

Anthracene-Induced Turnover Enhancement in the Manganese Porphyrin-Catalyzed Epoxidation of Olefins

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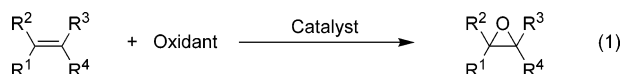
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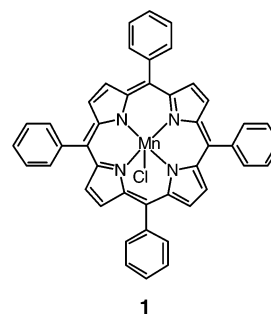
Anthracene and related compounds function as lifetime-extending cofactors in the (*meso*-tetraphenylporphine)Mn^{III} chloride-catalyzed epoxidation of olefins. An experiment with a chiral porphyrin catalyst shows that enantioselectivity is preserved in the presence of the cofactor. Additional experiments show that (a) turnover number enhancement is greatest for the least reactive substrates, (b) derivatization of anthracene at the 9 and 10 positions largely eliminates the enhancement effect, and (c) anthracene is ultimately converted to anthraquinone. The origin of the observed enhancements is in the reaction of anthracene with the normally unreactive dimeric oxo-bridged form of the catalyst. This reaction, which produces anthraquinone, regenerates the catalytically active monomeric form of the manganese porphyrin.

Introduction

We have been exploring the notion that reversible supramolecular complex formation (Lewis acid/Lewis base linked triads, molecular-square-based encapsulated assemblies, etc.) can usefully stabilize molecular catalysts, leading to longer catalyst lifetimes and increased numbers of catalyst turnovers.^{1,2} As a starting point, we have focused on olefin epoxidation reactions (eq 1) catalyzed by achiral manganese



porphyrins and by optically active manganese(salicyl)diamine complexes (“salens”). In the best cases, we find that catalyst lifetimes can be extended from minutes to greater than 24 h, while total catalyst turnover numbers (TON) can be increased by ca. 2 orders of magnitude. Recently, and unexpectedly, we have run across a second means of catalyst lifetime extension and TON amplification. With (*meso*-tetraphenylporphine)Mn^{III} chloride (MnTPP, **1**) as the catalyst in eq 1 and any of several compounds as the oxidant, we find that addition of anthracene, anthracene derivatives, and



related polyaromatic compounds at modest concentrations can increase total turnover numbers by up to an order of magnitude.

We report herein the details of the catalytic enhancement. Briefly, we find that the magnitude of the enhancement depends strongly upon the identity of the catalyst, as well as the composition of the olefinic substrate and the structure of the polyaromatic additive. Together with additional experimental information, the findings are sufficient to distinguish between several candidate mechanisms and to provide support for a mechanism entailing additive regeneration of expired catalyst species.

Results

Preliminary Observations. In a typical experiment, 100 equiv of the insoluble solid oxidant iodosylbenzene (PhIO) were added to a freshly made methylene chloride solution

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(1) (a) Merlau, M. L.; Grande, W. J.; Nguyen, S. T.; Hupp, J. T. *J. Mol. Catal. A: Chem.* **2000**, *156*, 79–84. (b) Morris, G. A.; Nguyen, S. T.; Hupp, J. T. *J. Mol. Catal. A: Chem.* **2001**, *174*, 15–20.
(2) Merlau, M. L.; del Pilar Mejia, M.; Nguyen, S. T.; Hupp, J. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4369–4242.

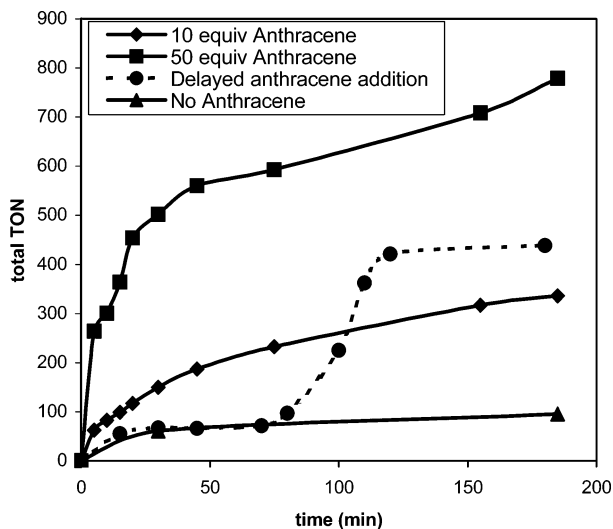


Figure 1. Enhancement of turnover number for the MnTPP-catalyzed epoxidation of styrene by substoichiometric amounts of anthracene [MnTPP (1 mM), styrene (2000 equiv), PhIO (2×400 equiv) added at $t = 0$ and 15 min]. Also shown in the figure is the effect of delayed anthracene addition on total turnover number. Note that the maximum TON is limited to 800 by oxidant availability.

of MnTPP (1 mM) and 500 equiv of styrene (substrate)—a protocol that minimizes side reactions. Under these conditions, the consequences of anthracene addition are particularly visually striking: After 5 min, in the presence of 10–50 equiv of anthracene, the solution has changed from red (characteristic of the inactive species) to green ($\text{Mn}^{\text{III}}\text{TPP}$) and the PhIO solid is no longer present. Subsequent additions of PhIO are also quickly and completely consumed. In contrast, in the absence of anthracene, the reaction mixture is still colored intensely red after 5 min and retains substantial amounts of unreacted solid oxidant. Analysis by gas chromatography shows that the primary products are styrene oxide (eq 1; typically 95%) and phenylacetaldehyde (typically 5%). Notably, the product distribution is unchanged by anthracene addition, although anthraquinone production is evident.

