gensen.[36] ΔG_{sol} for water is given in Table IV, and ΔG_{int} was determine to be −11.2 ± 0.5 kcal/mol. This gives an estimate of −5.2 ± 1.0 kcal/mol for the free energy associated with this process. Thus, in order to estimate the ΔG_{act} for the reverse of the two-water reaction all we need consider is the affect solvent has on **10** → **6**. Using the data from Table V we estimate ΔG_{act} for this reaction to be 15.2 ± 1.0 kcal/mol. Our computed value of 15.2 ± 1.0 kcal/mol is in excellent agreement with the experimental ΔG_{act} of 15.3 kcal/mol.[3] From both the forward and reverse directions it is clear that the two-water reaction is in better agreement with experiment than is the one-water reaction.

Conclusions

Using a combination of ab initio and statistical mechanical techniques we have been able to provide insight into how CO_2 reacts at neutral pH in water to form carbonic acid (i.e. uncatalyzed reaction of CO_2 with water). We have found that the reaction of two water molecules with CO_2 is significantly more favorable and is in better agreement with available experimental activation parameters than is the reaction of CO_2 with one water molecule. These results suggest that for hydrolysis reactions the participation of more than one water molecule is likely.[16] The present reaction is an example of what Jencks has called a preassociation mechanism,[16] where the reactants come together in an encounter complex, which subsequently undergoes a reaction step. Thus, two water molecules associate with CO_2 and then undergo a Woodward–Hoffmann allowed six-electron process that generates carbonic acid and water. While the entropic penalty paid in the two-water reaction in the gas phase is high (about 9.0 kcal/mol) it is not enough to disfavor this reaction. Thus for hydration and dehydration processes at neutral pH in water the two-water process has to be considered a viable pathway. Our results also demonstrate that solvent plays a significant role in favoring one reaction type over another even when the reactants and products are neutral. Finally, we find that when determining solvation corrections for reactions it is best to perturb between, for example, the reactant and transition state than it is to evaluate the absolute free energy of the separate molecules and then taking the difference.[31]

Acknowledgment. We would like to thank the Center for Academic Computing at the Pennsylvania State University for generous allocations of IBM 3090-600S computer time. Numerous discussions with Mark Maroncelli were also very helpful in completing this work. A grant from the NSF for the purchase of a Multiflow 14/300 is also acknowledged.

Mechanistic Studies of Olefin Epoxidation by a Manganese Porphyrin and Hypochlorite: An Alternative Explanation of "Saturation Kinetics"

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Abstract: The catalytic epoxidation of olefins with Mn(TMP)Cl with phase-transfer catalysis and hypochlorite has been reexamined from the point of view of material balance and stability of this system in the presence of three axial ligands. The efficiency (yield of epoxide formation based on OCl^- consumed) is found to fall off with decreasing olefin concentration and to be influenced by the nature of the axial base. With *t*-BuPy as the axial ligand, the stirred system in the absence of olefin is found to be stable over prolonged periods and does not lose OCl^- titer. This leads to the conclusion that, in the presence of low olefin concentration, the missing OCl^- equivalents must be consumed in a side reaction with the olefin. It is proposed that extensive byproduct oxidations account for loss of OCl^-, low efficiency, and apparent "saturation kinetics" we previously reported.

Many studies of catalytic olefin epoxidation have been inspired by interest in the enzyme family cytochrome P-450.[1] The mechanism by which an oxygen atom is transferred from a metalloporphyrin to an olefin has been widely debated.

Several years ago we studied catalytic olefin epoxidation with manganese porphyrins, hypochlorite anion, an axial ligand, and a phase-transfer agent in biphasic media.[2] This system was modelled after the efficient catalyst first developed by Meunier.[3] Under stringently controlled conditions we found evidence for saturation kinetics.[2c] At high olefin concentrations we showed the epoxidation rate to be zero order in olefinic substrate, whereas at low olefin concentrations the rate becomes first order in olefin. Furthermore, different olefins react at different rates. These observations led us to make a controversial proposal: that a metallaoxetane intermediate is in rapid equilibrium with a M=O species and olefin substrate and that this intermediate irreversibly breaks down to the epoxide product.

