ratio and number and type of residual alkali cations on the charge density residing on the oxygen atoms in the zeolite framework, all of which contribute to the crystal field sensed by, and the electron density located on, the transition metal cation. Ultimately this knowledge could assist with the understanding of metal-support effects and in the fine tuning of the electronic, magnetic, chemical and catalytic properties of transition metal loaded zeolites.

Acknowledgment. The financial assistance of the Natural Sciences and Engineering Council of Canada's Strategic Grants Programme and the Connaught Foundation of the University of Toronto is gratefully appreciated. The granting of a 3M Corp. scholarship and a Union Carbide Innovation Recognition Award to G.A.O proved to be invaluable. In addition, the donation of zeolite samples from, and helpful technical discussions with, Dr. Edith Flanigen (Union Carbide), Dr. Nicolas Spencer (W. R. Grace Co.) and Dr. Paul Kasai (IBM) is sincerely appreciated. W.S. is also indebted to Nankai University and the Government of the Peoples Republic of China for a 2-year leave of absence at the University of Toronto and financial assistance. We are indebted to Kate Helwig for preparation of the calcium sample.

Registry No. Ca^{2+}, 14127-61-8; Mn^{2+}, 16397-91-4; Fe^{2+}, 15438-31-0; Co^{2+}, 22541-53-3; Ni^{2+}, 14701-22-5; Cu^{2+}, 15158-11-9; Zn^{2+}, 23713-49-7.

Epoxidation of Olefins by Cytochrome P-450 Model Compounds: Kinetics and Stereochemistry of Oxygen Atom Transfer and Origin of Shape Selectivity

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Abstract: An analysis of the mechanism of the lithium hypochlorite epoxidation of olefins catalyzed by Mn(TPP)Cl is presented. We have previously reported that the oxygen atom transfer from manganese porphyrin to olefin occurs via an oxo-olefin intermediate whose breakdown is the rate-determining step of the catalytic cycle. Stereochemical and kinetic evidence presented here indicate that both formation of this intermediate and its subsequent breakdown to form epoxide are, in general, concerted processes. The rarely observed loss of stereoselectivity represents the presence of a minor leakage pathway in the breakdown of the oxo-olefin complex to form epoxide. Shape selective olefin epoxidation is achieved when the sterically hindered porphyrin, Mn(TMP)Cl, is used as a catalyst in the hypochlorite system. The observed shape selectivity parallels the large differences in binding energies for formation of the oxo-olefin complex.

Introduction and Background

The cytochrome P-450 enzyme family catalyzes the reaction of hydrocarbons with molecular oxygen, incorporating one oxygen atom into the substrate, the other being reduced to water[2] (eq 1).

$$RH + O_2 + NADPH + H^+ \rightarrow ROH + H_2O + NADP^+ \quad (1)$$

The active site contains an iron(III) protoporphyrin IX moiety with a cysteine thiolate as one axial ligand. Evidence to date indicates that the active species is an iron oxo complex in which the iron porphyrin system is two oxidation levels above the ferric state. The reactivity of this high-valent species is remarkable, P-450 being the only known hemoprotein capable of hydroxylating unactivated carbon-hydrogen bonds. The majority of steps in the catalytic cycle of the enzyme are reasonably well understood. However, the mechanism of the most significant step, oxygen atom transfer to the substrate, is the least understood and still quite speculative.

The observation that P-450 with suitable oxygen atom transfer agents will anaerobically oxygenate substrates[3] has spurred much interest in modeling studies using synthetic metalloporphyrins. High-valent metalloporphyrin species can be obtained directly from iron,[4] manganese,[5] and chromium[6] porphyrins with the use of various forms of reduced oxygen. On the basis of these findings, catalytic systems have been devised which oxygenate hydrocarbons in good yields.[7] Shape selective catalysts for both alkane hydroxylation and olefin epoxidation have been discovered[8] by using

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sterically hindered porphyrins. However, a kinetics analysis by Bruice of one such system reveals a problem common to many: the rate-determining step of the catalytic cycle is often formation of the oxo complex.[9] Thus the mechanism of the most important step, oxygen atom transfer from metalloporphyrin to substrate, is kinetically inaccessible in these interesting model systems.[10,11]

We recently described a highly efficient catalytic system for the epoxidation of olefin which employs manganese(III) tetraarylporphyrins, an imidazole ligand, a phase transfer catalyst, and sodium hypochlorite as the oxygen atom source in a two-phase (CH_2Cl_2/H_2O) system.[12] We found that the nature of the added axial ligand greatly influenced the selectivity of the oxidant toward olefins, the rate of the overall reaction, and the stability of the catalyst toward degradation. With the imidazole ligand, initial turnover rates of up to 10 per s are realized.[12] Stoichiometric reactions studied by Meunier have demonstrated the active oxidant to be a high-valent manganese oxo complex.[13] Previous studies with pyridine have indicated that the nitrogenous base acts as a ligand and not as a general base.[14]

A kinetic study of this system with Mn(TPP)Cl[15] revealed that even at saturating levels of hypochloride ion, the reaction rate is independent of the concentration of the olefin. However, different olefins are epoxidized at different rates.[16] *Therefore the olefin must be involved in the rate-determining step.* This kinetic scheme is frequently encountered in enzymology and is described by the Michaelis–Menten equation[17] (eq 2).