Figure 1 offers a more quantitative description, in this case based on 2000 equiv of substrate and 2×400 equiv of PhIO added at 0 and 15 min. Plotted in Figure 1 is the total catalyst TON under several conditions as a function of time after initiation of the reaction. Most striking is the large enhancement in TON in the presence of 50 equivalents of anthracene. After 15 min nearly 400 turnovers occur in the presence of anthracene, but only about 80 occur in its absence. Addition of the second 400 equiv of oxidant stimulates the production of additional styrene oxide and phenylacetaldehyde in the anthracene-containing solution—eventually ca. 800 equivalents—but has no effect upon the anthracene-free solution.

Figure 1 additionally shows that substantial TON amplification occurs even in the presence of 10 equiv of anthracene, although not to the extent seen with 50 equiv. Importantly, control experiments in which substrate is added to a mixture of anthracene and PhIO, without the manganese catalyst, result in no detectable oxidation of styrene.

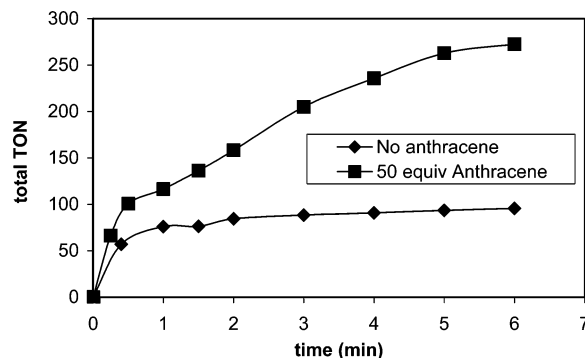
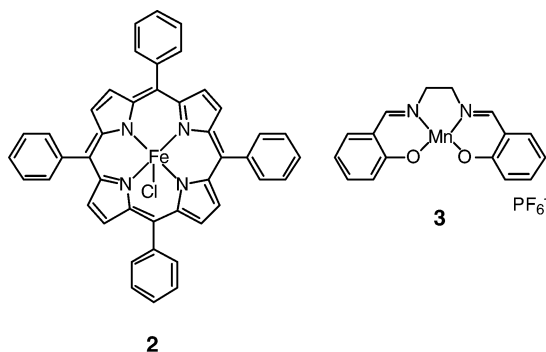


Figure 2. Initial reaction profile in the anthracene-induced TON enhancement of the MnTPP-catalyzed epoxidation of styrene.

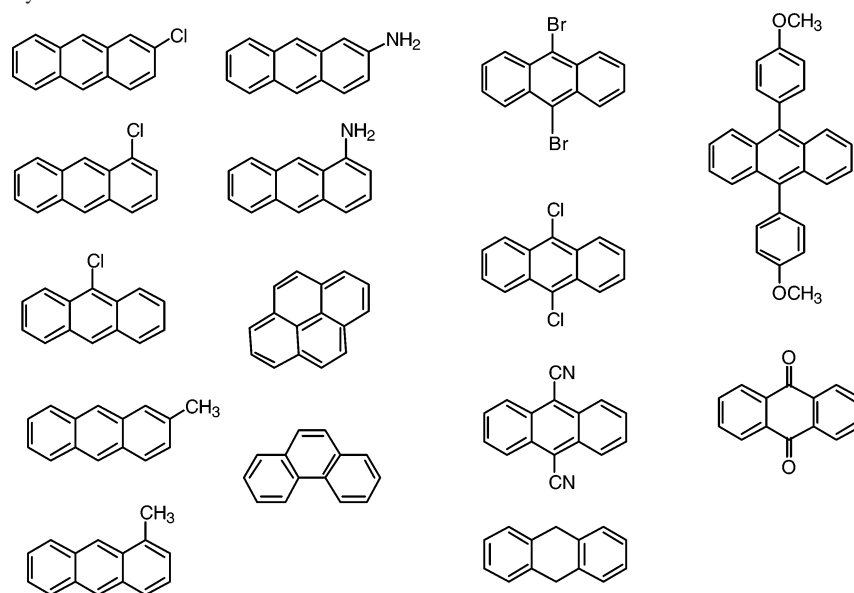
We reasoned that some insight into the mechanism of TON amplification might be obtained by examining the course of the reaction at early times. Figure 2 compares turnovers obtained during the first 6 min of the reaction in Figure 1, with and without 50 equiv of anthracene. The heterogeneous nature of the reaction mixture, together with the protocol used for product evaluation, prevented us from sampling the reaction at times shorter than about 20 s. While it is difficult or impossible—again, in the light of the heterogeneous nature of the reaction mixtures—to extract meaningful reaction rate constants from the figure's plots, they do indicate that the reactions, with and without added anthracene, proceed at similar relative rates at early times. In other words, the anthracene additive does not significantly alter the (unknown) catalytic rate constant, but instead acts solely to extend the catalyst lifetime.