Since that time, the kinetic behavior of this reaction has been examined by several research groups.[4-6] Diverse, conflicting interpretations have been advanced to explain this complicated system. Nolte and co-workers have proposed that Mn(V)–oxo formation is the rate-determining step in this system and suggest dimerization of the unhindered $Mn(TPP)^+$ catalyst may be responsible for the difference in rates for this catalyst.[4] They also

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suggest that the saturation behavior in alkene concentration may be due to a reversible formation of the Mn(V)–oxo from a hypochlorite complex.[4] Bruice and co-workers have argued that phase transfer of hypochlorite is the rate-determing step, but they cannot explain the apparent saturation kinetics behavior.[6] Both Bruice and Groves[5] and their co-workers have observed that both Mn(V) and Mn(IV) species can be present under catalysis; since the latter is a weaker oxidizing agent, the formation of Mn(IV) species may be responsible for the observed rate differences. There appears to be no good explanation for the apparent saturation kinetics of this system. Herein we describe (1) conditions under which there is good material balance and stability for the catalytic system, (2) that the efficiency of the catalyst is dependent on the nature and concentration of the olefin as well as the ligating base, and (3) that byproducts of olefin epoxidation are competitively oxidized and that when olefin concentration is low this competition reduces the efficiency of the system. These experiments provide an alternative explanation for the apparent saturation kinetics; the experimental foundation for the proposed metalloxetane intermediate has been abrogated.

Results

In this work we have measured the efficiency of olefin epoxidation by hypochlorite with the system Mn(TMP)Cl, the same phase-transfer agent as before (benzyldimethyltetradecylammonium chloride), and CH_2Cl_2 as the solvent. We define efficiency as moles of epoxide produced/mol of ClO^- consumed. Low hypochlorite concentrations, typically with $[OCl^-]/[Mn]$ ratios of 130:1, have been employed in order to obtain good mass balance and an accurate assay of changes in hypochlorite concentration during catalysis. In our prior work the high $[OCl^-]/[Mn]$ ratio (~1000:1) would have masked the subtle effects found in this study.

Three different axial ligands have been studied: 4-(imidazol-1-yl)acetophenone, NAPI (used in our previous work); 4-*tert*-butylpyridine, *t*-BuPy (which was subsequently shown by Meunier to be more resistant to oxidation);[3d] and *N*-phenylimidazole, Ph-Im. The latter was used to explore the possible reactivity of the methyl ketone in NAPI and as a substance conveniently followed by GLC analysis.

Since we wished to determine the fate of the oxidizing equivalents in ClO^-, we examined the head gas over these reaction mixtures for the possible formation of dioxygen—none was detected by GC analysis.

The aqueous hypochlorite containing phase was treated with Ba^{2+} to remove sulfates present in the lithium hypochlorite. In a separate report[7a] we have examined the role of another possible impurity, ClO_3^-, in the epoxidation reaction. Although chlorate is not an effective oxidizing agent itself, it does retard the rate of epoxidation by ClO^-, presumably by strongly complexing with the phase-transfer agent.

Effect of Olefin Concentration. Table I shows results for epoxidation of three different olefins at various olefin concentrations with NAPI as the axial ligand. The results for indene are also presented for the other two axial ligands, 4-*t*-BuPy, and Ph-Im. As shown in Table I, at higher olefin concentrations the material balance with respect to olefin is good for all combinations we examined. This material balance was calculated by measuring the olefin introduced, the olefin remaining after all OCl^- is consumed, and the epoxide formed. Typically, at higher olefin concentrations, roughly 90% of the olefin consumed can be accounted for as epoxide. At lower olefin concentrations (olefin to Mn ratio of 14000/1) the olefin material balance falls to a value as low as 80%.