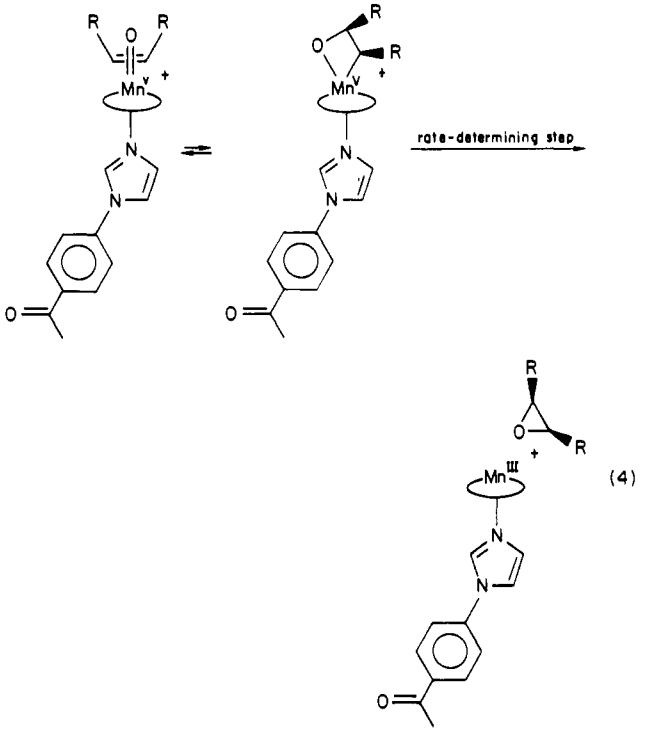
$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow[\text{rate-determing step}]{k_2} E + P \qquad (2)$$

The enzyme (E) and substrate (S) reversibly interact to yield a complex (ES) that breaks down in the rate-determining step.[18] The hyperbolic plot of initial velocity vs. substrate concentration is defined by two parameters, V_{max} and K_m, according to the mathematical relationship

$$\frac{d[P]}{dt} = \frac{V_{max}[S]}{K_m + [S]} \qquad (3)$$

V_{max} is equal to k_2 times the total enzyme concentration and gives a direct measure of the rate-determining step. K_m is defined as $(k_{-1} + k_2)/k_1$ and in the limit that $k_{-1} \gg k_2$ gives a measure of the binding affinity of the substrate. (A large binding affinity corresponds to a low K_m.)

In analogy to the above scheme, our kinetic results show that the olefin binds reversibly to the manganese oxo species, forming an oxo-olefin intermediate. The breakdown of this complex to epoxide and manganese(III) is the rate-determining step of the catalytic cycle. We have proposed that this intermediate is a metallaoxetane.[16]



(4)

To date, direct spectroscopic analysis of this interesting intermediate has not been possible. However, kinetic studies of the hypochlorite system have enabled us to show that the oxygen atom transfer from manganese porphyrin to olefin occurs in at least two steps. We can now separate the reactivity of the manganese oxo with olefins into two components: the binding energy for formation of the intermediate (K_m values) and the rate constant for the decomposition of the intermediate to products (V_{max} values). Using both kinetic and stereochemical probes, we herein provide evidence that both formation and decomposition of the oxo-olefin complex are principally concerted processes, in the sense that the stereochemical integrity of the olefin is maintained throughout and there are no kinetically detectable radical intermediates. We then argue that the metallaoxetane formulation for this species is most consistent with these data.

The promise which cytochrome P-450 model systems possess for use as efficient oxidation catalysts has not gone unnoticed. Of particular interest is the engineering of metalloporphyrins for the shape-selective and asymmetric catalytic oxygenation of hydrocarbons. A rational approach to the design of such catalysts is dependent upon a detailed understanding of how catalyst-substrate interactions affect each step in the catalytic cycle. When Mn(TMP)Cl is used as the catalyst in the hypochlorite system, the *o*-methyl groups on the porphyrin periphery provide sufficient steric hindrance to allow shape-selective, catalytic olefin epoxidation. Using the above kinetic analysis, we find the observed shape selectivity in this system parallels the large differences in binding energies (K_m values) for various olefins. The interpretation of these results corresponds conceptually to the lock and key model used to explain the high substrate specificities of many enzymes.

