"Intermolecular" Trapping of a Nonheme Fe(IV)═O Intermediate

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The reactions of Fe^{III}(TPA) (TPA = tris(2-pyridylmethyl)amine) complexes with 2-methyl-1-phenyl-2-propyl-hydroperoxide (MPPH) delivered by syringe pump under anaerobic conditions afford nearly quantitative conversion of MPPH to products derived from the benzyl radical. These results unequivocally show that MPPH breaks down by O−O bond homolysis, leading to the formation of the benzyl radical and a high valent Fe(IV)═O species. Without added substrates, the benzyl radical reacts with the high valent species to form benzyl alcohol or benzyl halides. The Fe(IV)═O species can also effect the two-electron oxidation of added substrates such as thioanisole, cyclohexanol, and cyclooctene under appropriate conditions. The oxidation of thioanisole and cyclohexanol is likely facilitated by pre-equilibrium binding of the substrate to the metal center, allowing these substrates to intercept the high valent iron−oxo species as it forms. These results suggest the importance of close proximity to direct the high valent metal center down a desired pathway.

Introduction

Iron(IV)−oxo species are proposed to be the key reactive species that effect substrate oxidation in many heme[1] and nonheme iron enzymes.[2−6] In cytochrome P450, the iron(IV)−oxo moiety is used in conjunction with a porphyrin radical to effect hydroxylations of alkanes and arenes. In methane monooxygenase (MMO), two iron(IV)−oxo species work in concert to achieve oxidation of methane to methanol. In contrast, mononuclear nonheme iron enzymes such as isopenicillin N synthase, 2-oxoglutarate-dependent enzymes, and the pterin-dependent aromatic amino acid hydroxylases are proposed to carry out two-electron oxidations of their respective substrates by a mononuclear iron(IV)−oxo moiety. However, there is thus far no direct spectroscopic evidence for a mononuclear iron(IV)−oxo intermediate in these enzymes, although indirect evidence has been obtained implicating the participation of such species in some enzyme reactions.[7,8]

In the past 10 years, many groups have made efforts to model the reactivities of these nonheme iron enzymes.[9] Although frequently invoked, no mononuclear high valent iron−oxo species has been observed. In our biomimetic efforts, we have explored the alkane hydroxylation activity of Fe(TPA) (TPA = tris(2-pyridylmethyl)amine) complexes, $[Fe_2O(TPA)_2(H_2O)_2]^{4+}$ (**1**) in particular, in concert with alkyl hydroperoxides.[10−12] The mechanism we initially proposed involving an Fe(V)═O species has been scrutinized and criticized by Ingold and co-workers.[13,14] From these discussions has evolved the consensus mechanism for this catalytic reaction, shown in Scheme 1.[15] Alkane hydroxylation with this system occurs via an Fe(III)−OOR intermediate, which undergoes O−O bond homolysis to afford an alkoxy radical and an Fe(IV)═O moiety. The alkoxyl radical then abstracts a hydrogen atom from the alkane to generate a

Scheme 1

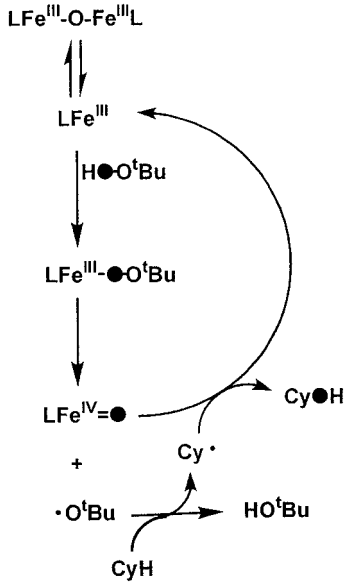

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Table 1. Product Distribution of Oxidation Reactions of **1**/10 Equiv MPPH in CH_3CN at 25 °C[a]

