

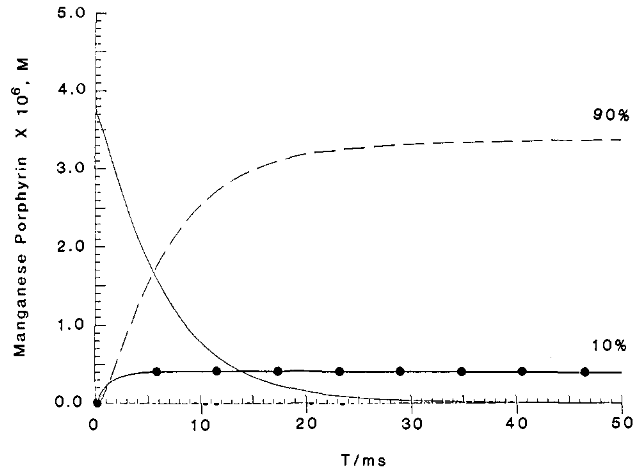

Figure 3. The computer-generated plot (based on Scheme I and associated rate constants) showing the time dependence for the concentrations of the three manganese porphyrin species present during the course of the reaction depicted in Figure 4. The solid line represents $(Me_{12}TPP)Mn^{III}(Cl)$; the broken line represents $(Me_{12}TPP)Mn^{IV}(X)$, and the solid line with circles represents $(Me_{12}TPP)Mn^{V}(O)$. The ratio of $(Me_{12}TPP)Mn^{IV}(X)$ to $(Me_{12}TPP)Mn^{V}(O)$ at the completion of the reaction is ca. 1:9. This agrees with the computer-assisted deconvolution of a spectrum of the reaction mixture produced in a similar run at completion of reaction (see the Experimental Section).

Table I. The Influence of Increasing $[NAcPhIm]_i$ on the Reaction of $(Me_{12}TPP)_{Mn}{}^{III}(Cl)$ and ClO^-

$[(Me_{12}TPP)Mn^{III}(Cl)]_i \times 10^6$, M	$[ClO^-]_i \times 10^4$, M	$[NAcPhIm]_i \times 10^5$, M	$k_1 \times 10^{-5}$, $M^{-1}\,s^{-1}$	k_4, s^{-1}
3.8	1.4	7.6	5.0	2.5
6.6	1.2	13	3.8	2.5
8.3	1.3	17	5.7	2.5
4.8	2.6	278	5.5	2.5
4.8	2.3	278	4.8	2.5
4.8	2.1	278	4.1	2.5

Scheme I

$$(Por)Mn^{III}(X) + ClO^- \xrightarrow{k_1 = (3.8 \pm 1.8) \times 10^5\ M^{-1}\,s^{-1}} (Por)Mn^{V}(O) + Cl^-$$

$$(Por)Mn^{V}(O) + (Por)Mn^{III}(X) \xrightarrow{k_2 = 2.0 \times 10^8\ M^{-1}\,s^{-1}} 2(Por)Mn^{IV}(X)$$

$$(Por)Mn^{V}(O) + Alkene \xrightarrow{k_3 = \text{variable}} (Por)Mn^{III}(X) + Epoxide$$

$$(Por)Mn^{V}(O) \xrightarrow{k_4 = \text{variable}} (Por)Mn^{III}(X)$$

All **computer simulations of the kinetic and epoxide yield** data have been carried out according to Scheme I, where Por = $(Me_{12}TPP)^{2-}$ and X = negatively charged axial ligands required to balance the charge on manganese (i.e., Cl^- and HO^-, etc.). The rate constants k_1 and k_2 of Scheme I were derived from experiments in which $[(Me_{12}TPP)Mn^{III}(Cl)]_i = (3.1–8.3) \times 10^{-6}$ M, $[ClO^-]_i = (1.1–5.4) \times 10^{-4}$ M, $[alkene]_i$ = 0–0.50 M, $[NAcPhIm]_i = (0–2.8) \times 10^{-3}$ M, and $[PTC]_i = 1.5 \times 10^{-2}$ M. The range of concentrations of ClO^- was restricted by a need for the reactions to exhibit reasonable absorbance changes and also by the large rate of the overall reaction. The value of k_1 provided in Scheme I represents the average for all kinetic runs in this study (i.e., presence and absence of alkene and NAcPhIm), and k_2 has been maintained at the given value. The ratios of k_1 and k_2 were chosen so that the value of $[(Me_{12}TPP)Mn^{V}(O)]/[(Me_{12}TPP)Mn^{IV}(X)]$ was equal (ca. 1:9, Figure 3) to that determined at the time of the complete disappearance of $(Me_{12}TPP)Mn^{III}(Cl)$ in the absence of alkene—about 50 ms (Figure 4). The value of $[(Me_{12}TPP)Mn^{V}(O)]/[(Me_{12}TPP)Mn^{IV}(X)]$ was estimated by computer deconvoluting (see the Experimental Section) the broad mixed Soret region (380–460 nm) upon the complete consumption of $(Me_{12}TPP)Mn^{III}(Cl)$. Value of k_3 and k_4 are dependent upon the nature of the given alkene or other added reagents. It is required to assume that $(Me_{12}TPP)Mn^{V}(O)$ carries out nonproductive $2e^-$ oxidations of solvent, trace impurities in PTC (vide infra), and alkene to yield products other than epoxide. Ex-

