DOI: 10.1002/ejoc.200600079

Kinetics of (Porphyrin)manganese(III)-Catalyzed Olefin Epoxidation with a Soluble Iodosylbenzene Derivative

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Keywords: Kinetics / Homogeneous catalysis / Supported catalysis / Epoxidation

We examined the kinetics of a well-behaved system for homogeneous porphyrin-catalyzed olefin epoxidation with a soluble iodosylbenzene derivative **1** as the terminal oxidant and Mn(TPFPP)Cl (**2**) as the catalyst. The epoxidation rates were measured by using the initial rate method, and the epoxidation products were determined by gas chromatography. The epoxidation rate was found to be first order with respect to the porphyrin catalyst and zero order on the terminal oxidant. In addition, we found the rate law to be sensitive to the nature and concentration of olefin substrates. Saturation kinetics were observed with all olefin substrates at high olefin concentrations, and the kinetic data are consistent with a Michaelis–Menten kinetic model. According to the observed saturation kinetic results, we propose that there is a complexation between the active oxidant and the substrate, and the rate-determining step is thought to be the breakdown of this putative substrate–oxidant complex that generates the epoxidation products and the resting state porphyrin catalyst. Competitive epoxidations further indicate a reversible complexation of the active oxidant and the olefin substrate. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the oxygen-transfer process (k_2) in the *cis*-cyclooctene epoxidation were determined to be 12.3 ± 0.9 kcal mol^{-1} and -15.6 ± 3.2 cal mol^{-1} K^{-1}, respectively. In addition, the Hammett constant ρ^{+} was measured for the epoxidation of *para*-substituted styrenes, and the value of -0.27 ± 0.04 is too low to be consistent with the involvement of a discrete carbocation in the transition state. We also prepared a (porphyrin)manganese catalyst immobilized on silica support, and found the epoxidation of *cis*-cyclooctene catalyzed by this heterogeneous catalyst proceeds at virtually the same turnover frequency as by the homogeneous porphyrin catalyst.

Introduction

Olefin epoxidation catalyzed by metalloporphyrins has been intensively investigated because of its mechanistic importance and potential synthetic applications.[1] These catalytic systems often employ sacrificial terminal oxidants such as iodosylbenzene (PhIO) and sodium hypochlorite to circumvent the two-electron reduction required for catalysis with O_2.[2] Despite the enormous amount of effort devoted to elucidating the mechanism of the metalloporphyrin-catalyzed olefin epoxidation, kinetic studies of the system have been hampered by competing side reactions and insolubility of terminal oxidants. Peracids such as *meta*-chloroperbenzoic acid (*m*CPBA) epoxidize olefins in the absence of porphyrin catalysts and therefore are not suitable for kinetic studies.[3] The partitioning between heterolytic and homolytic O–O bond cleavage of the porphyrin–hydroperoxo complex, and H_2O_2 dismutation also complicates kinetic studies with hydrogen peroxide.[4] Our group reported kinetic studies of olefin epoxidation with lithium hypochlorite (LiOCl) as the terminal oxidant in a biphasic (H_2O/CH_2Cl_2) system, but the phase-transfer process and other side reactions complicated the interpretation of the kinetic data and led to controversial conclusions.[5]

Montanari and co-workers demonstrated that by lowering the pH of the aqueous NaOCl solutions from 12.7 to 10.0 ± 0.5, HOCl can be extracted into the organic phase as a soluble terminal oxidant.[6] Under two-phase conditions in the absence of a phase-transfer catalyst, they also investigated the kinetic behavior of a (porphyrin)manganese-catalyzed olefin epoxidation system employing HOCl as the terminal oxidant and observed Michaelis–Menten saturation kinetics.[7]

Iodosylbenzene (PhIO) has been widely employed as the sacrificial terminal oxidant in oxygenation reactions catalyzed by metalloporphyrins as well as (salen)manganese complexes.[8,9] However, PhIO (and other iodosylarenes) is insoluble in non-reactive solvents because of its polymeric structure resulting from a strong intermolecular secondary I···O bond.[10] The exact concentration of PhIO in the reaction mixture is dependent upon many factors such as the particle sizes of the solid, stirring rate and so on, and its insolubility in most organic solvents has hindered the utilization of PhIO in kinetic studies. PhIO readily dissolves in methanol and forms hydromethoxy and dimethoxy derivatives.[11] There have been several kinetic studies of (porphyrin)iron-catalyzed olefin epoxidation with the soluble iodo-

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Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

dimethoxybenzene as the terminal oxidant.[12–14] However, the kinetic and mechanistic details observed with iododimethoxybenzene are expected to be different from those with PhIO, given the structure and reactivity differences between the parent PhIO and dimethoxyiodobenzene. Because of the importance of iodosylbenzene as a terminal oxidant in metalloporphyrin-catalyzed olefin epoxidation, a detailed and clean kinetic study of iodosylbenzene or its derivative is needed.