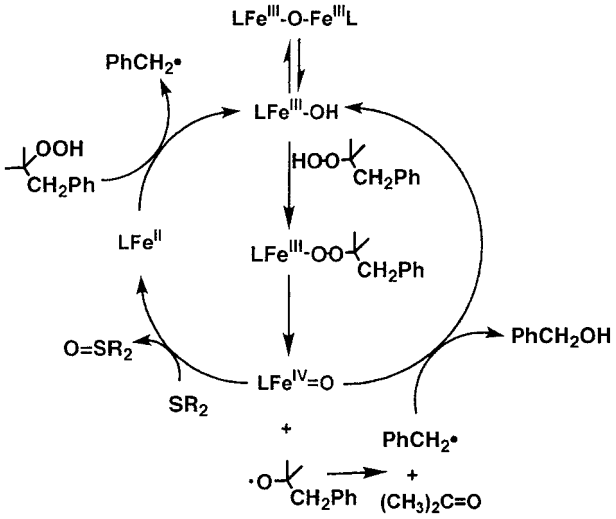
entry	substrate/trap	$PhCH_2OH$	PhCHO	$(PhCH_2)_2$	$PhCH_2Br$/ $PhCH_2Cl$	$PhS(O)CH_3$	$C_6H_{10}O$ or $C_8H_{16}O$
1	none	8.7(3)	0.2(1)				
2	cyclohexane	8.4(2)	0.2(1)				
3	cyclooctane	8.2(4)	0.2(1)				
4	cyclooctane/air	0.9(1)	7.4(1)				
5	35 mM PhSMe	3.1(2)	0.2(1)	1.9(1)		2.7(1)	
6	cyclohexane/35 mM PhSMe	3.1	0.2	1.9		2.7	
7	cyclooctane/35 mM PhSMe	2.7	0.2	1.9		2.7	
8	350 mM PhSMe	1.0(2)	0.2(1)	2.9(3)		4.4(8)	
9	cyclohexanol	8.1(1)	0.3(1)	0.5(2)			1.0(6)
10	cyclohexanol/air	2.1(1)	7.0(1)				6.0(1)
11	cyclohexanol/350 mM $CBrCl_3$				6.6(8)/2.0(2)		7.0(6)
12	cyclooctene	7.2(5)	0.4(2)				0.4(2)
13	cyclooctene/350 mM $CBrCl_3$		0.2(1)		7.1(1)/1.0(2)		1.0(4)

[a] See Experimental Section for reaction conditions. All reactions were run under Ar unless otherwise indicated. Values with error limits derive from data obtained from at least three runs, while values without error limits reflect single-run experiments. Yields are not corrected for the approximately 13% tertiary alcohol impurity present in the preparation of MPPH.

long-lived alkyl radical, which in the absence of other traps reacts with the Fe(IV)═O species to form the alcohol product. In support of this proposed mechanism, the alcohol product in cyclooctane oxidation was 93% ^{18}O-labeled when $^tBuO^{18}OH$ was used as oxidant.[15] Therefore, the O−O bond homolyzes in the Fe(III)−^{18}O−OR intermediate to give the Fe(IV)═^{18}O species that can transfer its terminal oxygen atom to an alkyl radical to form the alcohol.

Our realization that the Fe(IV)═O species can be readily trapped by the nascent alkyl radical has led us to devise strategies to learn more about its inherent reactivity. By introducing a pendant phenyl group on the α position of one of the pyridines of TPA, we have shown that the Fe(IV)═O moiety is capable of intramolecular arene hydroxylation,[16] modeling the chemistry of pterin-dependent hydroxylases such as phenylalanine hydroxylase.[4] In this paper, we demonstrate that the Fe(IV)═O species derived from **1** can carry out two-electron oxidations of exogenous substrates such as thioanisole, cyclohexanol, and cyclooctene.

Scheme 2



Results and Discussion

A key probe of the reaction of **1** with ROOH was the use of 2-methyl-1-phenyl-2-propyl-hydroperoxide (MPPH) as the oxidant.[13,15,17] The alkoxy radical formed upon O−O bond homolysis of MPPH rapidly undergoes β-cleavage (2×10^8 s^{-1}) to form a benzyl radical, a species incapable of hydrogen atom abstraction from inert alkanes such as cyclohexane and cyclooctane. Consistent with the earlier report of MacFaul et al.,[15] we observed no alkane oxidation with the combination of **1** and MPPH (Table 1, entries 2 and 3). In the experiments reported here, we used conditions in which O_2 was rigorously excluded, and its in situ production via in-cage collapse of dialkyltetroxides derived from dimerization of alkylperoxyl radicals was significantly suppressed by syringe pumping. We found that 10 equiv MPPH yielded 8.2−8.7 equiv benzyl alcohol (Table 1, entries 1−3), a nearly quantitative conversion considering that our preparation of MPPH contained an approximately 13% impurity of 2-methyl-1-phenyl-2-propanol. These results show that nearly all of the benzyl radicals produced from decomposition of the MPPH alkoxy radical can be trapped by the Fe(IV)═O species that must be formed in the homolysis of the O−O bond (Scheme 2). On the other hand, in the presence of air, the benzyl radical readily reacted with O_2 to form benzylperoxyl radical and produce the large quantity of benzaldehyde observed (Table 1, entry 4). Thus, the benzyl radical can be prevented from reacting with the Fe(IV)═O species in order to unmask the actual oxidizing potential of the latter.