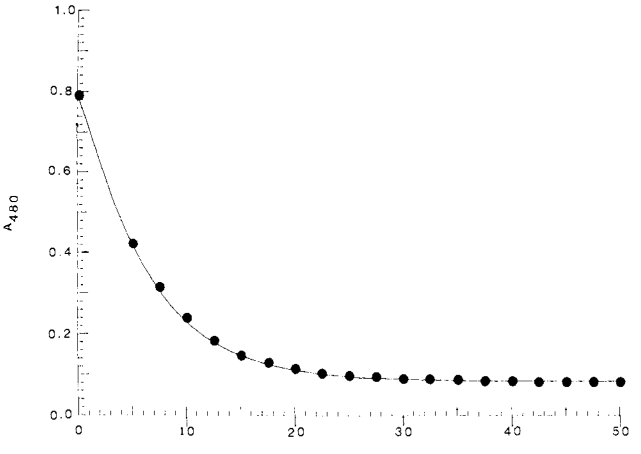

Figure 4. The time course, showing the decrease in (Me$_{12}$TPP)Mn^{III}(Cl) absorbance (λ_{max} = 480 nm), for the reaction of (Me$_{12}$TPP)Mn^{III}(Cl) (3.8 × 10^{-6} M) with ClO$^-$ (1.6 × 10^{-4} M). The line is computer generated with the rate constants given in Scheme I (k_1 = 5.5 × 10^5 M^{-1} s^{-1}) and the points are experimental.

Table II. The Effect of Increasing [PTC]$_i$ on the Reaction of (Me$_{12}$TPP)Mn^{III}(Cl) (8.5 × 10^{-6} M) and ClO$^-$ in the Presence of NAcPhIm (1.7 × 10^{-4} M)

[ClO$^-$]$_i$ × 10^4, M	[PTC]$_i$ × 10^4, M	k_1 × 10^{-5}, M^{-1} s^{-1}	k_4 × 10^{-2}, s^{-1}
3.0	5.0	2.5	1.0
2.3	30	1.0	18
1.1	110	1.0	21

Table III. The Rate Constants and Yields (Based on the Initial [ClO$^-$]) of Norbornene Oxide Produced in the Reaction of (Me$_{12}$TPP)Mn^{III}(Cl) (5.0 × 10^{-6} M) with ClO$^-$ in the Presence of NAcPhIm (1.0 × 10^{-4} M)

[ClO$^-$]$_i$ × 10^4, M	[Nb]$_i$, M	k_1 × 10^{-5}, M^{-1} s^{-1}	k_3 × 10^{-3}, M^{-1} s^{-1}	k_4 × 10^{-2}, s^{-1}	NbO, % yield
4.6	0.025	2.4	2.0	1.5	27
4.5	0.025	1.8	2.0	1.4	27
4.3	0.025	1.7	2.0	1.4	24
5.3	0.050	2.6	2.0	1.2	31
5.2	0.050	2.6	2.0	1.2	34
5.2	0.050	2.0	2.0	1.4	33
2.8	0.25	0.9	3.0	1.7	78
4.5	0.50	1.0	3.0	1.3	98
4.1	0.50	0.7	3.0	1.3	100

Table IV. The Yields (Based on the Initial [ClO$^-$]) of Norbornene Oxide Produced in the Reaction of (Me$_{12}$TPP)Mn^{III}(Cl) (5 × 10^{-6} M) with ClO$^-$ in the Absence (−) and Presence (+) of NAcPhIm (1 × 10^{-4} M)