Recently, Protasiewicz and co-workers reported the preparation of a soluble monomeric iodosylbenzene derivative in which the intermolecular secondary I···O bond in PhIO is replaced by intramolecular I···O interactions between the iodine atom and one of the sulfone oxygen atoms (**1** in Figure 1).[15] Compound **1** can be prepared in large quantities, is fairly soluble in CH_2Cl_2, and is an ideal terminal oxidant for our kinetic investigations. Metalloporphyrins with halogen substituents are electron-deficient and more resistant to oxidative degradation compared to metalloporphyrins with electron-donating substituents.[16] Herein, we employ this soluble PhIO derivative **1** and a robust (prophyrin)manganese catalyst MnTPFPPCl [TPFPP = dianion of tetrakis-(pentafluorophenyl)porphyrin] (**2**) and present kinetic and mechanistic results from this well-behaved, homogeneous olefin epoxidation system.

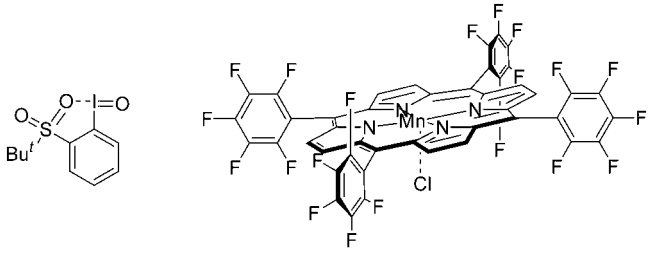

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Figure 1. Structures of the oxidant **1** and catalyst **2** employed in this study.

Results and Discussion

Epoxidation Procedures

The epoxidation involves an olefin substrate, the soluble iodosylbenzene derivative **1** and Mn(TPFPP)Cl (**2**) in CH_2Cl_2 at 0 °C unless otherwise indicated. The absence of exogenous axial ligands eliminates undesired side reactions associated with axial ligands. The addition of the catalyst **2** to a solution of **1** and the substrate was employed in this study. The other addition method, the addition of a solution of **1** to a solution of **2** and the substrate was shown to yield identical kinetic results. Olefin epoxidation does not take place in the absence of either oxidant **1** or porphyrin catalyst **2**. Although compound **1** disproportionates in the presence of the porphyrin catalyst in CH_2Cl_2, the disproportionation is significantly suppressed in the presence of olefin substrates.[15] The olefin epoxidation yields based on **1** are generally greater than 80%. Porphyrin catalyst **2** is stable under the oxidative conditions and UV/Vis measurements showed that the decrease of the Soret band (478 nm) is less than 5% after 200 turnovers (Table S-1 in the Supporting Information).

Epoxidation rates were determined by the initial rate method: aliquots were taken every minute during the early stage of the reaction (8–10 min, 200 turnovers or fewer) and the products were analyzed by gas chromatography (Figure S-1, Supporting Information). Epoxides were found to be the only major product in the epoxidation of *cis*-cyclooctene and 1-decene. In the epoxidation of styrene, a small amount of phenylacetaldehyde was formed in addition to styrene epoxide. We found that phenylacetaldehyde does not result from rearrangement of styrene epoxide, and the ratio of aldehyde/epoxide (1:4) is constant throughout different epoxidation conversions and changes in reagent concentrations. We presume that phenylacetaldehyde results from a common intermediate by the same mechanism as styrene oxide; both products are parallel oxidation products. The epoxides, phenylacetaldehyde, and the resulting iodobenzene byproduct are stable under the reaction conditions and do not undergo further reactions. Collman et al. observed that phenylacetaldehyde was oxidized vigorously by C_6F_5IO in the presence of (porphyrin)manganese.[17] Control experiments show the products do not inhibit or facilitate the epoxidation (Table S-2, Supporting Information). Nolte et al. demonstrated synergistic effects of phenylacetaldehyde on the epoxidation rates, which were not found in our study.[18] The rate accelerations of the epoxidation from the epoxide product observed by Banfi et al. were not observed in our catalytic reactions either.[7]