We have attempted to trap the putative Fe(IV)═O species with dialkyl sulfides. Previously, we reported that adding dimethyl sulfide inhibited the hydroxylation of cyclohexane with ^tBuOOH catalyzed by an Fe(TPA) complex.[10] This inhibition was incorrectly attributed at that time to the trapping of a proposed Fe(V)═O species derived from O−O bond heterolysis. In principle, a dialkyl sulfide could also inhibit the reaction by binding to the iron center and preventing coordination of the peroxide.[14] Alternatively, the inhibition of the reaction could result from sulfide trapping of either the Fe(III)−OOR intermediate or the Fe(IV)═O species derived from O−O bond homolysis. Indeed, a significant amount of $(CH_3)_2SO$ has been reported later by Kim et al.[12] under similar experimental conditions. We repeated the trapping experiment using **1** as catalyst, 50 equiv thioanisole as the trap, and 10 equiv ^tBuOOH as oxidant. Indeed 4.2(6) equiv phenyl methyl sulfoxide was identified as the oxidation product. Furthermore, we found that with $^tBuO^{18}OH$ (96% ^{18}O-enriched) as oxidant >92% of the resulting $PhS(O)CH_3$ contained ^{18}O, showing that the oxidation occurred by transfer of the terminal oxygen atom of ROOH.

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The use of MPPH instead of ^{t}BuOOH should allow us to determine whether O−O bond homolysis occurs prior to the oxidation of $PhSCH_3$.[17] Indeed, the syringe pump addition of 10 equiv MPPH to a CH_3CN solution of **1** in the presence of excess thioanisole resulted in the formation of the corresponding sulfoxide (Table 1, entries 5−8). An examination of the MPPH byproducts showed that the corresponding tertiary alcohol was not formed as would have been expected for an Fe(III)−OOR or an Fe(V)═O oxidant derived from subsequent O−O bond heterolysis. Instead, benzyl alcohol and bibenzyl were observed, indicating that the corresponding alkoxyl radical of MPPH was formed and underwent β-scission to afford the benzyl radical. The benzyl radical could then be trapped by the Fe(IV)═O species to form benzyl alcohol, or it could dimerize to form bibenzyl if no Fe(IV)═O species was present.[18] These results strongly suggest that dialkyl sulfides react with the **1**/ROOH combination by trapping the Fe(IV)═O species derived from O−O bond homolysis of the Fe(III)−OOR intermediate in competition with the benzyl radicals formed in the reaction (Scheme 2).

Further support for the trapping of the Fe(IV)═O species was obtained from ^{1}H NMR studies of the reaction, which were performed to determine the fate of the iron catalyst after the sulfoxidation reaction. The NMR spectrum of the solution at the end of the reaction of **1,** with 1 equiv MPPH and 50 equiv CH_3SCH_3 in CD_3CN, shows strong peaks with chemical shifts within 0−13 ppm, which are characteristic of a low spin Fe^{II}(TPA) complex such as $[Fe(TPA)(CD_3CN)_2]^{2+}$. The formation of the Fe(II) complex at the end of an oxidation reaction is counter-intuitive at first glance, but may be rationalized by invoking oxygen atom transfer from the [(TPA)Fe(IV)═O] moiety to R_2S, resulting in its reduction to $[Fe(TPA)(CH_3CN)_2]^{2+}$ (Scheme 2).[19]