Experimental Section

Instrumentation. All NMR spectra were recorded on a Nicolet NMC 300-MHz spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5880A gas chromatograph fitted with a 12 ft × $^1/_8$ in. column of 10% OV-101 on Chromasorb P. UV–vis spectra were recorded on a Cary Model 219 spectrometer from Varian.

Materials. Manganese(III) *meso*-tetraphenylporphyrin chloride [Mn^{III}(TPP)Cl][19] and manganese(III) *meso*-tetramesitylporphyrin chloride [Mn^{III}(TMP)Cl][20] were synthesized by literature methods and purified by recrystallization from methylene chloride/hexanes. 4′-(Im-

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(10) This appears to be true for the natural enzyme as well. Kinetic studies on cytochrome P-450 Cam have shown the rate-determining step of the catalytic cycle to be the addition of a second reducing equivalent from putidaredoxin to the iron(II) dioxygen complex of P-450. This step exhibits a rate of 17 s^{-1} and occurs before O–O bond cleavage of dioxygen and subsequent oxygenation of the substrate. Tyson, C. A.; Lipscomb, J. D.; Gunsalus, I. C. *J. Biol. Chem.* **1972**, *247*, 5777–5784.

(11) A possible exception is the robust oxygenation system reported by Traylor et al. which exhiibits fast rates, high turnovers, and unusual stability toward catalyst degradation. Traylor, P. S.; Dolphin, D.; Traylor, T. G. *J. Chem. Soc., Chem. Commun.* **1984**, 279–280.

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(14) Guilmet, E.; Meunier, B. *Tetrahedron Lett.* **1982**, 2449–2450.

(15) Abbreviations: TPP = *meso*-tetraphenylporphyrinato; TMP = *meso*-tetramesitylporphyrinato; NAcPhIM = 4′-(imidazol-1-yl)acetophenone.

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(20) Bortolini, O.; Meunier, B. *J. Chem. Soc., Perkin Trans. 2*, in press.

idazol-1-yl)acetophenone (NAcPhIm) (Aldrich) was twice recrystallized from methylene chloride/hexanes. Benzyldimethyltetradecylammonium chloride (Fluka) was used without further purification. Saturated linear hydrocarbons C_8–C_{14} were purchased from Aldrich (99%+) and used as internal standards without further purification. Methylene chloride was distilled from CaH_2. Olefins were purchased from ICN or Aldrich and passed through short alumina columns immediately prior to reaction to remove trace peroxides.

The hypochloride solution was prepared as follows. LiOCl (3.5 g) (30%) purchased from Fluka was dissolved in 50 mL of deionized water. To this solution was added 1.15 g of anhydrous $BaCl_2$ to remove sulfates. The $BaSO_4$ was allowed to settle, and the solution was filtered away from the precipitate. The pH was 11.8. The concentration of LiOCl was 0.31 M as determined by thiosulfate titration. These solutions were always used within 0.5 hr. Deviation from these conditions can lead to irreproducible results.

Kinetics. Standard conditions for kinetics experiments are as previously described.[16] Under these conditions the reaction was experimentally determined to be first order in manganese porphyrin[21] and independent of hypochlorite concentration. NAcPhIm (0.62 mmol), internal standard, and catalyst (0.007 mmol) were placed in a 100-mL round-bottom flask equipped with a 1 in. × $^1/_4$ in. stirbar. Sufficient methylene chloride was added such that the total volume was 10 mL. A constant temperature bath was used to maintain the temperature at 22 ± 0.5 °C. Twenty milliliters of the hypochlorite solution (6.2 mmol LiOCl) was then layered over the organic phase. The reaction was initiated by vigorous stirring, and aliquots were taken every minute by stopping both stirbar and timer for 0.1 min and sampling the organic phase. Longer sampling periods did not affect the measured epoxidation rates. In most olefins, direct analysis of the reaction mixture was possible using gas chromatography.

Experiments where *cis*-stilbene, *trans*-stilbene, or *trans,trans,cis*-1,5,9-cyclododecatriene was employed as a substrate could not be analyzed in this way. Therefore, 0.5-mL aliquots of the reaction mixture were loaded on $^1/_8$ in. × 2 in. alumina columns, and the organic products and unreacted olefin were eluted with 15 mL of pentane. The pentane was removed on a rotory evaporator, and the residue was taken up in $CDCl_3$. Analysis of the products and unreacted olefin was performed by 300-MHz ^1H NMR.

In all cases the epoxide was the major product with the selectivity ranging from 85 to 98%. One exception is styrene, from which both styrene oxide and phenylacetaldehyde are produced as primary products in a ratio of approximately 4 to 1. The other exception is 1-methylcyclohexene, giving a selectivity for epoxide of only 76%. No other products for this olefin could be detected in the organic phase.