[ClO$^-$]$_i$ × 10^4, M	[Nb]$_i$, M	NbO, % yield	NAcPhIm
4.1–5.4	0.025	12 ± 1	−
4.0–4.9	0.025	26 ± 6	+
4.1–5.2	0.050	15 ± 2	−
4.7–5.3	0.050	37 ± 5	+
2.4–3.2	0.25	42 ± 7	−
1.9–2.8	0.25	82 ± 7	+
3.2–4.5	0.50	97 ± 9	+

Table V. The Rate Constants of Scheme I for the Reaction of (Me$_{12}$TPP)Mn^{III}(Cl) with ClO$^-$ in the Presence of *cis*-Cyclooctene and 20 equiv of NAcPhIm

[(Me$_{12}$TPP)-Mn^{III}(Cl)]$_i$ × 10^6, M	[ClO$^-$]$_i$ × 10^4, M	[COT]$_i$ × 10^2, M	k_1 × 10^{-5}, M^{-l} s^{-1}	k_3 × 10^{-2}, M^{-1}, s^{-1}	k_4 × 10^{-2}, s^{-1}
4.8	2.5	4.8	4.7	6.6	1.4
5.5	2.2	5.0	7.0	7.0	1.5
4.8	2.1	4.8	5.0	5.0	1.0
4.8	1.9	4.8	4.5	5.0	1.0
5.5	1.7	5.0	6.8	7.6	1.3
5.0	1.2	5.0	5.5	6.0	1.0

Table VI. The Rate Constants of Scheme I for the Reaction of (Me$_{12}$TPP)Mn^{III}(Cl) with ClO$^-$ in the Presence of Cyclohexene and 20 equiv of NAcPhIm

[(Me$_{12}$TPP)-Mn^{III}(Cl)]$_i$ × 10^6, M	[ClO$^-$]$_i$ × 10^4, M	[CH]$_i$ × 10^2, M	k_1 × 10^{-5}, M^{-1} s^{-1}	k_3 × 10^{-2}, M^{-1} s^{-1}	k_4 × 10^{-1}, s^{-1}
5.0	3.3	5.0	7.0	1.0	5.0
4.4	3.0	4.4	7.0	1.0	5.0
5.0	2.9	5.0	6.0	1.0	5.0
4.4	2.8	4.4	6.0	1.0	5.0
5.0	2.7	5.0	5.0	1.0	5.0
5.0	2.5	5.0	4.5	1.0	5.0
4.4	2.5	4.4	5.5	1.0	5.0
4.4	2.2	4.4	5.2	1.0	5.0
5.0	1.7	5.0	7.0	1.0	5.0
5.0	1.2	5.0	4.5	1.0	5.0

penditure of (Me$_{12}$TPP)Mn^V(O) in such processes is incorporated into k_4.

The influence of NAcPhIm on the overall reaction of the manganese(III) porphyrin with ClO$^-$ is shown in Table I. The rate constant k_3 has no relevance in the absence of alkene. Examination of Table I shows that k_4 remains invariant with increasing [NAcPhIm]$_i$, which implies that NAcPhIm is inert toward oxidation by (Me$_{12}$TPP)Mn^V(O). It has been recorded,[7,13,14] when employing (TPP)Mn^{III}(Cl), that ligation of imidazole (in organic or aqueous media) is accompanied by substantial spectral changes from which the equilibrium constants for ligation were calculated. The species (Me$_{12}$TPP)Mn^{III}(Cl) does not complex with NAcPhIm (up to 580 equiv), as shown by spectral observations. Inspection of Table I shows that the rate constant (k_1) for reaction of (Me$_{12}$TPP)Mn^{III}(Cl) with ClO$^-$ is not changed by addition of increasing concentrations of NAcPhIm.

The influence of PTC concentration on the rate of disappearance of (Me$_{12}$TPP)Mn^{III}(Cl) in the absence of alkene is shown in Table II. The increase in k_4 is a function of PTC which was initially added to solution A (this is in addition to the usual 1.5 × 10^{-2} M PTC employed to solubilize the ClO$^-$). This is attributable to the oxidation of PTC or of an impurity present in the PTC.