Table I. Epoxide Yield Based on Oxidant

N-base	concn of N-base, mM	olefin	concn of olefin, mM	eff,[a] %	material balance,[b] %
(a) NAPI	11	indene	360	94	99
			35	84	101
			3.1	27	91
(b) NAPI	11	styrene	360	96	97.2
			27	34	
			10	9	93.8
			3.3	4	91.5
(c) NAPI	11	1-methylcyclohexene	360	34	93
			35	13	97
			3.6	6	82.1
(d) NAPI	50	indene	360	92	
			35	88	99.0
			3.2	39	89.2
(e) NAPI	2	indene	300	88	
			33	68	
			3.2	36	
(f) 4-*t*-BuPy	33	indene	320	76	
			26	88	
			2.2	49	95.1
(g) 4-*t*-BuPy	11	indene	350	88	97.2
			35	89	108
			3.2	57	80.7
(h) Ph-Im	11	indene	360	86	
			35	52	
			3.0	25	

[a] Eff = (mol epoxide)/(mol LiOCl added). [b] Material balance = {mol epoxide formed + mol recovered olefin}/(mol of olefin added). Both the efficiency and the material balance were determined after the hypochlorite was completely consumed.

Table I also shows the efficiency with respect to hypochlorite. We define efficiency as the percent OCl^- converted into epoxide [(mol epoxide formed)/(mol of LiOCl added)]. Entries (a) and (b) show efficiencies of ~95% when large amounts of indene or styrene are used. These experiments were done under 11 mM of NAPI, which is the same Mn/NAPI ratio we used in our earlier work.

Under these conditions the system is well behaved; both the olefin material balance and the OCl^- efficiencies are high. As entries (a), (d), and (e) show, this situation is not much affected by a 25-fold variation in the concentration of the axial base.

On the other hand, the data in Table I show that the efficiency is influenced by the *concentration* and by the *nature* of the olefin. Entries (a), (b), and (c) reveal that the three alkenes indene, styrene, and 1-methylcyclohexene show a remarkable dependence (entries (a)–(c)) of the efficiency on the olefin concentration under our previous reaction conditions (11 mM NAPI). This suggests that there may be an additional mechanism for the diminished rates at low alkene concentrations. The fate of the lost oxidizing equivalents will be discussed later.

Effect of the Axial Ligand. Nolte and co-workers have shown that the axial ligand NAPI, which we used for our earlier kinetic studies, is unstable and can be oxidized by this system.[4g,h] On the other hand, *t*-BuPy is not oxidized very slowly (1 day) by hypochlorite in the absence or presence of either the Mn(TMP)Cl catalyst or the olefin substrate. Nevertheless, as shown in Table I, at higher olefin concentrations in the presence of NAPI the efficiency of olefin epoxidation with respect to OCl^- is very high—sometimes higher than observed when *t*-BuPy is used as

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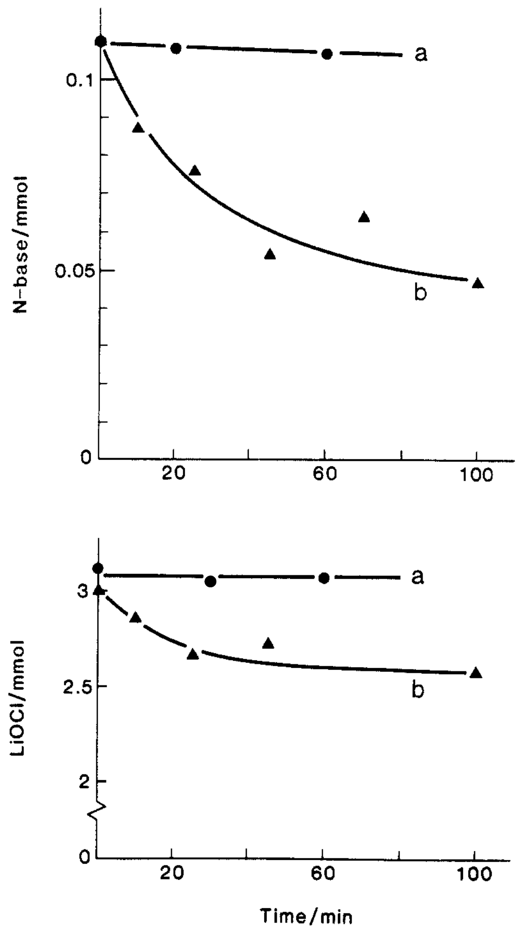