All concentration values are based on the volume of the organic phase. All reaction rates are determined at early reaction times (<50% conversion) and are reproducible to within 10%. V_{max} values are reported in mmol of epoxide produced per mmol of catalyst per s (turnovers per second).

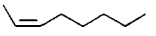
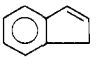
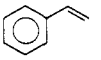
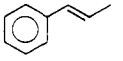
Determination of K_m and V_{max}: Mn(TPP)Cl (Method 1). For every olefin examined with use of Mn(TPP)Cl, the reaction rate was found to be zero order in the concentration of the olefin. V_{max} values were therefore determined under saturation conditions (>0.4 M in olefin) and are reproducible to within 10%. Relative K_m values were determined by allowing olefins to compete with cyclooctene. Under steady-state conditions for competitive inhibition, the ratio of rates for two competing substrates A and B is given by the following equation[22]

$$\frac{-d[A]/dt}{-d[B]/dt} = \frac{[A]V_{max}^{A}K_m^{B}}{[B]V_{max}^{B}K_m^{A}} \quad (5)$$

Thus a plot of the relative rates of epoxidation vs. the ratio of substrate concentrations will yield a straight line with slope equal to $(V_{max}^{A}/V_{max}^{B})(K_m^{B}/K_m^{A})$. By knowing V_{max}^{A} and V_{max}^{B}, the relative K_m values (K_m^{B}/K_m^{A}) can be calculated. These values were determined relative to cyclooctene. Note that a simple first-order competition of olefins for the oxo will yield a similar plot with slope equal only to $(V_{max}^{A}/V_{max}^{B})$. This is not observed.

Determination of V_{max} and K_m: MnTMPCl (Method 2). V_{max} and K_m could be obtained for most olefins by standard techniques. Initial velocity measurements were made at six or more olefin concentrations which normally ranged from 0.5 to 5 times the K_m of the particular substrate. The parameters were calculated from these measurements by the method of Lineweaver and Burk.[23] V_{max} and K_m for cyclooctene were determined by method 1 in competition with *cis*-2-octene.

Table I. Kinetic Parameters for Epoxidation Catalyzed by Manganese Porphyrins

olefin	Mn(TPP)Cl K_M(rel), M	Mn(TPP)Cl V_{max}, turnovers/s	Mn(TMP)Cl K_M, M	Mn(TMP)Cl V_{max}, turnovers/s
	1.0	1.0	0.02	4
	1.0	1.0	0.04	5
	1.5	3.1	0.08	8
	2.1	1.5	0.8	11
	0.32	0.37	8	6
	1.8	1.4	*a*	*a*

[a] Could not be determined.

Results and Discussion

Mechanism of Oxygen Atom Transfer. For every olefin examined with use of the less hindered catalyst, Mn(TPP)Cl, the reaction rate was found to be zero order in the concentration of the olefin. Under these conditions the epoxidation rate could not be increased by the further addition of phase-transfer catalyst or by increasing the concentration of aqueous lithium hypochlorite. As the organic phase is not starved for hypochlorite, the saturation conditions of the olefin imply that all of the manganese catalyst is present as the oxo-olefin complex. UV–vis spectra of the catalytic reaction under these conditions are dominated by a strong absorbance at about 420 nm. This broad Soret band is common to many oxidized manganese porphyrins, and being insensitive to the ligands coordinating the metal, it confirms only that the steady state of the catalyst is a manganese porphyrin in the +4 or +5 oxidation state.[5d,7h]

Studies in which the concentration of the olefin was lowered in an attempt to reach the linear part of the Michaelis–Menten curve only resulted in unacceptable catalyst degradation. This can be followed by UV–vis spectra taken of organic aliquots removed from the reaction mixture that no longer contain a source of hypochlorite. These spectra reflect the resting state of the catalyst and are identical with the starting manganese(III) porphyrin having a Soret band at 480 nm. With insufficient olefin present in the reaction mixture, spectra of aliquots taken after 1 min of the catalytic reaction no longer exhibit this Soret at 480 nm, indicating that the porphyrin macrocycle has been destroyed. Therefore, while absolute V_{max} values could be obtained under saturation conditions in olefin, only relative K_m values were obtained by means of competition experiments with use in each case of cyclooctene as a competitive inhibitor (cf. the Experimental Section). Absolute V_{max} and relative K_m values for Mn(TPP)Cl are reported in Table I.