Saturation Kinetics

The order of the reaction with respect to the catalyst was obtained by measuring the initial rate of epoxidation at 0 °C as the concentration of **2** was varied while the concentrations of **1** and the substrate were kept constant. As shown in Table S-3 and Figure S-2 (Supporting Information), the reaction is first order in the catalyst, implying the comproportionation of the active (porphyrin)manganese intermediate with resting state catalyst **2** does not take place within the catalyst concentration range studied ($2\cdot10^{-6}$ M to $2\cdot10^{-5}$ M).[19,20] The reaction was found to be zero order with respect to the terminal oxidant (Table S-4, Supporting Information). This implies that the formation of the active oxidant cannot be rate-determining. On the other hand, the epoxidation rate was found to be dependent on the concentration of the olefin substrate, and a nonlinear relationship between the epoxidation rate and olefin concentration was observed. Furthermore, the epoxidation rate is sensitive to the nature of the olefin substrate. As shown in Figure 2 and Table S-5 (Supporting Information), for each olefin substrate, the epoxidation rate increases substantially at low concentrations and then levels off at higher concentrations. Electron-rich olefins such as *cis*-cyclooctene and styrene undergo epoxidation much faster than 1-decene,

which is a less electron-rich terminal olefin. Control experiments show that the epoxidation yields at low and high olefin concentrations are similar and are all greater than 80%. Therefore the slower epoxidation rates at lower olefin concentrations do not result from lower epoxidation yields or catalyst degradation (Table S-1, Supporting Information).[5c] The experimental data shown in Figure 2 can be fitted nicely into the Michaelis–Menten kinetic model (Scheme 1) using nonlinear least squares.[21] The parameters such as K_m and V_{max} are calculated and listed in Table 1 (see also Table S-6, Supporting Information).[22] The pseudo-first-order rate constants (k_2) for *cis*-cyclooctene, styrene, and 1-decene epoxidation under saturation conditions at 0 °C are 0.36, 0.49, and 0.15 s^{-1}, respectively. The saturation kinetics of olefin substrates have also been observed in several other studies on metalloporphyrin-catalyzed olefin epoxidations.[5,7,13,23,24]

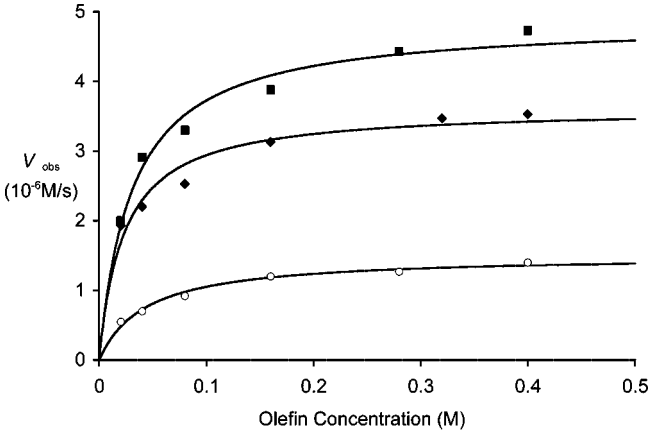


Figure 2. Initial rates of the epoxidation as a function of substrate concentrations at 0 °C. [**2**] = $1 \cdot 10^{-5}$ M; [**1**] = 0.01 M. Diamonds: *cis*-cyclooctene; squares: styrene; circles: 1-decene. See Supporting Information for non-linear fitting results.

$$\underset{(2)}{Por_{red}} + \underset{(1)}{ArIO} \xrightarrow{k_0} Por_{ox} + ArI \quad (1)$$

$$Por_{ox} + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Por_{ox}S \xrightarrow{k_2} Por_{red} + P \quad (2)$$

$$V_{obs} = \frac{V_{max}[S]}{K_m + [S]} \quad (3)$$

$$V_{max} = k_2[por]_0 \qquad K_m = \frac{k_{-1} + k_2}{k_1}$$

$$V_{obs,\,a} = \frac{V_{max,\,a}[S]_a}{K_{m,\,a}(1+[S]_b/K_{m,\,b}) + [S]_a} \quad (4)$$

Scheme 1. Michaelis–Menten kinetic model.

Table 1. Non-linear fitting results of rate data at 0 °C in Figure 2 and Table S-4 (Supporting Information).[a]

	K_m [M]	V_{max} [10^{-6} M/s]	k_2 [s^{-1}]
cis-Cyclooctene	0.023 ± 0.005	3.62 ± 0.16	0.36 ± 0.02
Styrene	0.031 ± 0.004	4.87 ± 0.16	0.49 ± 0.02
1-Decene	0.043 ± 0.006	1.50 ± 0.06	0.15 ± 0.01

[a] See also Table S-5 in the Supporting Information.