Returning to Figure 1, an experiment involving delayed addition of anthracene shows that an inactive catalyst can be revived and made to function for many more cycles than initially obtained. Additional preliminary experiments included evaluation of anthracene's effect upon styrene epoxidation using either FeTPP (**2**) or Mn(salen) (**3**) as the catalyst. In neither case is an increase in TON or catalyst lifetime is observed.³



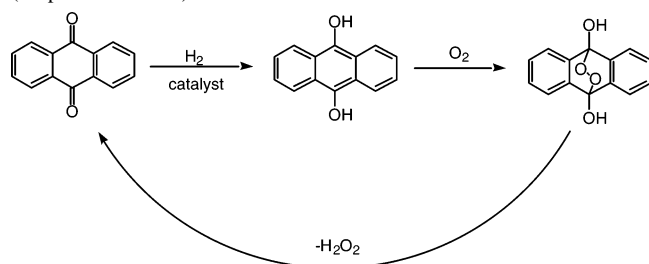
Other experiments entailed evaluation of several substituted anthracenes, as well as pyrene and phenanthrene, as TON enhancement agents. As summarized in Chart 1, many of the compounds displayed significant enhancements based

(3) That the anthracene amplification effect is not absolutely unique to $\text{Mn}^{\text{III}}\text{TPP}$, however, is shown by experiments with with 5,10-dipyridyl and 5,10,15,20-tetrapyridyl analogues of the tetraphenylporphyrin catalyst.

Chart 1. Candidate Cocatalysts^a

^a Of the four columns, the most effective are those in the two columns on the left-hand side of the chart.

Scheme 1. Proposed Mechanism for Commercial H₂O₂ Production (adapted from ref 5)

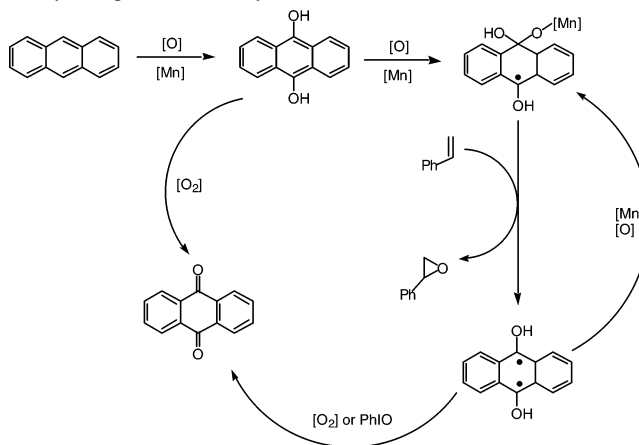


on product concentration measurements after 5 min of reaction,⁴ but some did not. The distinguishing feature appears to be the presence (or not) of an easily oxidizable carbon atom. Those anthracene derivatives featuring substituents in the 9 and 10 positions (making quinone formation difficult) engender little TON enhancement. Those that easily add oxygen engender significant enhancement.

An Anthracene-Mediated Oxygen-Shuttle Mechanism?

From Figure 1 anthracene clearly is functioning as a cocatalyst for styrene epoxidation, albeit with eventual consumption. For example, after 3 h under the conditions described above, 10 equiv of anthracene stimulates the production of an additional 240 equiv of styrene oxide and phenylacetaldehyde. An interesting mechanistic possibility—in part suggested by the formation of anthraquinone—is the involvement of anthracene as an oxygen shuttle. As illustrated in simplified form in Scheme 1, anthraquinone is employed commercially as a catalytic shuttle for formation of hydrogen peroxide from H₂ and O₂: Anthraquinone is first reduced to 9,10-dihydroxyanthracene, which then reacts rapidly with dioxygen to form a peroxo intermediate.⁵ Adapting the scheme to the epoxidation reaction studied here,

Scheme 2. A Hypothetical Oxygen-Shuttle Mechanism for the Anthracene-Induced Enhancement of Turnover Number for the MnTPP-Catalyzed Epoxidation of Styrene



we postulated that 9,10-dihydroxyanthracene could bind to MnTPP, with the resulting radical transferring an oxygen atom to an olefinic substrate and releasing the anthracene-derived intermediate as a highly reactive diradical (Scheme 2). The intermediate could then either bind another manganese porphyrin and repeat the epoxidation step or react directly with PhIO or O₂ to form anthraquinone, thereby terminating the cycle.