By using the sterically hindered porphyrin, Mn(TMP)Cl, it proved possible to measure rate data in which the reaction order with respect to olefin concentration varied from one to zero for many olefins. Thus absolute K_m and V_{max} values could be obtained from Lineweaver–Burk analyses, and these are also reported in Table I. As an example, the data for the epoxidation of indene catalyzed by Mn(TMP)Cl and the corresponding double reciprocal

(21) In the Mn(TPP)Cl concentration range 3.0×10^{-4} to 2.0×10^{-3} M, the reaction order in catalyst decreases from 1 to 0 with standard conditions with cyclooctene as a substrate. At high catalyst concentrations the rate could not be increased by the addition of more phase transfer agent or by an increase in the concentration of the aqueous hypochlorite solution. Mn(TMP)Cl in the same concentration range exhibits linear first-order behavior. We do not fully understand the implications of these results, but manganese porphyrins are known to dimerize under similar oxidizing conditions.[5d,7h] For Mn(TPP)Cl, we believe some of the catalyst may be present in an inactive state at higher catalyst concentrations; therefore, all epoxidations were performed at a manganese porphyrin concentration of 7.0×10^{-4} M, where the reaction is first order with respect to catalyst.

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(23) Lineweaver, H.; Burk, D. *J. Am. Chem. Soc.* **1934**, *56*, 658–666.

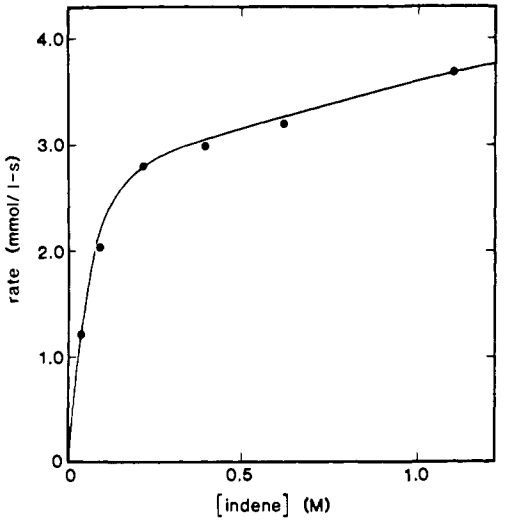


Figure 1. Plot of initial velocity vs. olefin concentration for the Mn(TMP)Cl catalyzed epoxidation of indene.

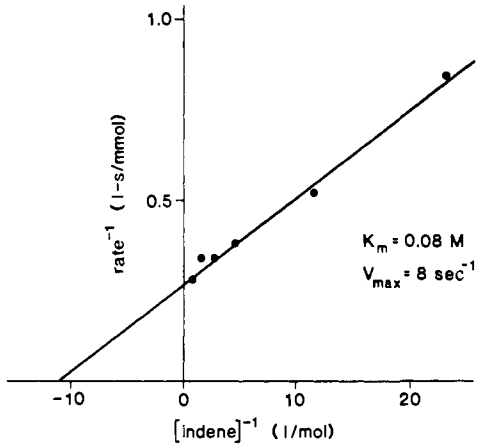
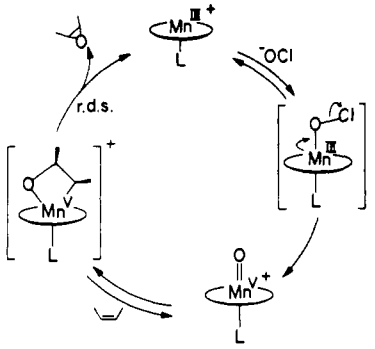


Figure 2. Double reciprocal plot for the Mn(TMP)Cl catalyzed epoxidation of indene.

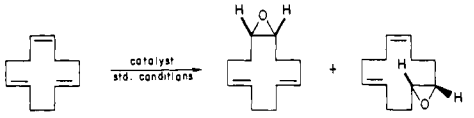
Scheme I



plot are shown in Figures 1 and 2. These results further substantiate our previously published mechanism shown in Scheme I, where the rate-determining step of the catalytic cycle is a breakdown of the oxo-olefin complex.[24]

Inspection of the K_m and V_{max} values in Table I for the unhindered Mn(TPP)Cl reveals that electron-rich olefins bind somewhat more efficiently (lower K_m) than do electron-poor olefins. Small geometric preferences are observed, cis olefins binding better than trans olefins. In general, however, only modest differences in K_m values and V_{max} values are observed. This is further illustrated by the fact that the Mn(TPP)Cl catalyzed epoxidation of *trans,trans,cis*-1,5,9-cyclododecatriene gives only a 1.4 to 1 preference for the cis epoxide (corrected for the number of double bonds, Table II).