Proposed Mechanism

According to the saturation kinetic results observed above, we propose the following mechanistic insights [Scheme 1, Equations (1) and (2)]. The reaction between the soluble iodosylbenzene derivative (ArIO, **1**) and the resting state of the porphyrin catalyst (Por_{red}, **2**) rapidly forms the active oxidant (Por_{ox}). The formation of this active intermediate is fast compared to subsequent steps involving the olefin substrate. In addition, because the concentration of the terminal oxidant **1** is not present in the rate law, the formation of the active intermediate therefore cannot be the rate-determining step. The formation of the active intermediate was proposed to be the rate-determining step in other metalloporphyrin-catalyzed epoxidation studies with oxidants such as hypochlorite and *p*-cyano-*N*,*N*-dimethylaniline.[25,26] The olefin substrate (S) and the active oxidant (Por_{ox}) are proposed to form an intermediate ($Por_{ox}S$) that irreversibly breaks down to the epoxide product (P) and the porphyrin catalyst (Por_{red}). At high substrate concentrations, Por_{ox} exists almost entirely as $Por_{ox}S$, and the epoxidation rate reaches its maximum value ($V_{max} = k_2[Por]_0$). Clearly, the epoxidation rates are dependent on the nature of the olefins at the same catalyst and oxidant concentrations, suggesting that the olefin substrate is involved in the rate-determining step in the catalytic cycle.

Competitive Epoxidation

To further support the premise of the reversible complexation of the active oxidant and the olefin substrate, competitive epoxidations were carried out. In a competitive epoxidation one olefin substrate should competitively inhibit the epoxidation of the other. Under steady-state conditions for competitive inhibition, the reaction rate for competing substrates is given by Equation (4) in Scheme 1.[21] Therefore, the competitive epoxidation rate depends on not only the epoxidation rate (V_{max}) when epoxidized alone, but also the binding constant (K_m).

When epoxidized separately, styrene reacts 1.5 times faster than *cis*-cyclooctene, and *cis*-cyclooctene 3 times faster than 1-decene (Table 2, column 1). When a 1:1 mixture of *cis*-cyclooctene and styrene is epoxidized competitively, the reactivity is reversed and *cis*-cyclooctene is epoxidized faster than styrene (Table 2, column 2, experiment 1). On the other hand, the epoxidation of *cis*-cyclooctene is almost 8 times faster than that of 1-decene in the competitive epoxidation of *cis*-cyclooctene and 1-decene (Table 2, column 2, experiment 2). These observations are consistent with the saturation kinetics and demonstrate that *cis*-cyclooctene binds the active oxidant more efficiently than styrene and 1-decene. The observed competitive epoxidation rates

are in good quantitative agreement with the calculated epoxidation rates by using V_{max} and K_m values from Table 1 in Equation (4) of Scheme 1 (Table 2, column 3).

Table 2. Rates of competitive epoxidations [10^{-6} M/s] at 0 °C.[a]

		1: separate[b]	2: competitive[c]	3: calculated[d]
Experiment 1	*cis*-cyclooctene	2.53 ± 0.07	2.00 ± 0.10	1.8 ± 0.4
	styrene	3.30 ± 0.07	1.30 ± 0.05	1.7 ± 0.4
Experiment 2	*cis*-cyclooctene	2.53 ± 0.07	2.15 ± 0.10	2.0 ± 0.4
	1-decene	0.92 ± 0.03	0.30 ± 0.03	0.4 ± 0.1

[a] [**1**] = 0.01 M; [**2**] = $1 \cdot 10^{-5}$ M; [olefin] = 0.08 M. [b] Epoxidation rates when epoxidized separately. [c] Epoxidation rates when epoxidized competitively. [d] Competitive epoxidation rates calculated from Equation (4) in Scheme 1.

Eyring and Hammett Studies

To shed further light on the nature of the oxidant–substrate complex, we carried out temperature dependence and free energy correlation studies.[27] The rates of the epoxidation of *cis*-cyclooctene were measured at four different temperatures (–9, 0, 10, 20 °C). Michaelis–Menten behavior was observed at all temperatures, and k_2 values at those temperatures were obtained by non-linear least-square fitting to the Michaelis–Menten equation (Tables S-7, S-8, and S-9, Supporting Information). The $\Delta H^{\ddagger}$ value of k_2 in the *cis*-cyclooctene epoxidation was found to be 12.3 ± 0.9 kcal mol^{-1} (Figure 3). The $\Delta S^{\ddagger}$ value was determined to be –15.6 ± 3.2 cal mol^{-1} K^{-1} (eu), which is consistent with the proposed bimolecular nature of the formation of the putative complex between the active oxidant and the substrate.