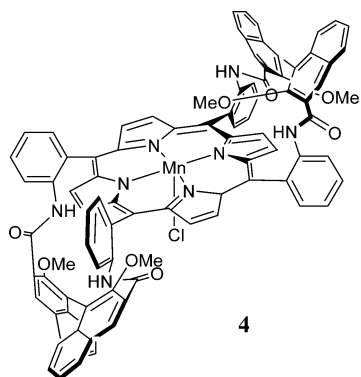
Consistent with the Scheme 2, anthraquinone—in contrast to anthracene—is ineffective as a cocatalyst. The results of other experiments, however, fail to support the shuttle mechanism. For example, exclusion of O₂ from Scheme 2 should enhance the lifetime of dihydroxyanthracene (by preventing direct formation of the quinone) and permit additional epoxidation reaction turnovers. Instead, O₂ exclusion has no effect, suggesting that the dihydroxy species is not a participant in the cocatalysis process. As a more direct

(4) Included as Supporting Information are extended TON versus time plots for all additives examined. Consistent with Figure 1, those showing TON amplification after 5 min showed additional amplification at longer times.

(5) Weissmermel, K.; Arpe, H. J. *Industrial Organic Chemistry. Important Initial and Intermediate Products*; Verlag Chemie: Weinheim, 1976; pp 324–326.

check, dihydroxyanthracene was independently synthesized. As an epoxidation reaction additive, it yields a modest increase in TON but is considerably less effective than anthracene itself. Hence, we conclude that Scheme 2 is not the basis for the observed anthracene-induced TON amplification and catalytic lifetime extension.

To test whether anthracene might be functioning as an oxygen shuttle via some other mechanism, we prepared a chiral manganese porphyrin catalyst, **4**.⁶ We reasoned that



any enantiomeric excess (ee) associated with the direct epoxidation via the chiral catalyst would be lost if oxygen transfer instead occurred via the intermediacy of an achiral cocatalyst. In the absence of anthracene, styrene epoxidation proceeds with 76% ee in favor of the *S* enantiomer, in excellent agreement with an earlier report.⁶ In the presence of anthracene (50 equiv) a modest increase in TON is observed after 5 min, but the reaction enantioselectivity is unchanged. We conclude, therefore, that anthracene does not function as an oxygen shuttle in the epoxidation reaction.

Alternative Mechanisms: Oxidant and Substrate Compositional Effects. A possibility not yet considered is that the cocatalytic role of anthracene is simply to solubilize the oxidant, for example, via charge-transfer complex formation.⁷ If oxidant solubilization were rate-limiting, complex formation presumably would accelerate the rate of epoxidation and increase the total TON by effectively increasing the concentration of catalyst-available oxidant. To test this idea, three additional oxidants were examined: a perfluorinated analogue of iodosylbenzene (PhF_5IO , also a poorly soluble polymeric species), 2-(*tert*-butylsulfonyl)iodosylbenzene (“sol. PhIO”, a methylene chloride soluble oxidant), and *m*-chloroperbenzoic acid (*m*-CPBA, also a methylene chloride soluble oxidant). As shown in Table 1, while the number of turnovers obtained during the first 5 min of reaction varies significantly as a function of oxidant used, all are enhanced by anthracene. Furthermore, the degree of enhancement is not correlated with oxidant (in)solubility; we conclude that oxidant solubilization is not the factor responsible for TON enhancement.

Additional experiments, featuring PhIO as oxidant, focused on substrate compositional effects—in particular, para-

Table 1. Anthracene-Induced TON Enhancement at $t = 5$ min in the MnTPP-Catalyzed Epoxidation of Styrene with Various Oxidants

entry	oxidant	TON enhancement		conditions ^a
		no anthracene	50 equiv of anthracene	
1	PhIO	28	296	a
2	PhF_5IO	154	385	a
3	sol. PhIO	52	302	a
4	<i>m</i> -CPBA	13	106	b

^a Conditions: (a) CH_2Cl_2 , ambient temperature; (b) CH_2Cl_2 , -78 °C.

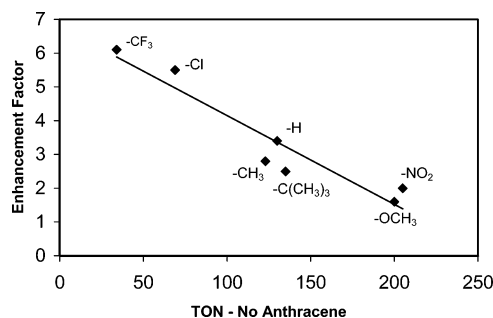


Figure 3. Correlation of anthracene-induced epoxidation TON enhancement factor for 4-substituted styrene compounds with catalytic TON in the absence of anthracene.

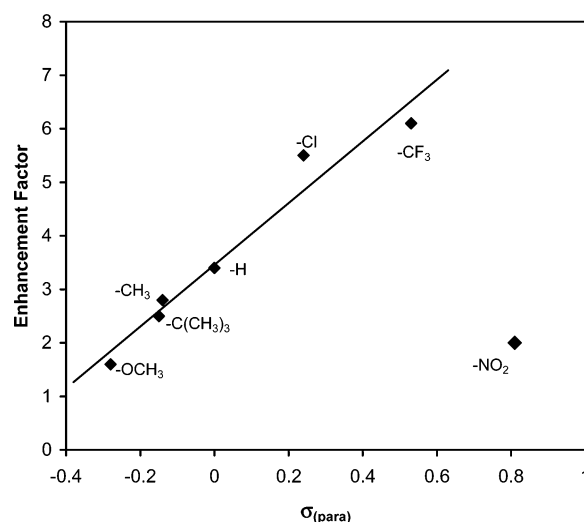


Figure 4. Correlation of anthracene-induced epoxidation TON enhancement factor with Hammett σ_{para} parameter for 4-substituted styrene compounds as substrates. The line drawn is a fit omitting 4-nitrostyrene.