Figure 1. Stabilities of N-bases to the manganese porphyrin/hypochlorite system. Conditions: see Experimental Section: a, 4-*t*-BuPy (●) and b, 1-phenylimidazole (▲). The upper panel shows the concentration of each axial ligand with time for the Mn(TMP)Cl catalyst. The lower panel shows the corresponding time course of the OCl^- concentration in the presence of two different ligands.

the axial ligand. Entries (f) and (g) show that the efficiencies also fall off as the olefin concentration is lowered; a similar pattern is seen with Ph-Im (entry (h)). Note that it is convenient to follow the concentration of *t*-BuPy and Ph-Im over the course of a reaction with GLC, but NAPI is difficult to analyze for.

The role of Ph-Im as an axial base and a substrate was studied (in the absence of olefin substrate). As shown in Figure 1, hypochlorite is consumed in a time course parallel to Ph-Im. However, for each mol of Ph-Im used up several moles of OCl^- are consumed! We were unable to find the oxidation products and suppose that these fragments, possibly including CO_2, remain in the basic (pH ~11) aqueous phase.

The behavior of this system in the presence of *t*-BuPy is very interesting. As shown in figure 1, in the absence of olefinic substrate very little hypochlorite is consumed when *t*-BuPy is used as the axial ligand. Under the same conditions of high concentration of olefinic substrate, hypochlorite is consumed, and good yields of epoxide are obtained. With lower olefin concentrations lower yields of epoxide are detected; however, hypochlorite is still consumed. The results with *t*-BuPy in the absence of olefin are very significant; little oxidation occurs over the time span of the usual olefin epoxidation reaction. As shown in figure 1, little OCl^- is consumed over a 60-min period in the absence of any olefinic substrate. That is, in the absence of olefin substrate, the system does not oxidize *t*-BuPy, Mn(TMP)Cl, the phase-transfer catalyst,[6b] nor the CH_2Cl_2 solvent. Nor is hypochlorite consumed under these conditions. We have previously shown that under these conditions ClO^- itself does not disproportionate into ClO_2^- or ClO_3^- and Cl^-.[7a]

Catalyst Stability. We then examined the above mentioned system to determine whether it had lost its catalytic activity. A CH_2Cl_2 solution containing Mn(TMP)Cl, 4-*t*-BuPy, and the phase-transfer catalyst was divided into two portions; each was placed in contact with aqueous LiOCl. Indene, 0.1 M, was injected into one portion and stirred for 50 min, during which time indene epoxide was measured at brief intervals. The other portion was stirred for 33 min, then the same quantity of indene was injected, and the formation of indene epoxide was monitored. The yield of epoxide and the rate profile of epoxide formation for the two experiments were the same within experimental error. We repeated this type of experiment, incubating the solutions for 1 min and for 155 min before adding indene. Again, the results were very similar. We conclude that the system loses neither OCl^- titer nor catalytic activity upon incubation (with stirring).

We carried out a similar incubation with NAPI as the axial base. In the absence of olefin all of the OCl^- is consumed within 25 min. At this point indene was injected; of course no epoxide is formed. However, addition of more OCl^- immediately results in the formation of epoxide and the consumption of OCl^-. The activity of the catalyst is not distinguishable from the "normal" system. Enough NAPI remains to sustain the active catalyst.

Discussion

There have been several proposals to account for the fact that, with the Meunier system, the rate of olefin epoxidation shows first-order dependence on olefin concentration at low olefin concentration and that different olefins exhibit different rates of epoxidation.