The dependence of the spectral time course, as well as the yields of norbornene oxide (NbO), upon norbornene (Nb) concentration in the presence of NAcPhIm were computer simulated according to Scheme I. The values of the rate constants k_1, k_3, and k_4 (Table III) were obtained by iteration using the change in A_{480} due to the disappearance of (Me$_{12}$TPP)Mn^{III}(Cl) with the requirement of providing the experimentally determined yield of NbO (Figure 5). Only *exo*-norbornene oxide was detected. Due to the reaction of (Me$_{12}$TPP)Mn^{III}(X) with (Me$_{12}$TPP)Mn^V(O), the latter does not accumulate but, of course, (Me$_{12}$TPP)Mn^{IV}(X) does. The variation in the concentration of ClO$^-$ in the experiments of Table III is fortuitous. It is quite difficult to control this concentration at the time of initiation, although the concentration is accurately known at this time. The average values in Table III of k_1, k_3, and k_4 are (1.7 ± 0.7) × 10^5 M^{-1} s^{-1}, (2.3 ± 0.5) × 10^3 M^{-1} s^{-1}, and (1.4 ± 0.2) × 10^2 s^{-1}, respectively. The standard deviations of these rate constants (42%, 22%, and 11%, respectively) should be considered acceptable considering the difficulty of the experiments, which include the short time (~50 ms) elapsed before their completion.

As shown in Table IV, the yields of norbornene oxide are higher in the presence of NAcPhIm. Each percentage yield of NbO recorded in Table IV is the average obtained from six experiments. A plot of the percentage yield of NbO produced in the presence of NAcPhIm (*y* axis) vs the percentage yield of NbO produced in the absence of NAcPhIm (*x* axis) is linear with a slope of ~2 for [Nb]$_i$ = 0.025–0.25 M. An improved epoxidation efficiency, with the inclusion of NAcPhIm, is consistent with previous

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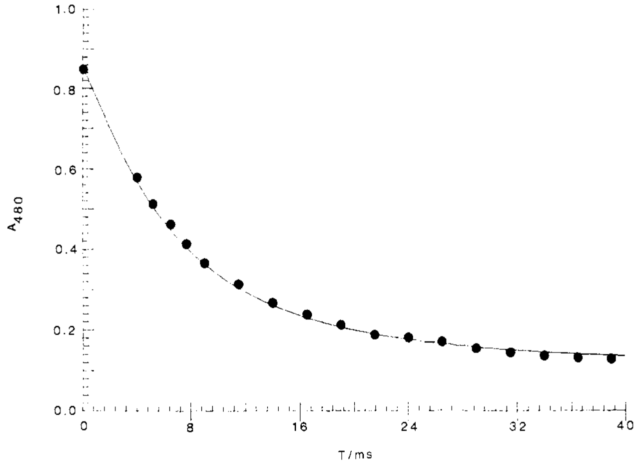

Figure 5. The time course, indicated by the decrease in absorbance (λ_{max} = 480 nm), for the reaction of $(Me_{12}TPP)Mn^{III}(Cl)$ (4.8×10^{-6} M) and ClO^- (4.5×10^{-4} M) in the presence of Nb (0.025 M). The line is computer generated with the rate constants given in Scheme I ($k_1 = 2.8 \times 10^5$ M^{-1} s^{-1}, $k_3 = 2.0 \times 10^3$ M^{-1} s^{-1}, and $k_4' = 120$ s^{-1}) and the points are experimental.

Table VII. The Rate Constant, k_5, for the Reappearance of $(Me_{12}TPP)Mn^{III}(X)$ in the Presence of Alkene and 20 equiv of NAcPhIm

$[(Me_{12}TPP)Mn^{III}(Cl)]_i$ $\times 10^6$ M	alkene	$[alkene]_i$	$[ClO^-]_i$ $\times 10^4$, M	k_{obsd} $\times 10^4$, s^{-1}
5.0	Nb	0.05	2.0	100
5.0	CH	0.05	2.0	6.0
5.0	COT	0.05	2.0	1.4
6.0	COT	0.085	6.1	32
8.0	COT	0.17	5.4	120

studies[9g,15] when employing phase-transfer conditions. Computer simulations were carried out for the epoxidation experiments performed in the absence of NAcPhIm. The values of k_1 were similar to those obtained in experiments performed with the inclusion of NAcPhIm.

The time course for disappearance of $(Me_{12}TPP)Mn^{III}(Cl)$ and yields of *cis*-cyclooctene oxide (COTO) and cyclohexene oxide (CHO) in the presence of NAcPhIm have been computer simulated. The yields of COTO produced (Table V) in these experiments were ~20% (based on $[ClO^-]_i$). The yields of CHO produced (Table VI) in these epoxidation experiments were ~9%, based on $[ClO^-]_i$. There was noted to be a lack of allylic oxidation products (2-cyclohexen-1-ol and 2-cyclohexen-1-one) by GC analyses.