substituted derivatives of styrene. To provide a common reference point, turnover numbers for each substrate, with and without 50 equiv of anthracene, were evaluated 5 min after reaction initiation. As shown in Figure 3, a remarkable inverse correlation exists between the degree of anthracene-induced TON amplification (enhancement factor) and the number of turnovers obtained in the absence of anthracene. In other words, the most reactive substrates (in terms of total TON after 5 min) are least susceptible to anthracene-based reactivity amplification. Figure 4 shows that the enhancement factor correlates reasonably well with electronic properties, the most electron deficient olefins (as measured by the Hammett σ_{para} parameter⁸) being the most susceptible to

(6) Collman, J. P.; Wang, Z.; Straumanis, A.; Quelquejeu, M.; Rose, E. *J. Am. Chem. Soc.* **1999**, *121*, 460–461.

(7) We thank Prof. Craig Hill for suggesting this interesting possibility.

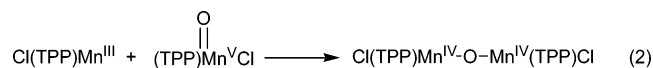
(8) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; 4th ed.; Wiley: New York, 1992; pp 1495.

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anthracene-induced enhancement. (The lone exception is 4-nitrostyrene; we lack an explanation for its departure from the electronic correlation other than to note its higher-than-expected reactivity in the absence of anthracene.) If we equate relative TONs with relative epoxidation rate constants, the results in Figures 3 and 4 are strongly suggestive of mechanistically relevant, competitive rate processes, an idea that is explored further in the Discussion section.

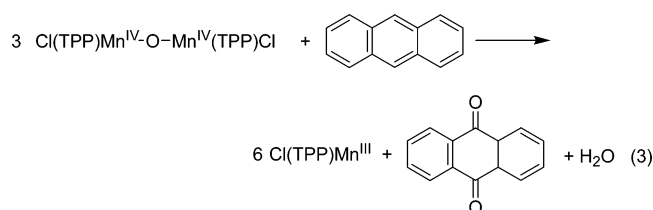
Discussion

The primary mechanisms for Mn^{III} porphyrin catalyst inactivation are (a) formation of a μ -oxo dimer (Mn^{IV}-O-Mn^{IV}; eq 2),⁹ and (b) destructive oxidation of the porphyrin



ligand of one catalyst molecule by a second.¹⁰ We assume that the second process is chemically irreversible, so will be unaffected by subsequent introduction of anthracene. The first process, dimer formation, is problematic in catalysis because the dimer lacks the oxidizing strength of the high-valent manganese-oxo monomer species. Nevertheless, the μ -oxo dimer is known to behave as a weak oxidant under some conditions.¹¹

We speculated, as shown in eq 3, that the dimer would be capable of oxidizing anthracene to anthraquinone, thereby



regenerating the original Mn(III) catalyst. The regenerated catalyst would then continue to epoxidize styrene through formation of the active metal-oxo species with PhIO.

Support for this hypothesis is provided by experiments involving an intentionally preformed and isolated complex of the μ -oxo dimer with iodosylbenzene, [Cl(TPP)-Mn^{IV}(OIPh)]₂O.¹¹ The complex rapidly oxidizes anthracene to anthraquinone. In contrast, addition of the complex to a mixture of PhIO and styrene results in very little substrate oxidation. As shown in Figure 5, however, anthracene addition triggers the rapid catalytic conversion of styrene to styrene oxide and phenyl acetaldehyde, consistent with regeneration of the monomeric MnTPP catalyst. Notably, both the corresponding dimer of FeTPP, [Fe^{III}(TPP)]₂O, and a doubly oxo-bridged dimer of Mn(salen), [Mn^{IV}(salen)]₂(O)₂, proved unreactive with anthracene.¹²

The proposed catalytic and cocatalytic sequences are summarized by cycles B and C in Scheme 3. If the second

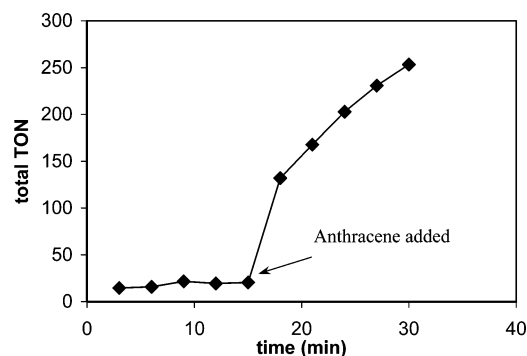


Figure 5. Reaction profile for the epoxidation of styrene in the presence of [Cl(TPP)Mn^{IV}(OIPh)]₂O. Anthracene was added at $t = 15$ min.

catalyst degradation pathway, mentioned above, can be neglected, then from the two cycles each equivalent of added anthracene should be capable of triply reproducing the original TON. In other words, 10 equiv of anthracene would yield a 30-fold increase in TON and so on. Behavior well below this limit is observed: 50 equiv of anthracene yields a 10-fold increase in TON.