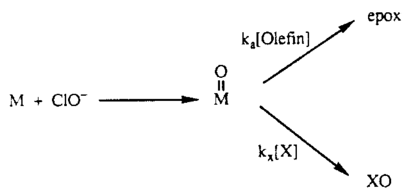
The reversible formation of a μ-oxo dimer (por)$Mn^{IV}OMn^{IV}$(por) has been suggested by Nolte and co-workers[4d,e] as one explanation for the observed kinetic phenomenon. We have chosen Mn(TMP)Cl as a catalyst for two reasons: (1) the inherent steric hindrance of the porphyrin prevents μ-oxo dimer formation, and (2) Mn(TMP)Cl is stable to oxidative degradation over extended reaction times; we earlier reported that less hindered porphyrins such as Mn(TPP)Cl are bleached in this system in the lower olefin concentration range. Thus, Mn(TPP)Cl itself could be a surrogate substrate.

The reversible breakdown of a $Mn^{III}OCl$ complex into $Mn^{V}{=}O$ and chloride, which has also been proposed by Nolte's group,[4] seems unreasonable on thermodynamic grounds. To date, no transition-metal hypochlorite complexes have been identified or characterized.

The idea that the rate differences between various olefins involve the formation of a less reactive Mn(IV) complex does not offer a plausible explanation of our results. For example, we have found that the catalyst system with 4-*t*-BuPy as a ligand is stable and does not lose titer over periods of time sufficient for extensive olefin epoxidation. When olefin is added to such a stirred system, catalytic epoxidation commences at once and continues at a rate indistinguishable from that of a sample which was immediately treated with olefin. The same yields of epoxide were obtained in each case. Furthermore, Groves has found that pyridine derivatives suppress the equilibrium between Mn(V) and Mn(IV).[5]

We now offer an alternative explanation for the olefin concentration dependence on the rate. This is that oxo formation is the rate-limiting step but that the diminished rate of epoxide formation at low alkene concentration is due to the presence of a competing reaction at low alkene concentrations (eq 1). An unknown reductant, X, is oxygenated; subsequent oxidations of X occur more rapidly. At high olefin concentrations the efficiency of epoxide formation (percent yield based on hypochlorite consumed) would be very high since $k_a[\text{olefin}] \gg k_x[X]$. At lower olefin concentrations the efficiency would fall off as surrogate substrate X oxidation becomes competitive with the olefin; ($k_a[\text{olefin}] \sim k_x[X]$). This is qualitatively consistent with the data in Table I. At higher olefin concentrations the efficiencies are quite high; at lower olefin concentrations the efficiencies fall off.

Table I shows that the three alkenes indene, styrene, and 1-methylcyclohexene show a remarkable dependence (entries (a)-(c)) of the efficiency on the olefin concentration under our previous reaction conditions (11 mM NAPI). The concentrations of olefin where the efficiency is 50% are roughly 0.01 M for indene,



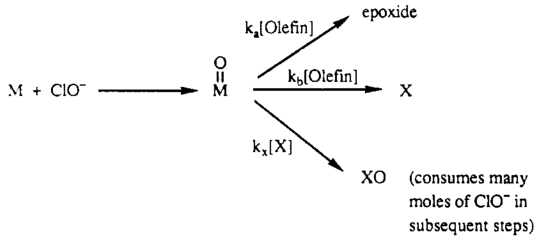
(1)

0.1 M for styrene, and >0.4 M for 1-methylcyclohexene. This trend resembles the trend in the apparent "K_m" values we reported for these alkenes, 0.08, 0.8, and 8 M, respectively. Since the K_m value in Michaelis–Menten kinetics is the concentration of substrate for which the rate is half that of the maximal rate, and since the 50% efficiency value presumably reflects the concentration of alkene where the rate of epoxidation is half of its value when the efficiency is near 100%, the 50% efficiency values should therefore be close to our reported K_m values. Although 1-methylcyclohexene is consistent with this scheme, the 50% efficiency values are much lower than the K_m values for indene and styrene. For indene and styrene thus it appears that an additional mechanism may be operating to lower rates of epoxidation at low alkene concentrations. One possible mechanism would be the reduction of the Mn(V)–oxo to a Mn(IV) species. Both Bruice and Groves and their co-workers have observed the formation of Mn(IV) species, and Groves has reported them to be weaker oxidizing agents.[5] We have found that with *t*-BuPy as a ligand, a stirred "incubated" system retains its full activity, which would not be the case if this resting system were in an unreactive Mn(IV) state, but this does not rule out the participation of Mn(IV) during the catalytic process.