A study of the oxidation of thioanisole by **1** as a function of thioanisole concentration showed the oxidation mechanism to be more complex than a simple attack on the substrate by the Fe(IV)═O species. As illustrated in Figure 1a, the yield of sulfoxide increased with increasing amounts of thioanisole and then reached a plateau above 0.1 M. Concomitantly, the yield of bibenzyl increased, while the yield of benzyl alcohol decreased. The amounts of both of these products also reached a plateau at the same thioanisole concentration. The saturation behavior of the various products is corroborated by the double reciprocal plots in Figure 1b, where straight lines are obtained for the appearance of $PhS(O)CH_3$ and bibenzyl and for the disappearance of benzyl alcohol. These results show the presence of a pre-equilibrium involving dialkyl sulfide and the iron center prior to sulfoxidation. We propose that thioanisole binds to the iron center in a fast equilibrium, and an association constant of approximately 60(10) M^{-1} can be estimated from the *x*-intercepts of the double reciprocal plots. With sulfide in close proximity to the metal center, sulfoxidation can effectively compete with the reaction of the benzyl radical with the Fe(IV)═O species.

We also investigated the oxidation of other potential substrates that are more difficult to oxidize than thioanisole. Under the same conditions as the oxidation of thioanisole, only 1 equiv of cyclohexanol was oxidized to cyclohexanone (Table 1, entry 9). Concomitantly formed was 0.5 equiv bibenzyl, showing that cyclohexanol can partially compete with the benzyl radical for the Fe(IV)═O species. The yield of cyclohexanone increased when a radical trap was added into the reaction mixture to intercept the benzyl radical and prevent it from reacting with the Fe(IV)═O species. For example, when the cyclohexanol oxidation was carried out in air, rather than under Ar, the major products were cyclohexanone and benzaldehyde (Table 1, entry 10). Similarly, the addition of 500 equiv of $CBrCl_3$, another good radical trap, to the reaction of **1** and 10 equiv MPPH under Ar resulted in the predominant formation of cyclohexanone and benzyl halides (Table 1, entry 11). The nearly quantitative interception of the benzyl radical, that can form from the homolysis of MPPH by O_2 or $CBrCl_3$ to give benzaldehyde or benzyl halides, respectively, shows that the alkoxyl radical derived from homolysis of MPPH is not involved in alcohol oxidation. These results leave the Fe(IV)═O moiety as the only reasonable oxidant capable of abstracting the α-hydrogen of the alcohol. The thus-generated hydroxycyclohexyl radical can afford cyclohexanone either via a radical chain reaction in the presence of O_2 or through a one-electron oxidation by the metal complex. The fact that comparable amounts of cyclohexanone are formed with either O_2 or $CBrCl_3$ favors the latter mechanism. Support for the hydrogen abstraction step in the oxidation of cyclohexanol comes from a competition experiment using a 1:3 ratio of cyclohexanol and cyclohexanol-d_{11}; product analysis shows an isotope effect of 3.4 in the cyclohexanone formation, demonstrating that C−H bond breaking is an important component of the rate-determining step in the mechanism. Since alcohols have been shown to bind to the Fe(III)(TPA)−OOR intermediate,[20] it seems likely that the oxidation of the alcohol, as with thioanisole, is facilitated by its coordination to the iron center.

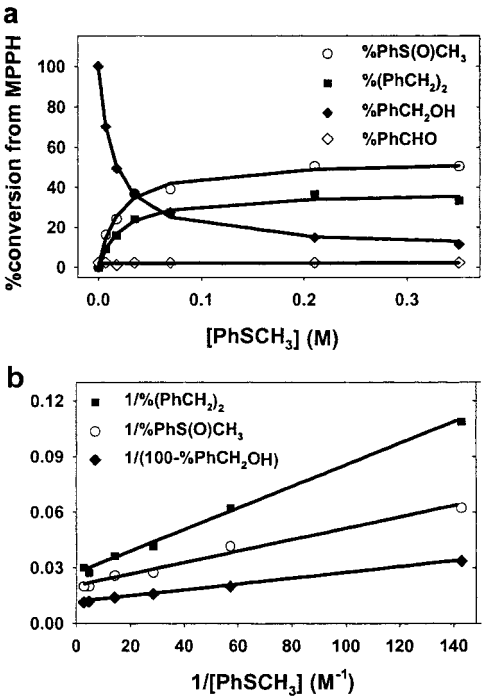

Figure 1. (a) Plot of the amounts of products formed relative to MPPH in the reactions of **1** and 10 equiv of MPPH as a function of $PhSCH_3$ concentration. (b) Double reciprocal plots showing the correlation of product formation with thioanisole concentration. The percent conversion values were corrected for the 13% impurity of tertiary alcohol present in the MPPH oxidant.