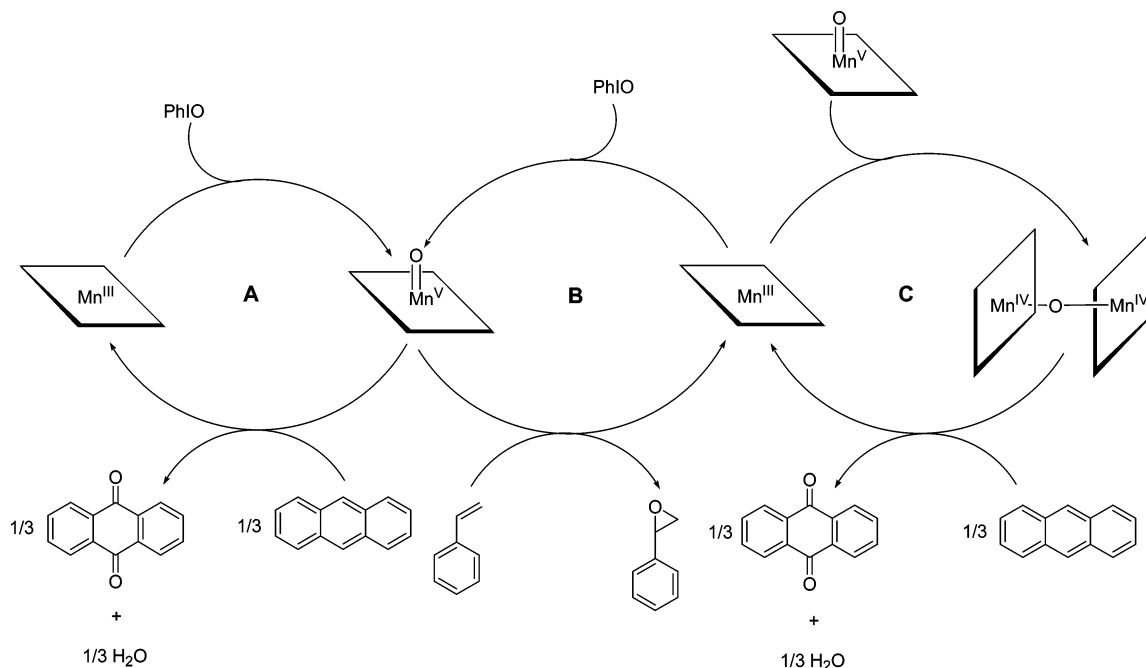
Less than the anticipated maximum TON amplification would be observed, however, if anthracene were additionally consumed by direct reaction with the monomeric catalyst, as shown in cycle A of the scheme. That cycle A does not completely define the chemistry of anthracene consumption here is, in part, a consequence of the large concentration advantage enjoyed by the substrate. For a given sequence, cycle B rather than A (or C) usually accounts for the fate of the active monomeric metal-oxo species, although clearly both A and C do occur to some extent. Note further that once anthracene is exhausted, pathway C terminates with catalyst inactivation (dimer formation) rather than catalyst regeneration. Competition between cycles also provides an attractive explanation for the behavior summarized in Figure 3, where the most reactive substrates proved least susceptible to anthracene-induced TON amplification. Highly reactive substrates are capable of cycling the catalyst many more times than poorly reactive substrates before the inactive dimer is formed. If the dimer is only rarely formed, it follows that anthracene will tend to be consumed by the catalytically unproductive cycle A, rather than the regenerative cycle C.¹³ Consequently, fewer instances of regeneration (less TON amplification) will result from addition of a given number of equivalents of anthracene cocatalyst to a reaction mixture.

Finally, to clarify our interpretation of the various elements of Scheme 3, we emphasize the following: (a) As noted by Bruce and co-workers,¹⁴ among many others, the Mn^{III} +

(9) See, for example: Meunier, B. *Chem. Rev.* **1992**, *92*, 1411–1456.
(10) Chang, C. K.; Kuo, M.-S. *J. Am. Chem. Soc.* **1979**, *101*, 3413–3415.
(11) (a) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3510–3515. (b) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3515–3521.

(12) Presumably the oxo-bridged iron dimer is thermodynamically more stable with respect to dissociation into monometallic components, via oxygen atom transfer, than is the manganese porphyrin dimer. While the doubly bridged salen compound may be similarly stabilized, such stability is probably less relevant, since loss of salen catalytic activity appears to be due mainly to irreversible ligand oxidation.
(13) More rapid cycling through B will also diminish the rate of anthracene consumption via cycle A. An additional factor, however, may be an ability of the most reactive substrates to react also with the dimer (albeit slowly), thus supplanting to some extent the role of anthracene as catalyst regenerator.
(14) Lee, R. W.; Nakagaki, P. C.; Bruce, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 1368–1372.