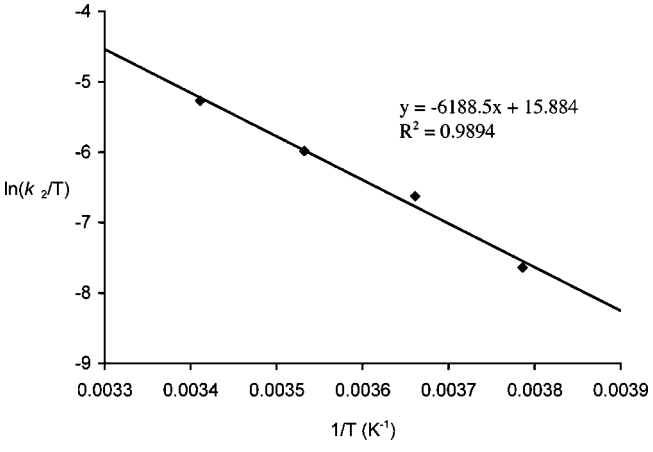


Figure 3. Eyring plots for the epoxidation of *cis*-cyclooctene.

The Hammett plot was also constructed by measuring the k_2 values from four different *para*-substituted styrenes (Tables S-10, S-11, and S-12, Supporting Information). The rate difference between these *para*-substituted styrenes is assumed to result from the electronic properties because the steric effects should be essentially constant. The ρ^+ values of –0.27 ± 0.04 indicates that here is no significant charge separation in the transition state and does not support the involvement of a cationic intermediate (Figure 4). For comparison, a ρ^+ value of –0.93 was obtained from olefin epoxidation catalyzed by a (porphyrin)iron(III) catalyst and iodosylbenzene.[28] It is worthy noting that larger negative ρ^+ values were found for stoichiometric olefin epoxidation by putative (oxo)iron(V)[29] and (oxo)chromium(V)[30] intermediates (–1.9). However, we cannot propose a definite structure of the olefin-active intermediate complex based on our available experimental data.[27]

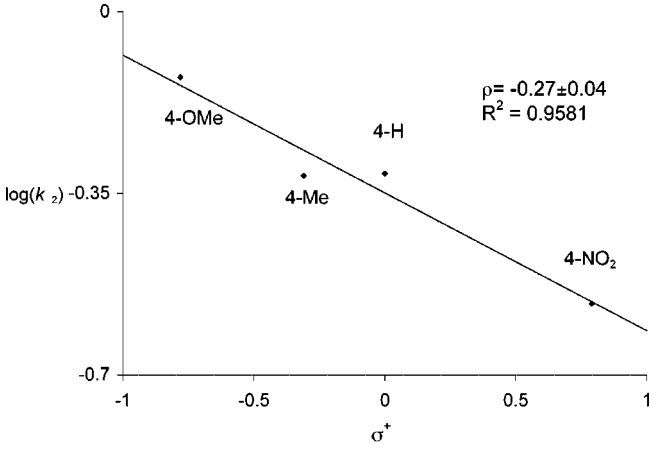
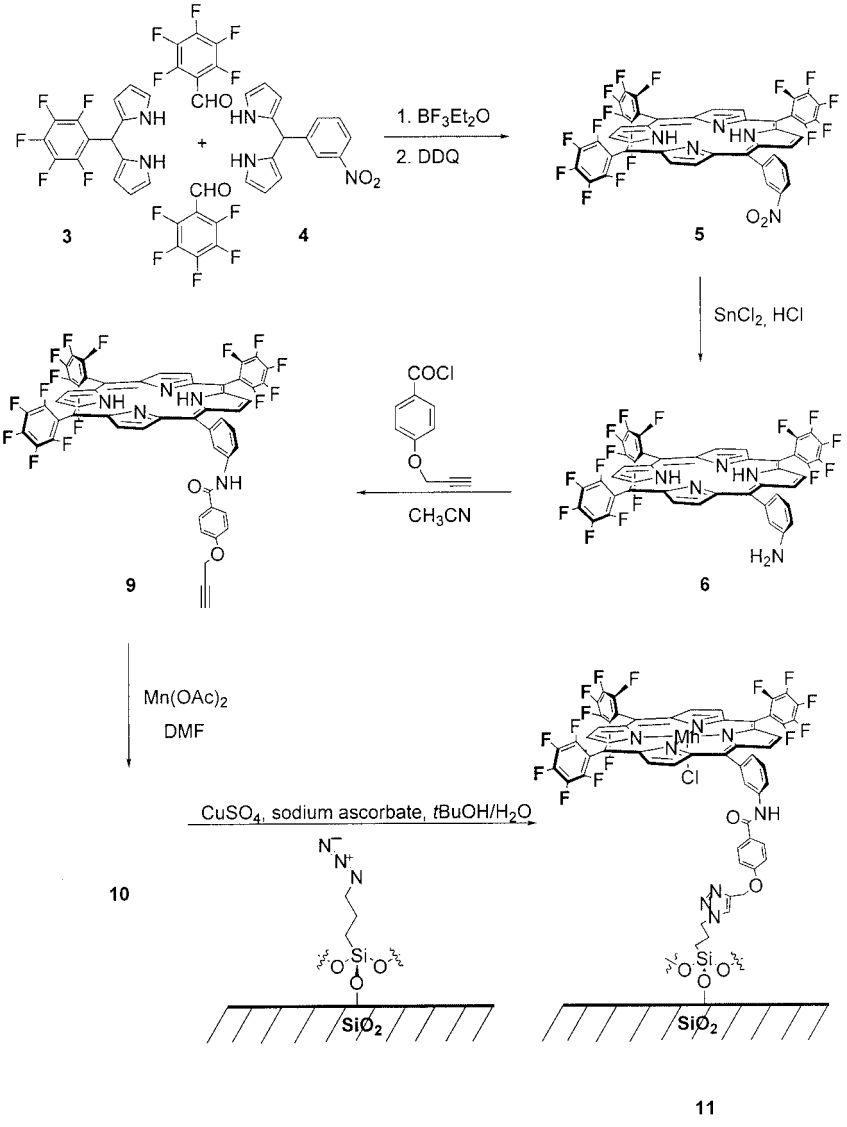