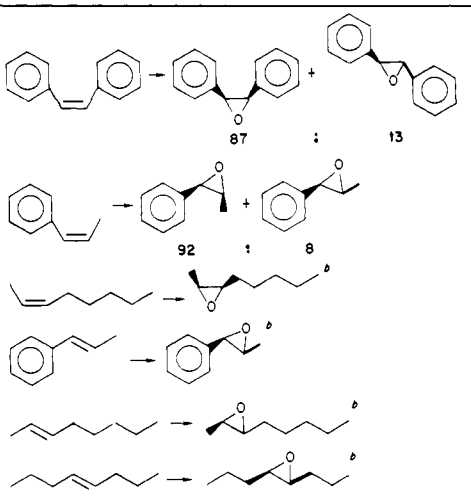
Table II. Manganese Porphyrin Catalyzed Epoxidation of *trans,trans,cis*-1,5,9-Cyclododecatriene



catalyst	% cis[a]	% trans[a]	cis/trans[b]
MnTPPCl	41	59	1.4
MnTMPCl	88	12	15

[a] Observed ratio of products at 40% conversion. [b] Cis/trans selectivity accounting for the two trans double bonds and one cis double bond in the starting olefin.

Table III. Stereochemistry of Epoxidation Formation (Mn(TPP)Cl)[a]



[a] Product ratios at 40% conversion. [b] Only isomer produced >98% of epoxide product.

The epoxidation of *cis*-stilbene has been widely used as a probe of the stereoselectivity of P-450 model systems, due to the large strain manifested in the cis arrangement of the two phenyl substituents.[5b,7a,j,l] In many related oxygenation systems, a mixture of cis and trans epoxides has been observed, the exact ratio depending upon the nature of the catalyst and the reaction conditions. This has been taken as evidence for the presence of radical species in the general reaction scheme. In view of the uncertain nature of the oxo-olefin complex, we were interested in determining if this loss of stereoselectivity occurs during the formation of the intermediate or its subsequent breakdown to products. Under our standard conditions, using Mn(TPP)Cl, a series of cis and trans olefins was epoxidized; the ratio of products is shown in Table III. For *cis*-stilbene and *cis*-β-methyl styrene, some trans epoxide is observed. However, for *all* of the olefins shown, *analysis of the olefin pool at low conversion showed no loss of olefin stereochemistry*. As the cis olefins react faster than the trans, any build up of the trans olefin would be detected under our reaction conditions. These results argue that the reversible formation of the intermediate is a rigorously concerted process and any loss of stereochemistry occurs during breakdown of the intermediate, which is the rate-limiting step.

Since a mixture of epoxides is produced during the oxygenation of *cis*-stilbene, it seems plausible to postulate that decomposition of the oxo-olefin intermediate might proceed via a transient radical species which would allow a limited amount of rotation about the former olefinic bond prior to closure (Figure 3). However, several pieces of evidence argue against this postulate. In only two cases was any loss of stereochemistry observed in the epoxide product. Furthermore, Table I demonstrates that while different substrates are epoxidized at different rates, the spread in the rate constants for decomposition of the intermediate (V_{max}) is very small. If the rate-determining step involved the generation of a radicaloid or carbonium ion species, one would expect that the various sub-

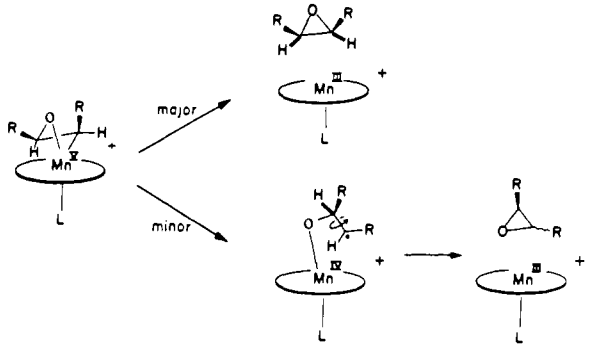
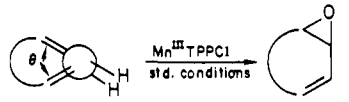


Figure 3. Pathways for epoxide formation.

Table IV. Mn(TPP)Cl Catalyzed Epoxidation of Cyclic 1,3-Dienes



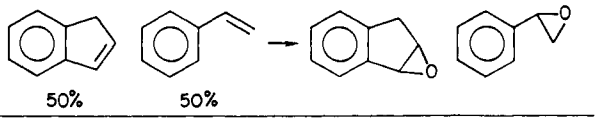
olefin	θ	V_{max}, turnovers/s
	10	3.4
	22	2.1
	55	0.8

stituents on the substrates examined would have a larger effect on the rate.