Scheme 3. Proposed Mechanism for the Cocatalytic and Competitive Degradative Reactivity of Anthracene during MnTPP-Catalyzed Epoxidation of Styrene



$\text{Mn}^{\text{V}}=\text{O} \rightleftharpoons \text{Mn}^{\text{IV}}-\text{O}-\text{Mn}^{\text{IV}}$ equilibrium (eq 2) lies far to the right. (b) The dimer-consumption/anthraquinone-formation equilibrium (eq 3) also lies far to the right, consistent with an observed lack of reactivity of anthraquinone with $\text{Mn}^{\text{III}}\text{TPP}$. In other words, cycle C circulates only in the direction indicated. (c) Except at early times, most of the catalyst likely exists in the inactive dimer form. While anthracene regenerates the active catalyst, it does so slowly enough (relative to redimerization) that even when anthracene is present in excess most of the catalyst exists in the inactive dimer form. Consistent with this assumption, the extra turnovers engendered by anthracene (Figure 2) occur much more slowly than the initial turnovers. (d) Some of the $\text{Mn}^{\text{III}}\text{TPP}$ released in cycle C could be reconverted to inactive dimer via encounter with a $\text{Mn}^{\text{V}}=\text{O}$ complex, without first circulating through cycle B. We assume, on average, that the regenerated catalyst is no less and no more reactive with the substrate than is the initially used catalyst. We also assume that permanent inactivation (mainly by dimerization) is the eventual fate of every regenerated catalyst.

Conclusions

Anthracene and related polyaromatic compounds substantially extend the lifetime of MnTPP as a catalyst for olefin epoxidation. Up to 10-fold increases in catalytic reaction turnover number have been observed (i.e. ~ 700 additional turnovers). The origin of the TON enhancement is regeneration of the catalyst from a catalytically ineffective oxo-bridged dimer. Despite the very limited reactivity of the dimer with respect to olefin epoxidation, oxygen transfer to generate, eventually, anthraquinone and the monomeric catalyst readily occurs. Substrate-based differences in efficacy of anthracene as a cocatalyst can be understood in terms of competitive reaction pathways where some fraction

of the available anthracene is lost to direct oxidation by the monomeric catalyst. Other additives such as pyridine are well-known to influence favorably the performance of manganese porphyrin epoxidation catalysts, for example, by enhancing the oxidizing strength of the catalyst or by forcing substrates to bind at a spatially confined site defined by a chiral-strapped structure.¹⁵ In the light of the new results, and given the ease of oxidation of additives such as pyridine, it is conceivable that a secondary role for these additives is to regenerate active monomeric catalysts from essentially unreactive dimers.^{16,17}

Experimental Section

General Information and Materials. GC-MS experiments were recorded on a Hewlett-Packard HP6890 series instrument equipped with an HP-5 column. GC analyses were carried out on a Hewlett-Packard HP6890 series instrument equipped with an FID detector and HP7683 series autosampler and injector and analyzed using HP Chemstation software. The column was a 30-m HP-5 (cross-linked 5% PH ME siloxane) capillary column with 0.32-mm inner diameter and 0.25- μm film thickness (inlet pressure = 13.9 psig; column flow = 1.2 mL/min; temperature program for

- (15) (a) Liu, S.-Q.; Pecaut, J.; Marchon, J.-C. *Eur. J. Inorg. Chem.* **2002**, 1823–1826. (b) Lai, T.-S.; Ng, K.-H.; Liu, H.-Y.; Chang, C. K.; Yeung, L.-L. *Synlett* **2002**, 1475–1478. (c) Gross, Z.; Ini, S. *J. Org. Chem.* **1997**, *62*, 5514–5521. (d) Collman, J. P.; Lee, V. J.; Kellen-Yuen, C. J.; Zhang, X.; Ibers, J. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1995**, *117*, 692–703.
- (16) Consistent with this suggestion, pyridine addition to a deactivated porphyrin catalyst is observed to restore activity for styrene epoxidation, although less efficaciously than anthracene addition. Accompanying the restored catalytic activity is pyridine *N*-oxide formation. Addition of the *N*-oxide to a deactivated catalyst, on the other hand, has no restorative effect.
- (17) Collman and co-workers (*Inorg. Chem.*, **2000**, *39*, 4625–4629) have presented evidence for another interesting role for pyridine. They find that conversion of pyridine to pyridine *N*-oxide renders the ligand a better donor to manganese, thereby enhancing its catalytic activity.

all analyses, initial temp = 50 °C, initial time = 0 min, rate = 5 °C/min, final temp = 150 °C, final time = 5 min). Catalyst TON values were determined by GC through the use of experimentally measured response ratios versus an internal standard. Retention times for various components of the reaction mixture were assigned by injection of pure samples of each component.

Chiral GC analysis of styrene oxide was performed on a Hewlett-Packard HP6890 GC equipped with FID detector and HP7683 series autosampler and injector and analyzed using HP Chemstation software. The column used was a 30-m Supelco BetaDex 220 column with 0.25-mm inner diameter and 0.25- μ m film thickness (inlet pressure = 21.5 psig; column flow = 2.4 mL/min; temperature program for all chiral GC analyses, initial temp = 30 °C, initial time = 0 min, rate = 5 °C/min, final temp = 150 °C, final time = 10 min).