Figure 4. Hammett plot of the epoxidation of 4-substituted styrenes at 0 °C with σ^+ values.

Epoxidation Catalyzed by an Immobilized (Porphyrin)-manganese Catalyst

The deactivation of the (porphyrin)manganese catalyst caused by the comproportionation of the active epoxidizing intermediate with (por)Mn^{III} has been observed in some catalytic epoxidations as reported by Bruice and other groups.[19,20,31] Site isolation of (porphyrin)manganese catalysts should prevent the formation of the less reactive dimers resulting from the comproportionation. To this end, we have synthesized an immobilized (porphyrin)manganese catalyst **11** by Sharpless' "click chemistry" between an azide moiety on the silica surface and an alkyne moiety on the (porphyrin)manganese complex (Scheme 2, see also Supporting Information for the preparation of **5**–**10**).[32] The catalyst loading was determined by ICP analyses to be $9.5 \pm 0.5 \cdot 10^{-4}$ mmol/g of silica. As shown in Table 3, the immobilized heterogeneous catalyst catalyzes the epoxidation of *cis*-cyclooctene at the same turnover frequency (TOF) as the homogeneous catalyst within experimental error. This observation, along with the fact that the homogeneous epoxidation is first order in the concentration of catalyst **2**, strongly suggests that comproportionation of the active oxidant with (por)Mn^{III} to form inactive dimers does not take place in the homogeneous catalytic epoxidation.



Scheme 2. Synthesis of the immobilized (porphyrin)manganese catalyst **11**.

Table 3. Comparison of the reactivity of homogeneous catalyst **2** and heterogeneous catalyst **11** in the epoxidation of *cis*-cyclooctene.[a]

Catalyst	[catalyst] [M]	V [10^{-6}M /s]	V/[catalyst] (TOF) [s^{-1}]
2 (homogeneous)	$1 \cdot 10^{-5}$	2.53 ± 0.07	0.253
11 (heterogeneous)	$7.6 \cdot 10^{-7}$[b]	0.22 ± 0.02	0.289
11 (heterogeneous)	$1.9 \cdot 10^{-6}$[c]	0.57 ± 0.05	0.299

[a] [**1**] = 0.01 M, [*cis*-cyclooctene] = 0.08 M, 0 °C, 25 mL of CH_2Cl_2. [b] 20 mg of silica. [c] 50 mg of silica.