This argument was further substantiated by examining the rates of epoxidation of cyclic 1,3-dienes by Mn(TPP)Cl as shown in Table IV. The ground-state conformations of these molecules have been thoroughly studied both experimentally[25] and theoretically.[26] It has been found that the degree of conjugation decreases with ring size due to the conformational preferences of the carbocyclic ring. If the geometry of the ring is even roughly maintained upon binding to the manganese oxo species, one might expect substantially different degrees of allylic stabilization were the oxo-olefin complex to decompose via a radicaloid path. In addition, one would expect unusually high rates of epoxidation in these cases, since allylic stabilization would lower the energy of a carbon-based radical and the activation energy barrier of the rate-determining step by approximately 12–15 kcal/mol.[27] Although the predicted trend in epoxidation rates is observed, the differences are quite small, merely a factor of 4 between the C_6 and C_8 dienes. More importantly, a large rate enhancement over simple olefins is not observed.

These results argue against the presence of radical species in the dominant reaction pathway and against the oxo-olefin intermediate having radicaloid character. We believe that the small amount of isomerization observed during the epoxidation of *cis*-stilbene and *cis*-β-methylstyrene represents the presence of a minor, parallel reaction path and that these experiments are not indicative of the general reaction mechanism. In addition, the relative insensitivity of V_{max} to olefin substitution in general indicate that the concerted decomposition has an early transition state, similar in structure to the oxo-olefin intermediate.

Table V. Mn(TMP)Cl Catalyzed Competitive Epoxidation of Indene and Styrene



predicted[a]	87%	13%
observed[b]	91%	9%

[a] Product ratios predicted by using eq 5 and kinetic parameters reported in Table I. [b] Observed products determined at 10% conversion.

Origin of Shape Selectivity. Several groups have reported the use of sterically hindered porphyrins as shape-selective catalysts for the oxygenation of hydrocarbons.[8] In particular Groves has noted the strong preference for cis olefins in iodosylbenzene epoxidations catalyzed by iron tetramesityl porphyrin.[7a,8b] Mn(TMP)Cl shows similar properties under our catalytic conditions. Whereas the Mn(TPP)Cl catalyzed epoxidation of *trans,trans,cis*-1,5,9-cyclododecatriene yields a 1.4 to 1 ratio of cis and trans epoxides, a ratio of 15:1 is achieved when MnTMPCl is employed (corrected, Table II). Two possibilities for the origin of this selectivity exist. The first is that the ratio of products is determined by the relative binding affinity of the olefins to the manganese oxo complex (K_m values). That is, the predominant olefin oxo complex in solution becomes the major epoxide product. This is conceptually equivalent to the lock and key model proposed to explain the high substrate specificities of many enzymes. The second possibility is that the ratio of products is determined by a large difference in the activation energies for decomposition of the two intermediates (V_{max}). In this case the minor oxo-olefin complex in solution reacts faster to become the major epoxide product. Such a phenomenon was encountered by Halpern in the asymmetric hydrogenation of α-acetamidocinnamic acid derivatives catalyzed by Rh(I) phosphine complexes.[28] From a knowledge of the K_m and V_{max} values for the manganese porphyrin olefin epoxidation catalyst, these possibilities can be distinguished. Examination of the data in Table I for the two catalysts used shows that whereas large differences in K_m and V_{max} do not occur for Mn(TPP)Cl, *the range of binding constants for Mn(TMP)Cl varies over 300-fold*! Thus the shape selectivity afforded by the sterically encumbered catalyst arises from large differences in the binding energies for formation of the oxo-olefin complex. Furthermore, the differences are completely due to steric interactions, as evidenced by the fact that the most electron rich but sterically demanding substrate, 1-methylcyclohexene, is the poorest binder.

Interestingly, the K_m values in Table I lead us to predict the existence of catalyst–substrate interactions far more subtle than simple cis vs. trans selectivity. For example, while the V_{max} values in the Mn(TMP)Cl catalyzed epoxidations of indene and styrene are quite similar, the two binding constants differ by an order of magnitude. These data and eq 5 lead to the expectation that the initial rates of epoxidation of indene and styrene in a one-to-one competition should differ by a factor of roughly 10 to 1. Indeed, as shown in Table V, this is exactly the result obtained, providing a striking example of the predictive powers inherent in our kinetic model. The existence of such subtle shape selectivity sets these biomimetic catalysts apart from conventional synthetic reagents. A detailed understanding of the factors governing porphyrin–substrate interactions will allow the rational design of new, specific catalysts for selective hydrocarbon oxygenation.

Conclusion

We have shown that the reactivity of manganese oxo porphyrins with olefins can be separated into two components: the reversible formation of an intermediate oxo-olefin complex and its subsequent irreversible breakdown to form epoxide. Our stereochemical and kinetic results indicate that both the binding and breakdown steps are, in general, concerted processes; the rarely observed scrambling represents a minor leakage pathway in the breakdown step.