Column chromatography was performed on EM Reagents silica gel 60 (230–400 mesh) under positive nitrogen pressure. Commercially available styrene (Aldrich) and styrene derivatives were passed through a plug of inhibitor remover (Aldrich) and checked by GC for purity before use. Dichloromethane was purchased from VWR Scientific and used without purification in most cases. For air-free reactions, dichloromethane was distilled over calcium hydride, stored in a Strauss flask, and saturated with nitrogen prior to use. 4-Nitrostyrene was purchased from Pfaltz and Bauer Chemical Co. and purified as described above for styrene. Iodosylbenzene,¹⁸ pentafluoriodosylbenzene,¹⁹ 2-(*tert*-butylsulfonyl)iodosylbenzene,²⁰ 9,10-dihydroxyanthracene,²¹ chiral manganese(III) porphyrin,⁶ [Fe^{III}TPP]₂O,²² [Cl(TPP)Mn^{IV}(OIPh)]₂O,¹¹ and (*N,N'*-bis(salicylidene)ethane-1,2-diamine)Mn(PF₆)₂²³ were synthesized using literature procedures. All other chemicals were purchased from Aldrich Chemical Co. and used as received.

[Mn^{IV}(salen)]₂O₂. The synthesis of this compound was adapted from a literature procedure²⁴ as follows: The free-base salen ligand *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminobenzene (1.0 g, 1.9 mmol) was suspended in MeOH (200 mL). To this was added NaOH pellets (296 mg, 7.4 mmol) and the solution was warmed in a water bath until all NaOH and most of the salen ligand dissolved. Mn(OAc)₃·2H₂O (496 mg, 1.9 mmol) was added as a solid in one portion. The solution became dark reddish brown immediately and was stirred at 40 °C, open to the air, for 4.5 h. A dark brown precipitate was collected on a glass frit, rinsed with water (3 × 10 mL) and MeOH (3 × 10 mL), and dried in air to yield a brown solid (0.86 g, 76%). FABMS: *m/z* = 1218.6 (calcd *m/z* = 1218.6 for [M⁺]) and *m/z* = 1202.6 (calcd *m/z* = 1202.6 for [M–O]⁺). Anal. Calcd for C₇₂H₉₂Mn₂N₄O₆: C, 70.92; H, 7.60; N, 4.59. Found: C, 70.99; H, 7.20; N, 4.23.

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Standard Procedure for Synthesis of Epoxides for GC Calibration. In a 50-mL round-bottom flask equipped with a magnetic stir bar was dissolved the appropriate olefin (300 mg) in methylene chloride (25 mL). The mixture was cooled to 0 °C in an ice bath. Excess *m*-CPBA was added, and the stirred solution was allowed to come to room temperature. After all the olefin had reacted (as checked by thin-layer chromatography), CH₂Cl₂ (25 mL) was added. The solution was then washed with 10% aq K₂CO₃ (5 × 15 mL) to remove benzoic acid byproducts. When further purification was necessary, the products were separated by column chromatography on silica gel using mixtures of hexanes and ethyl acetate as eluant. The products were analyzed by GC–MS and ¹H NMR spectroscopy. Data for the following compared favorably with reported spectral characterization: 4-methoxystyrene oxide,²⁵ 4-methylstyrene oxide,²⁶ 4-*tert*-butylstyrene oxide,²⁵ 4-chlorostyrene oxide,²⁶ 4-trifluoromethylstyrene oxide,²⁷ 4-nitrostyrene oxide,²⁶ 1,4-dihydronaphthalene oxide,²⁸ and 1,2-dihydronaphthalene oxide.²⁴

General Procedures for Epoxidation Reactions. In a typical procedure, 100 μ L of a stock solution containing the catalyst (3 × 10^{−6} mol, 1 equiv) and the internal standard (octane, 30 equiv) was added to a 10-mL round-bottom flask equipped with a magnetic stirbar. The solvent (3 mL) was then added along with the anthracene additive (50 equiv) and styrene (0.624 g, 2000 equiv). The mixture was stirred until the anthracene derivative was dissolved. Solid iodosylbenzene (0.264 g, 400 equiv) was added at 0 and 15 min. Samples were taken periodically over 3 h. Each sample was first filtered through a silica plug to remove the catalyst. The plug was then washed with additional methylene chloride (2 × 0.75 mL). The filtrates were combined and analyzed by quantitative GC analysis.

Alternatively, 100 μ L of a stock solution containing MnTPP (3 × 10^{−6} mol, 1 equiv) and the internal standard (chlorobenzene, 30 equiv) was added to a 10-mL round-bottom flask equipped with a magnetic stirbar. Methylene chloride (3 mL) was then added along with anthracene (50 equiv) and the olefin (2000 equiv). The reaction was stirred until the anthracene was dissolved. Solid iodosylbenzene (0.528 g, 800 equiv) was added to initiate the reaction. Samples were taken periodically and treated as described above. The filtrates were combined and analyzed by quantitative GC analysis.

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Supporting Information Available: Figures showing the effect of anthracene derivatives on the time course of styrene epoxidation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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