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(19) As shown in Scheme 2, the Fe(II)TPA complex can re-enter the catalytic cycle by reaction with MPPH to afford the Fe(III)TPA catalyst and the benzyl radical. Indeed, the control experiment with 7 mM $[Fe(TPA)(CH_3CN)_2]^{2+}$ and one equiv MPPH via syringe pumping under Ar afforded 0.46 equiv benzyl alcohol, 0.17 equiv bibenzyl, and 0.06 equiv benzaldehyde, all of which accounted for all the benzyl radicals generated during the oxidation of Fe(II) to Fe(III).

Table 2. Reactions of $[FeX_2((TPA)]^+$ (X = Br, **2**; Cl, **3**) with One Equivalent of MPPH[a]

entry	complex/trap	$PhCH_2Br$	$PhCH_2Cl$	PhCHO	PhS(O)Me
1	**2**	0.83(2)		0.03(1)	
2	**2**/air	0.34(1)		0.50(1)	
3	**2**/350 mM PhSMe	0.78(2)		0.02(1)	0.01(1)
4	**3**		0.73(1)	0.03(1)	
5	**3**/35 mM $CBrCl_3$	0.12(6)	0.59(2)	0.01(1)	
6	**3**/140 mM $CBrCl_3$	0.26(3)	0.48(1)	0.01(1)	
7	**3**/350 mM $CBrCl_3$	0.35(2)	0.36(6)	trace	

[a] See Experimental Section for reaction conditions. All reactions were run under Ar unless otherwise indicated. Yields derive from data obtained from at least three runs and are not corrected for the approximately 13% tertiary alcohol impurity present in the preparation of MPPH.

The oxidizing potential of the Fe(IV)═O species was further probed with substrates incapable of coordinating to the metal. Neither cyclohexane nor cyclooctane was hydroxylated (Table 1, entries 2 and 3). However, we observed some epoxidation of cyclooctene, 0.4 equiv of epoxide in the absence of any trap and 1.0 equiv in the presence of 500 equiv $CBrCl_3$ (Table 1, entries 12 and 13). The negligible formation of benzaldehyde shows that little O_2 is present in the reaction and autoxidation is not responsible for the small but significant increase of the epoxide product in the presence of a radical trap. Instead, these results demonstrate that alkene epoxidation can be effected by this nonheme Fe(IV)═O species, albeit rather inefficiently. The low epoxidation yield, in comparison to that for thioanisole oxidation, may result from the fact that alkenes are more difficult to oxidize than dialkyl sulfides. However, we have found that *intramolecular* hydroxylation of a pendant aryl group of a Fe(6-Ph-TPA) complex by the corresponding Fe(IV)═O species can occur facilely,[16] an oxidation comparable in difficulty to epoxidation. Thus, it seems likely that the [Fe(IV)(TPA)═O] species may have the oxidizing power to epoxidize alkenes, but the lack of a mechanism to bring it into close proximity with the Fe(IV)═O moiety when the latter is formed may significantly hamper efficient oxygen atom transfer to the alkene.

In parallel with the studies of the reaction of **1** and MPPH, we also investigated the reactions of $[FeBr_2(TPA)](ClO_4)$ (**2**) and $[FeCl_2(TPA)](ClO_4)$ (**3**) with one equivalent of MPPH (Table 2). These complexes were shown previously to carry out the stoichiometric halogenation of cyclohexane with 1 equiv ^{t}BuOOH as oxidant.[11] The halogenating species at that time was also incorrectly ascribed to an [X−Fe(V)═O] species derived from the heterolysis of a putative [X−Fe(III)−OOR] intermediate (X = Br, Cl). With the probe MPPH, MacFaul et al. subsequently showed that this reaction must involve O−O homolysis, as with **1**, and proposed that the halogenated product resulted from the reaction of freely diffusing alkyl radicals with the starting Fe(III) halide complex.[14] However, this earlier study was carried out in excess ROOH added all at once, conditions that lead to the in situ generation of O_2. With the subsequent demonstration that alkyl radicals can indeed react with Fe(IV)═O species in the absence of O_2,[15] we decided to re-examine the reaction of **2** and MPPH, but with a 1:1 stoichiometry and syringe pumping, so that in situ formation of O_2 was minimized. Under these conditions, only 0.03 equiv benzaldehyde was observed, and the only other product was 0.83 equiv benzyl bromide (Table 2, entry 1). With the 13% impurity of tertiary alcohol in the MPPH preparation, all the benzyl radicals that could be formed in the reaction are accounted for. This result demonstrates that MPPH is essentially quantitatively converted to its alkoxy radical via O−O bond homolysis, as observed in the case of **1** + MPPH (Table 1, entries 1−3). In support, the same reaction carried out in air afforded 0.34 equiv benzyl bromide and 0.50 equiv benzaldehyde (Table 2, entry 2), showing that O_2 can trap some of the benzyl radicals formed in the reaction.