(24) A report (Razenberg, J. A. S. J.; Nolte, R. J. M.; Drenth, W. *Tetrahedron Lett.* **1984**, *25*, 789–792) of a preliminary kinetic study on this same system with pyridine had concluded that the rate-determining step of the catalytic cycle is manganese oxo formation from a manganese hypochlorite complex. This is consistent with the limited results reported therein but *not* consistent with our studies which show dependence of the rate constant on the nature of the olefin.

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Second, the sterically hindered catalyst Mn(TMP)Cl exhibits substantial shape selectivity in the catalytic epoxidation of olefins, and this is shown to be directly attributable to the differences in binding energies for formation of the intermediate. Our observations suggest a strategy for the development of other shape-selective, as well as asymmetric, porphyrin catalysts for olefin epoxidation.

These findings in turn argue that the oxo-olefin complex does not contain carbon-based cationic or radicaloid centers. The formation of this complex is rather insensitive to electronic effects of the olefin, but it is markedly influenced by steric interactions when the more sterically demanding catalyst, Mn(TMP)Cl, is used. These conclusions are consistent with our postulate that the intermediate is a metallaoxetane, which we speculate is formed by a concerted antarafacial 2 + 2 cycloaddition.[29] On the basis of the evidence presented here, it appears the normal mode of decomposition of this species is a concerted reductive elimination. Complete substantiation of these postulates awaits direct structural and spectroscopic analysis of the intermediate. Such studies are currently being pursued in our laboratories.

Finally, these studies have shed light on the general reactivity of high-valent manganese oxo porphyrins. At this point, the possible extension of this mechanism to other metals is not proven, but it seems plausible. In view of the similar reactivities of cytochrome P-450 and other model systems as evidenced by N and O demethylation,[30] the NIH shift,[31] and alkane hydroxylation,[32] it would not be suprising to find other similar stereoselective olefin epoxidations occurring by this general route.

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Registry No. Mn(TPP)Cl, 32195-55-4; Mn(TMP)Cl, 85939-49-7; lithium hypochlorite, 13840-33-0; cytochrome P-450, 9035-51-2; monooxygenase, 9038-14-6; cyclooctene, 931-88-4; (*Z*)-2-octene, 13389-42-9; indene, 95-13-6; 1-ethenylbenzene, 100-42-5; 1-methylcyclohex-1-ene, 591-49-1; (*E*)-1-propenylbenzene, 873-66-5; *trans,trans,cis*-1,5,9-cyclododecatriene, 706-31-0; *cis*-stilbene, 645-49-8; (*Z*)-1-propenylbenzene, 766-90-5; (*E*)-2-octene, 7642-04-8; (*E*)-4-octene, 14850-23-8; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0; 1,3-cyclooctadiene, 1700-10-3.

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Homogeneous Catalysis of the Photoreduction of Water. 6. Mediation by Polypyridine Complexes of Ruthenium(II) and Cobalt(II) in Alkaline Media[1]

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Abstract: The emission of (polypyridine)ruthenium(II) complexes (S) is quenched by (polypyridine)cobalt(II) (CoL_3^{2+}) complexes via parallel oxidative, reductive, and energy-transfer paths, giving $CoL_3^{+} + S^{+}$, $CoL_3^{3+} + S^{-}$, and $^*CoL_3^{2+} + S$, respectively. The oxidative route provides the basis for a new water photoreduction sequence: in mixed acetonitrile–water solvents relatively high cage-escape yields of $Ru(4,7\text{-}(CH_3)_2phen)_3^{3+}$ and $Co(bpy)_3^{+}$ (S = $Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}$, phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine) are obtained. The Ru(III) complex is reduced by triethanolamine (TEOA), and the $Co(bpy)_3^{+}$ reacts with water and/or $TEOAH^{+}$ to give H_2. The maximum H_2 quantum yield obtained is 0.29 in 50% acetonitrile–water. Unusual features of the system are the fact that, at low TEOA, $Co(bpy)_3^{2+}$ scavenging of Ru(III) reduces the H_2 yield and that the cage-escape and limiting H_2 yields are strongly solvent dependent: for the $Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}$–$Co(bpy)_3^{2+}$–TEOA system the H_2 yield increases from ~0.02 in H_2O to 0.29 in the mixed solvent. Reduction potentials for $CoL_3^{3+/2+}$ and $CoL_3^{2+/+}$ couples are also reported.

Cobalt–polypyridine complexes are of interest in a number of contexts [L = polypyridine, i.e., 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy)]: the cobalt(I) complexes reduce water to H_2[2-4] and CO_2 to CO[5] depending upon conditions. Since the cobalt(I) species may be generated by the reduction of the corresponding cobalt(II) or cobalt(III) species, catalytic systems incorporating this chemistry are possible. When RuL_3^{2+} complexes[6-8] are used as sensitizers, cobalt(I) complexes may be generated either via reductive (eq 2) or oxidative (eq 3) quenching of the excited state in the presence of an electron donor (D).

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