The value of the rate constant, k_5, for the reversion of $(Me_{12}TPP)Mn^{IV}(X)$ to $(Me_{12}TPP)Mn^{III}(X)$, after most ClO^- has been consumed, is dependent on the composition of the reaction solutions. On completion of the reactions which have been discussed, there is a slow return of $(Me_{12}TPP)Mn^{IV}(X)$ to the $(Me_{12}TPP)Mn^{III}(X)$ state. The reappearance of $(Me_{12}TPP)Mn^{III}(X)$ apparently results from slow 1e⁻ reduction of $(Me_{12}TPP)Mn^{IV}(X)$ by alkene, solvent, or an impurity present in the reaction mixtures (eq 3). In the presence of alkene, the

$$(Me_{12}TPP)Mn^{IV}(X) \xrightarrow{k_5 = \text{variable}} (Me_{12}TPP)Mn^{III}(X) \quad (3)$$

reappearance of $(Me_{12}TPP)Mn^{III}(X)$ exhibited first-order behavior and is dependent on the concentration and identity of alkene (Table VII). Since these reactions are quite slow, the rate constants k_5 for disappearance of $(Me_{12}TPP)Mn^{IV}(X)$ is not critical to the computer fitting of the time course for $(Me_{12}TPP)Mn^{III}(X)$ disappearance.

Conclusions

The kinetics of the oxidation of $(Me_{12}TPP)Mn^{III}(Cl)$ in a wet-dichloromethane monophase employing hypochlorite as the oxygen atom donor solubilized by phase-transfer reagent have been studied. With use of Scheme I to computer simulate the experimental data, the rate constants for the following processes were obtained: (1) the oxidation of $(Me_{12}TPP)Mn^{III}(Cl)$ by hypochlorite [$(3.8 \pm 1.8) \times 10^5$ M^{-1} s^{-1}], (2) the comproportionation of $(Me_{12}TPP)Mn^{V}(O)$ with $(Me_{12}TPP)Mn^{III}(X)$ to yield 2-$(Me_{12}TPP)Mn^{IV}(X)$ (2×10^8 M^{-1} s^{-1}), and (3) the rate of alkene epoxidation by $(Me_{12}TPP)Mn^{V}(O)$. The rate constant for the epoxidation of norbornene is $(2,3 \pm 0.5) \times 10^3$ M^{-1} s^{-1} while that for the epoxidation of *cis*-cyclooctene is $(6.2 \pm 1.1) \times 10^2$ M^{-1} s^{-1} and, in the case of cyclohexene, 1.0×10^2 M^{-1} s^{-1}.

The ligating agent 4′-imidazol-1-ylacetophenone (NAcPhIm) does not appear to take part in the oxygen transfer from hypochlorite to $(Me_{12}TPP)Mn^{III}(Cl)$ nor is it oxidized by $(Me_{12}TPP)Mn^{V}(O)$. There is no spectral evidence for the ligation of NAcPhIm to $(Me_{12}TPP)Mn^{III}(Cl)$ in wet CH_2Cl_2. In the catalytic epoxidation cycle using norbornene as the substrate, the inclusion of NAcPhIm improves the yield of norbornene oxide by ~2-fold. This effect is relatively small when compared to results obtained with a H_2O/CH_2Cl_2 biphase and hypochlorite as the oxygen atom donor.[9g,15] Comparison of the rate constants for epoxidation of norbornene (Nb), *cis*-cyclooctene (COT), and cyclohexene (CH) shows that Nb is ~4-fold more reactive than COT and ~20-fold more reactive than CH. The rate constant (k_4) for nonproductive 2e⁻ oxidations are similar for the three alkenes.

At high concentrations of Nb (0.25 to 0.50 M), and in the presence of NAcPhIm, the yields of epoxide are quite respectable (Table IV). It is not possible to compare these values to those obtained in a CH_2Cl_2/H_2O biphase[15b,16] due to the different methods of determining the yields of epoxides. In this study, yields are based on initial $[ClO^-]$ under conditions such that $[alkene]_i > [ClO^-]_i$, while in investigations using the CH_2Cl_2/H_2O biphase, yields were based on the percent of alkene epoxidized when $[ClO^-]_i > [alkene]_i$. The values of the rate constants for alkene epoxidation are orders of magnitude greater for the homogeneous system when compared to experiments in a CH_2Cl_2/H_2O biphase. This discrepancy casts considerable doubt on previous[12b,12c,17] interpretations of the kinetics of the CH_2Cl_2/H_2O biphasic system. Although the homogeneous system is not a high-yielding epoxidizing "machine", it does provide a clearer picture of the events that occur during the course of the catalytic epoxidation cycle. Even with the limitations and nonideality of this system, it allows for a good approximation of otherwise inaccessible rate constants (Scheme I).

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