Analogous studies with $[FeCl_2(TPA)](ClO_4)$ (**3**) confirm the observations made with **2**. The reaction of **3** and 1 equiv MPPH afforded 0.73 equiv benzyl chloride in the absence of any trapping agent (Table 2, entry 4). When the reaction was repeated in the presence of the trap $CBrCl_3$, the yield of benzyl chloride formed diminished with the addition of increasing amounts of $CBrCl_3$ (Table 2, entries 5−7). Concomitantly, the amount of benzyl bromide observed increased, showing that $CBrCl_3$ can compete for the nascent benzyl radical.[21]

We propose a mechanism analogous to that proposed for **1** + MPPH. MPPH displaces one of the halide ligands to form an X−Fe(III)−OOR intermediate (X = Br or Cl), which undergoes O−O bond homolysis. The alkoxy radical thus formed decomposes via β-scission to form acetone and benzyl radical, which then reacts with the high valent iron−oxo species. But the reaction of MPPH with **2** or **3** differs from that with **1** in some respects. Unlike for **1**, the benzyl radical is trapped by the corresponding Br−Fe(IV)═O or Cl−Fe(IV)═O intermediate not by forming a C−O bond but by forming a C−Br or C−Cl bond instead. Secondly, the addition of 50 equiv thioanisole to the reaction of **2** and MPPH led to the formation of only 0.01 equiv $PhS(O)CH_3$ and had little effect on the yield of benzyl bromide (Table 2, entry 3), in contrast to the significant sulfoxidation of thioanisole observed for **1** (Table 1, entry 5). This comparison shows that thioanisole cannot effectively compete with the benzyl radical for the trapping of the high valent intermediate in the case of **2**/MPPH. In line with observations discussed in the previous section, we attribute the inefficiency of sulfoxidation by **2**/MPPH to the lack of a binding site for thioanisole on the iron center, as thioanisole must displace the remaining bromide ligand to gain access to the iron center.

Our proposed mechanism for the reaction of $[FeX_2(TPA)]^+$ and MPPH differs from that suggested by Ingold and coworkers[14] with respect to the nature of the species involved in the halogenation. They proposed that alkyl halide formed by the reaction of freely diffusing alkyl radicals with the starting Fe(III) complex. However, it is important to point out that the reactions were investigated under different conditions. Ingold and co-workers investigated the reaction with a 140-fold excess MPPH, where all the alkyl hydroperoxide was added all at once. Only 0.4 equiv benzyl halide and 6−7 equiv PhCHO were observed, consistent with the fact that such conditions promote radical chain propagation and the in situ formation of O_2 from alkylperoxyl radicals. Indeed, the total amount of products derived from benzyl radical accounted for less than 15% of the MPPH added. In contrast, we studied the reaction of stoichiometric amounts of catalyst and alkyl hydroperoxide, where the latter was delivered by syringe pump over a 45 min period in order to minimize O_2 formation. Under these conditions, only a very small amount of PhCHO (0.03 equiv) was formed, and almost all of the MPPH was converted to benzyl halide (0.83

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(21) Although some of the benzyl chloride could be also generated by the trapping of benzyl radicals by $CBrCl_3$, the majority of the benzyl chloride observed comes from the Cl−Fe(III)−OOR species, as evidenced by the lower amounts of $PhCH_2Cl$ formed with increasing $CBrCl_3$ added.

equiv for **2** and 0.73 equiv for **3**). The two mechanistic conclusions are not necessarily incompatible. Our study focused on the first turnover, while the Ingold study involved multiple turnovers. Under the latter conditions, the nature of the iron complex is ambiguous, as it must change over the course of the reaction once the halide transfer occurs.