We have found that (a) efficiencies depend on the nature of the olefin and its concentration; (b) efficiencies depend on the nature of the axial base; (c) efficiencies do not depend on the concentration of axial base; (d) no oxidation occurs (e.g., in the *t*-BuPy system) in the absence of olefin; (e) when side product oxidations do occur, many equivalents of ClO$^-$ are reduced. These results require that the surrogate oxidant, X, does not derive from the usual components of the oxygenating catalyst system when *t*-BuPy is used as the axial ligand. Under such conditions X appears to be formed from the olefin; for example, it may be a byproduct of olefin oxidation. This suggests a more complete mechanistic scheme, eq 2. Note that the magnitude of k_x and k_b should also depend on the nature of the olefin if X derives from the olefinic substrate. The supposition that k_a, k_b, and k_x should all depend on the nature of the olefin accounts for the sensitivity of the efficiency to the nature of both the substrate and axial ligand (Table I). It is also consistent with reports from other laboratories that different olefins sometimes manifest different rates of epoxidation.[4d]

The material balance data based on epoxide as well as OCl$^-$ conversion provide some further evidence about the stoichiometry of the oxidation of X. At high olefin concentrations, the material balance of organics is about 90%. Thus, about 10% of the olefin is lost, suggesting that $k_a \sim 10k_b$. At low olefin concentrations, the efficiency based on OCl$^-$ drops to less than 24%. If X reduced only 1 mol of OCl$^-$, the efficiency based on OCl$^-$ would be at most 80%. In order to get an efficiency as low as 25%, X must ultimately reduce more than 6 mol of OCl$^-$. Although this is a crude estimate, it is consistent with the observation of extensive degradation once intermediates begin to be oxidized.

Although the scheme in eq 2 can qualitatively account for all our observations, the quality of our data is insufficient to validate the mechanism. Among the problems associated with this reaction is the extraction of intermediate oxidation products, derived from X, into the aqueous medium. Our results using Ph-Im in the absence of olefin show that surrogate substrates can be consumed in a burst of oxidation; several equivalents of OCl$^-$ are used up for each Ph-Im consumed. This is a paradigm for the rapid subsequent oxygenations of other substrates, X.[7b] Following the first oxygenation step for any surrogate reductant X, the subsequent oxygenation steps can be very fast; also, since the products are unknown, the stoichiometry may also be olefin dependent.



(2)

We have tested candidates, unsuccessfully, for the surrogate reductant X with the *t*-BuPy system. Addition of the following generic candidates for X in the absence of olefinic substrate did not lead to appreciable reaction on a time scale commensurate with olefin epoxidation. Cyclohexanone, cyclohexen-3-ol, cyclohexene epoxide, and 1,2-dihydroxyhexane were not appreciably consumed under these conditions. All of these substrates are plausible products or byproducts from cyclohexene epoxidation. The 1,2-diol might not have been expected to be a substrate since we earlier found such diols to be competitive inhibitors of these oxygenating systems.[8] However, X may be a reactive intermediate such as a free radical.

Conclusion

By studying the material balance of the phase-transfer Mn(TMP)Cl-catalyzed OCl$^-$ olefin epoxidation, we have discovered that the efficiency of olefin epoxidation falls off in the range of olefin concentrations in which the latter appears in the rate law. This provides an alternate explanation which does not require saturation kinetics. We have, however, also shown that in the presence of the axial ligand *t*-BuPy and the absence of olefin substrate major components of this system (the porphyrin, the solvent, and the phase-transfer agent) do not act as substrates. We have demonstrated that one surrogate substrate, Ph-Im, undergoes a series of fast, multiple oxygenation steps, and we suggest that this phenomenon may occur in other cases.