Active Intermediate

In recent studies, Groves and Newcomb independently reported the chemical and photolytic generation of (oxo)-Mn^V species and determined the rate constants for stoichiometric epoxidation of carbamazepine and *cis*-stilbene to be $6.5 \cdot 10^5$ M^{-1} s^{-1} at 25 °C.[33,34] As their stoichiometric rate constants are second order whereas our catalytic rate constants are first order, we chose an olefin concentration of 0.08 M to make meaningful comparisons. When the substrate concentration is 0.08 M, the stoichiometric epoxidation of carbamazepine and *cis*-stilbene reported by Groves and Newcomb at room temperature takes place at a turnover frequency of $5.2 \cdot 10^4$ s^{-1}, whereas that of the catalytic epoxidation of *cis*-cyclooctene at 0 °C in the present study is 0.25 s^{-1}. Their second order stoichiometric rate constants are not in agreement with our first order catalytic rate constants after proper adjustments of temperature and the nature of the substrate. We believe that the active oxidant involved in our catalytic reactions is different from the (oxo)-Mn^V intermediate Groves and Newcomb have observed. However, our kinetic study does not lead to an unambiguous assignment of the active intermediate in the catalytic reaction. It should be noted that the turnover frequency observed in the present catalytic study is in agreement with

Table 4. Turnover frequencies in homogeneous porphyrin-catalyzed olefin epoxidation.[a]

Catalyst	Substrate	Oxidant	T	r. d. s.	TOF [s^{-1}]	Ref.
MnTPPCl	cyclooctene	NaOCl	r.t.	olefin epoxidation	0.54	[5a]
MnTDCPPCl	cyclooctene	HOCl	r.t.	olefin epoxidation	0.17	[7]
FeTDCPPCl	norbornene	PhIO/MeOH	r.t.	catalyst oxidation	1.4	[12]
FeTMpyP	cyclooctene	PhIO/MeOH	r.t.	olefin epoxidation	0.06	[13a]
MnTPFPPCl	cyclooctene	**1**	0	olefin epoxidation	0.25	[b]

[a] Some values are calculated from the data reported in the references. [b] From this study.

those in other metalloporphyrin-catalyzed epoxidation studies in the literature (Table 4).[5,7,12,13b] The participation of multiple oxidants has been proposed in (porphyrin)iron-catalyzed oxidations.[35] However, the selectivity was found to be independent on the nature of the terminal oxidant in the competitive epoxidation catalyzed by MnTPFPPCl, implying the involvement of multiple oxidants is not operative in MnTPFPPCl-catalyzed olefin epoxidation.[36]

Conclusions

In conclusion, we have explored the kinetics of a well-defined porphyrin-catalyzed olefin epoxidation system. This epoxidation system meets all the criteria required for kinetic studies and consists of a soluble oxidant and a robust porphyrin catalyst. The epoxidation yield is high with minimal side reactions or interfering byproducts. The epoxidation rate was found to be first order on the porphyrin catalyst and zero order on the terminal oxidant. The observation that the epoxidation rates depend on the nature and the concentration of olefin substrates clearly demonstrates oxygen transfer from the active oxidant to the olefin substrate is the rate-determining step. Saturation kinetics is observed and a complexation of an active oxidant and a substrate is proposed. The breakdown of this putative oxidant–substrate complex is speculated to be the rate-determining step, in which the epoxide product is released. The identity of the active oxidant during the catalytic reaction will be investigated in due course. It is noteworthy that saturation kinetics have also been found in other oxygenation systems, such as single turnover experiments of compound Q of methane monooxygenase with CH_3NO_2, and sulfide oxidation by (oxo)(salen)Mn species.[37,38]

Experimental Section

Materials: All reagents were purchased from Aldrich unless otherwise noted. CH_2Cl_2 (VWR) was distilled under N_2 from CaH_2 (Acros). All olefins [*cis*-cyclooctene, styrene, 1-decene, 4-methoxystyrene, 4-methylstyrene, 4-nitrostyrene (TCI)] were passed through short alumina columns immediately prior to reaction to remove traces of epoxides and/or inhibitors. All epoxide standards (*cis*-cyclooctene oxide, styrene oxide, 1,2-epoxydecane), phenylacetaldehyde, and 1,3-dichlorobenzene (the internal standard) were used as received without further purification. The soluble iodosylbenzene derivative **1** was synthesized according to Protasiewicz's method and stored at –20 °C in a vial protected by aluminum foil.[15] The purity of **1** was determined to be greater than 98% by iodometric titrations.[39] The (porphyrin)manganese catalyst MnTPFPPCl (**2**) was synthesized and purified according to literature procedures.[40]