In summary, the reactions of Fe(TPA) complexes with MPPH delivered by syringe pump under rigorously anaerobic conditions afforded nearly quantitative conversion of MPPH to products derived from benzyl radical. As expected from the work of Ingold,[17] there is unequivocal evidence for O−O bond homolysis, leading to the formation of benzyl radicals and a high valent iron(IV)−oxo species. The high valent species can react with the benzyl radical to form benzyl alcohol, in the case of **1**, or benzyl halide, in the cases of **2** and **3**. Under appropriate conditions, the high valent species can also effect two-electron oxidations of added substrates, such as thioanisole, cyclohexanol, and cyclooctene. This oxidation occurs efficiently provided the substrate is in close proximity with the metal center so that it can intercept the high valent iron−oxo center as soon as it forms. This requirement for close juxtaposition rationalizes the hydroxylation of the pendant phenyl moiety in the reaction of $[Fe(6\text{-}PhTPA)(CH_3CN)_2]^{2+}$ with ROOH [16] and may also apply to the mechanisms of a number of mononuclear nonheme iron enzymes that are proposed to utilize an Fe(IV)═O oxidant.[6]

Experimental Section

Materials and Synthesis. All chemicals were purchased from Aldrich and used as received, unless otherwise noted. Thioanisole, $CBrCl_3$, cyclohexane, and cyclooctane were purified by silica gel chromatography (Aldrich 70−230 mesh) just before the reaction to remove oxidized impurities. Cyclooctene was purified by distillation. Acetonitrile (HPLC grade) was distilled from P_2O_5 prior to use. $^tBuO^{18}OH$ (96% atom % ^{18}O) was synthesized by Dr. E. H. Appelman of Argonne National Laboratory.[18] 2-Methyl-1-phenyl-2-propyl hydroperoxide (MPPH) was synthesized according to published procedures[13] and included 13% 2-methyl-1-phenyl-2-propyl alcohol as an impurity. $[Fe_2O(TPA)_2(H_2O)_2](ClO_4)_4$ (**1**), $[FeBr_2(TPA)](ClO_4)$ (**2**), $[FeCl_2(TPA)](ClO_4)$ (**3**), and $[Fe(TPA)(CH_3CN)_2](ClO_4)_2$ were prepared as previously reported.[11,18,22] ***Caution: Perchlorate salts with organic ligands are potentially explosive and should be handled with care.***

Instrumentation. Product analyses were performed using a Perkin−Elmer Autosystem Gas Chromatograph equipped with a capillary column (AT-1701, Alltech) and a flame-ionization detector. GC mass spectral measurements were obtained using a Finnigan MAT 95 with 4% NH_3/CH_4 as a reagent gas for CI-GC MS. ^1H NMR spectra were recorded on a Varian Unity-300 and referenced to solvent acetonitrile protons (1.94 ppm).

Oxidation Reactions. For the reactions with **1**, the appropriate amounts of **1**, substrate, and/or trap were dissolved in 2.7 mL of CH_3CN, and the solution was degassed by four freeze−pump−thaw cycles. Then 0.3 mL of a similarly degassed 70 mM ROOH solution in CH_3CN was added to the vigorously stirred solution of catalyst by syringe pump over a 30 min period at 25 °C. The following final concentrations were used for the various components of the reaction as required: 0.7 mM **1**, 7.0 mM MPPH, 700 mM cyclohexane, cyclooctane, cyclohexanol, or cyclooctene. Analogous reactions with 7 mM **2** or **3** were carried out over a 45 min period with 7 mM MPPH. Various amounts of $PhSCH_3$ or $CBrCl_3$ were added as indicated. All product solutions were stirred for an additional 5 min under argon at 25 °C, with chlorobenzene then added at this point as an internal standard. The solution was passed through a silica gel (Aldrich 70−230 mesh) column to remove the catalyst. The organic products were eluted by CH_3CN or CH_3OH (0.6 mL x 5) and analyzed by gas chromatography. Retention times for product peaks were compared directly to those of authentic compounds and confirmed by GC MS.

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