Other reports of apparent saturation kinetics in metal-catalyzed oxygenations have appeared in recent literature.[12,13] Our results suggest that more stringent criteria must be used to demonstrate reversible complex formation.

Finally we comment on the rate behavior of the present system. There are many experimental variables which have been shown to affect this rate: the nature and concentration of the axial base,[2,3] the nature and concentration of the porphyrin, the concentration and purity of the hypochlorite salt, the concentration of the phase-transfer agent,[6] the stir rate, and the possibility of rapid chain reactions. Subsequent deactivation of the catalyst by diol byproducts, by μ-oxo formation, and by formation of a less active Mn^{IV}=O state[5,6] can also affect these kinetics. It is thus not surprising that so many apparently inconsistent, conflicting results have been observed. Under many circumstances the rate-limiting step appears to be the formation of a Mn^{V}=O species. For example, Nolte has suggested that this involves a hypochlorite complex which he proposes to be in equilibrium with Mn^{V}=O and Cl$^-$.[4g,h] Whatever the details, the most probable rate-limiting step is not understood.

Experimental Section

Instrumentation. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5880A FID fitted with 6 ft × 1/8 in. column of 10% OV 101 on Chromosorb WHP or 6 ft × 1/8 in. column of 10% Carbowax 20M on Supelcoport and a Hewlett-Packard Model 5890 TCD fitted with a 10 ft × 1/8 in. column of molecular sieve 5A. UV-Vis spectra were recorded on a Hewlett-Packard model 8452A.

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Materials. Manganese(III) *meso*-tetramesityl chloride[(Mn^{III}-(TMP)Cl] was synthesized by literature methods[9] and purified by recrystallization. 4′-(Imidazol-1-yl)acetophenone (NAPI) (Aldrich) was twice recrystallized from methylene chloride/hexane. 4-*tert*-Butylpyridine (4-*t*-BuPy) (Aldrich) and benzyldimethyltetradecylammonium chloride (PTC) (Fluka) were used without further purification. *N*-Phenylimidazole was prepared by literature methods[10] from imidazole and bromobenzene. Saturated hydrocarbons which were used as internal standards were purchased from Aldrich and used without further purification. Olefins (Aldrich) were distilled and passed through neutral alumina columns immediately prior to reaction to remove trace peroxides.

The hypochlorite solution was prepared as follows: 30% LiOCl (3.5 g) 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 concentration of LiOCl was ca. 0.3 M, and it was diluted with deionized water to the desired concentration.

Analysis of LiOCl. LiOCl was determined by iodometric titration with standard sodium thiosulfate solution. Dilute LiOCl solutions were determined spectrometrically from the concentration of I_3^- ion (360 nm) formed with sodium iodide.[11]

Analysis of O_2. Mn(TMP)Cl (0.03×10^{-6} mol), PTC (15×10^{-6} mol), and Ph-Im (60×10^{-6} mol) were dissolved with methylene chloride (1.5 mL) in a 4-mL vial sealed by a rubber septum and flushed rigorously with helium. LiOCl (45×10^{-6} mol in 1.5 mL of H_2O) was added, and the mixture was stirred virorously. The reaction was followed by gas chromatographic analysis at room temperature (molecular sieve 5A, activated by baking at 240 °C for 230 h) of the gas layer, and no dioxygen was detected.

Determination of Epoxidation Efficiencies. Typical conditions of epoxidation with a limited amount of lithium hypochlorite were as follows: Mn(TMP)Cl (2.3×10^{-7} mol), PTC (1×10^{-4} mol), N-base (1.1×10^{-4} mol), and olefin ($0.03 \sim 3 \times 10^{-3}$ mol) were dissolved in 10 mL of methylene chloride and stirred vigorously, when lithium hypochlorite aqueous solution (3 mM × 10 mL) was dropped in at room temperature. The complete consumption of hypochlorite required a few minutes to an hour depending upon the olefin and was signalled by a brown-to-green color change of the organic phase. These final solutions have $\lambda_{max} = 478$ nm which indicates the presence of Mn^{III}(TMP)X species.