Catalytic Epoxidation and Product Analysis: In a typical experiment, **1** (85 mg, 0.25 mmol) was added to a solution of an olefin substrate (2.0 mmol) and 1,3-dichlorobenzene (10 μL) in CH_2Cl_2 (25.0 mL) at 0 °C. After **1** was completely dissolved (within seconds), 250 μL of a 1.0 mmol/L solution of MnTPFPPCl **2** (0.25 μmol) was quickly added to the solution, and the reaction mixture was stirred rapidly at 0 °C. Aliqouts (ca. 50 μL) were drawn from the reaction mixture, and the aliquots were then eluted with hexane/ethyl acetate (v/v = 3:1, 0.50 mL) through a short silica gel column (ca. 30 mg) and the epoxidation was quenched by triphenylphosphane (Acros) dissolved in the eluents (ca 2.5 mg or 10 μmol, 20 equiv. with respect to **1** in each 0.50 mL). The eluents were then analyzed with a Hewlett–Packard 6850 gas chromatograph equipped with an HP-INNOWax Polyethylene Glycol capillary column (Agilent, 19091N-133E, 30.0 m × 250 μm × 0.25 μm nominal). Product concentrations were determined using calibration plots with stock solutions of product standards.

Competitive Epoxidation: To a solution of **1** (85 mg, 0.25 mmol), *cis*-cyclooctene (2.0 mmol), and styrene (2.0 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added a solution of MnTPFPPCl (**2**, 250 μL of a 1.0 mmol/L solution, 0.25 μmol) and the resulting reaction mixture was stirred rapidly at 0 °C. The reaction kinetics was monitored by methods mentioned above. The reaction was repeated with *cis*-cyclooctene and 1-decene (2.0 mmol each).

Eyring Plots: To a solution of **1** (85 mg, 0.25 mmol) and *cis*-cyclooctene (2.0 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added a solution of MnTPFPPCl (**2**, 250 μL, 1.0 mmol/L solution, 0.25 μmol) and the resulting reaction mixture was stirred rapidly at 0 °C. The reaction kinetics was monitored by methods mentioned above. The k_2 value was obtained by fitting the epoxidation rates at several different olefin concentrations with the Michaelis–Menten equation. The epoxidation was then carried out at three different temperatures: –9, 10, and 20 °C. The data were plotted as $\ln(k_2/T)$ vs. $1/T$.

Hammett Plots: To a solution of **1** (85 mg, 0.25 mmol) and styrene (2.0 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added a solution of MnTPFPPCl (**2**, 250 μL7L of a 1.0 mmol solution, 0.25 μmol) and the resulting reaction mixture was stirred rapidly at 0 °C. The reaction kinetics was monitored by methods mentioned above. The k_2 value was obtained by fitting the epoxidation rates at several different olefin concentrations with the Michaelis–Menten equation. The epoxidation was then carried out with three different *para*-substituted styrenes: 4-nitrostyrene, 4-methylstyrene, and 4-methoxystyrene. The data were plotted as $\log k_2$ vs. σ^+.

Si (1000)-N_3 Silica Resin: 3-(Chloropropyl)triethoxysilane (10 mmol), NaN_3 (10 mmol) and PTC were mixed in freshly distilled MeCN (50 mL). The mixture was refluxed under nitrogen for 12 h and was cooled to room temperature. To the mixture was

added 10 g of SiO_2 (1000), and the mixture was stirred at room temperature for an additional 12 h. After removing MeCN under vacuum, the residue was washed with H_2O (5×30 mL), MeOH (5×20 mL), acetone (2×20 mL) and CH_2Cl_2 (2×20 mL). The collected solid was then dried under vacuum overnight.

Click-Chemistry (Porphyrin)manganese Catalyst 11: (Porphyrin)-manganese complex **10** (2.2 mg) (see Supporting Information for the preparation of **10**) and Si (1000)-N_3 (100 mg) were mixed in *t*BuOH (10 mL) and H_2O (10 mL). To the stirred solution were added sodium ascorbate (0.2 umol) and $CuSO_4$ (0.1 μmol), and the resulting reaction mixture was stirred at room temperature for 24 h. The solid was collected by filtration and thoroughly washed with MeOH (5×10 mL), acetone (3×10 mL), and CH_2Cl_2 (2×10 mL) and dried under vacuum overnight.

ICP Analysis: The loading of the (porphyrin)manganese catalyst on the silica support above was determined by ICP analysis. ICP analysis was conducted with a TJA IRIS Advantage/1000 Radial ICAP Spectrometer operated by the Geological and Earth Sciences Department's soil chemistry laboratory at Stanford University. See Supporting Information for details on the preparation of standard solutions and samples.

Supporting Information (see footnote on the first page of this article): Synthesis of the immobilized (porphyrin)manganese catalyst, data tables and figures, and non-linear least-square fitting results.

Acknowledgments

This material is based upon work supported by the National Science Foundation under Grant No. CHE0131206. The authors thank Prof. T. Dan P. Stack and Ms. Tracy Terry for their help with the catalyst immobilization processes and ICP analyses.

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Received: February 1, 2006
Published Online: April 25, 2006