Stabilities of N-Bases. Stabilities of N-bases were examined in the absence of olefins. Mn(TMP)Cl (5.7×10^{-7} mol), PTC (1×10^{-4} mol), and N-base (1.1×10^{-4} mol) were dissolved in methylene chloride (10 mL). LiOCl solution (20 mL × 0.15 M) was layered on the organic solution, and then the reaction was initiated by vigorous stirring. The reactions were followed by determining the concentration of N-base (gas chromatograph) and the concentration of hypochlorite (iodometric titration). The stabilities of cyclohexanone, cyclohexen-3-ol, cyclohexene epoxide, and 1,2-dihydroxyhexane were examined by the same procedure in the presence of 4-*t*-BuPy.

Stabilities of Catalytic Mixtures: *t*-BuPy. Two solutions each with Mn(TMP)Cl (2.1×10^{-6} mol), PTC (3.8×10^{-4} mol), and *t*-BuPy (4×10^{-4} mol) in 10 mL of CH_2Cl_2 were prepared. Indene (2.1×10^{-3} mol) was added to one, and both solutions were then treated with 36 mL of 0.1 M solution of lithium hypochlorite. The incubation solution was treated with 2.1×10^{-3} mol of indene after 33 min, and the formation of epoxide was followed by GC. The total yield of epoxide was 90 and 91% for the incubated and unincubated cases, respectively.

NAPI. Mn(TMP)Cl (2.3×10^{-7} mol), NAPI (1.1×10^{-4} mol), and PTC (1.1×10^{-4} mol) were dissolved in 10 mL of CH_2Cl_2 and treated with 10 mL of a 3 mM solution of lithium hypochlorite. Iodometry of aliquots taken from the aqueous phase indicated that hypochlorite was consumed within 25 min. Addition of 50 μL of cyclooctene to this mixture led to the formation of *no* epoxide after 80 min. However, when additional lithium hypochlorite (0.1 mL of 0.3 M) was added, cyclooctene oxide was formed, and after 80 min the hypochlorite was again consumed.

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Unusual Activity and Selectivity in Alkyne Hydrosilylation with an Iridium Catalyst Stabilized by an O-Donor Ligand

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Abstract: Catalytic alkyne hydrosilylation has been found for iridium in the O-donor ligand environment of Grim's triso ligand (=tris(diphenyloxophosphoranyl)methanide). The reaction is selective for 1-alkynes and regioselective for β-products and gives the thermodynamically less favored *cis*-vinylsilane products by an unexpected anti addition of Si–H to the triple bond. Mechanistic studies suggest that the alkyne first inserts into the M–Si, not the M–H, bond and that a trans to cis rearrangement occurs via an η^2-vinyl intermediate before reductive elimination. A number of Rh and Ir complexes of the type [(triso)ML_2] are prepared. IR studies on the CO complexes show that the donor power of triso compares with that of other related ligands in an unexpected order: Tp < $P_3O_9^{3-}$ < triso < Cp.

Soft, high-field ligands such as Cp, CO, and PR_3 are used very extensively in homogeneous catalysis and in organometallic chemistry. In contrast, heterogeneous catalysts most commonly employ oxide supports. Yermakov, Schwartz, and others[1] have developed a class of site-isolated oxide-supported catalysts in which a mononuclear organometallic fragment bound to the oxide surface catalyzes various hydrocarbon conversions including alkane functionalization. We have become interested in how the properties of organometallic compounds change on moving to the much less studied O-, N-, and S-donors as supporting ligands, for which very little organometallic chemistry or catalysis is known. We report here some results with an O-donor ligands.

Wolczanski,[2] Chisholm,[3] Klemperer,[4] Finke,[5] Shapley,[6] and others have studied organometallic chemistry in an O-donor ligand environment. These ligands tend to bind most strongly to the oxophilic early and middle transition metals, but complexes of

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