Biomimetic oxidation studies. 7. Alkane functionalization with a MMO structural model, $[Fe_2O(OAc)(tris((1\text{-methylimidazol-2-yl})methyl)amine)_2]^{3+}$, in the presence of *t*-butyl hydroperoxide and oxygen gas[☆]

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A biomimetic structural model of the active site of methane monooxygenase enzyme, $[Fe_2O(OAc)(tris((1\text{-methylimidazol})\text{-}2\text{-methyl})amine_2]^{3+}$, 1, has been shown to functionalize cyclohexane, toluene, adamantane, propane, and ethane in the presence of *t*-butyl hydroperoxide and oxygen gas. A mechanism is proposed to account for these results which implicates an alkyl hydroperoxide intermediate to the alcohol, ketone, and aldehyde products in an oxygen gas dependent reaction, while aldehyde and ketone products can also be formed from the further oxidation of the alcohols in an oxygen gas independent reaction.

Keywords: Biomimetic oxidation; alkane functionalization; MMO models; alkyl hydroperoxide intermediates

Recent studies on methane monooxygenase enzymes (MMO) have shown that the active site has a diiron μ-oxo or a μ-hydroxo structure [$Fe_2(\mu\text{-O})$ or $Fe_2(\mu\text{-OH})$], a possible μ-carboxylate anion, and that histidine appears to be a terminal ligand [2,3]. These enzymes are active in the conversion of a variety of alkanes, including methane, primarily to their respective alcohols [4]. Like cytochrome P450, MMO lacks substrate specificity in the alkanes it functionalizes, i.e., methane to adamantane [4c]. Interestingly, this type of diiron μ-oxo (μ-hydroxo) structure has also been proposed for other iron containing biomolecules such as hemerythrin [5], purple acid phosphatase [6], and ribonucleotide reductase [7].

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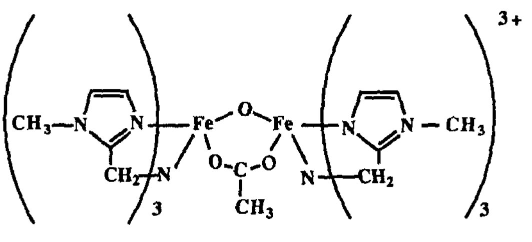
While the mechanistic details for alkane functionalization are still to be elucidated for MMO, an $[(L^{\cdot+})Fe^{IV}{=}O]$ intermediate has been implicated for both P450 porphyrin [8a] and MMO non-porphyrin [8b] biomimetic systems. In 1988, we demonstrated that FeOFe biomimetic active site model structures with μ-carboxylate anions were capable of functionalizing hydrocarbons to their corresponding alcohols, ketones, and aldehydes in the presence of *t*-butyl hydroperoxide (TBHP) [1a]. However, this previously reported biomimetic alkane functionalization study, and others that were published subsequently with non-porphyrin Fe complexes and TBHP, have not clearly specified the mechanistic details concerning the active Fe oxidant, the identity of any definitive oxidized organic intermediates that may provide alcohols, ketones, or aldehydes, and the critical role of oxygen gas during the functionalization reaction[#1] [1a].

In this communication, we report on pertinent mechanistic aspects of the C–H bond functionalization reaction of several hydrocarbons by a new MMO active site analogue, $[Fe_2O(OAc)(tmima)_2](ClO_4)_3$, **1**,(tmima = tris[((1-methylimidazol-2-yl)methyl) amine]) with TBHP in the presence of oxygen gas (O_2) using acetonitrile (CH_3CN) as the solvent. Moreover, compound **1** represents the first structurally characterized μ-oxo–μ-carboxylato bridged FeOFe complex containing biologically relevant polyimidazole ligands that shows C–H functionalization activity[#2] [1] (scheme 1).

Table 1 provides all the results of these alkane functionalization reactions and includes product identification (>95%) and mmol of product formed/mmol of complex **1**. Cyclohexane provided two major oxidation products, cyclohexanol (CyOH) and cyclohexanone (CyONE), and studies at different concentrations of cyclohexane indicate that as the concentration of cyclohexane is lowered, both the mmol of product/mmol of **1** and the CyOH/CyONE ratio similarly decrease



Scheme 1.

[#1] Other representative studies on Fe, Co, Mn, Ru, and Co complexes / TBHP systems are given in refs. [9a–e], respectively.

[#2] Crystal data for 1 : $C_{38}H_{54}Cl_3Fe_2N_{17}O_{15}$, triclinic, P 1, $a = 15.420(5)$ Å, $b = 16.005(5)$ Å, $c = 12.060(5)$ Å, $\alpha = 100.07(3)°$, $\beta = 108.11(3)°$, $\gamma = 102.35(3)°$, $V = 2668.4$ Å^3, $Z = 2$, $D_c = 1.50$ g/cm^3, $\mu = 7.7$ cm^{-1}, $R = 8.1\%$. The oxo bridge Fe–O lengths are 1.781(4) Å and 1.785(4) Å. The Fe–Fe separation is 3.314(1) Å and the FeOFe angle is 128.7(2)°. We have also recently isolated and characterized the μ-oxo bridged complex, $[Fe_2O(H_2O)_2(tmima)_2](ClO_4)_3$, via X-ray crystallography.

Table 1
Oxidation of alkanes with $[Fe_2O(OAc)(tmima)_2]^{3+}$ and TBHP in the presence of oxygen gas[a]

Substrate	Products	mmol product/ mmol $[Fe_2O(OAc)(tmima)_2]^{3+}$
cyclohexane	cyclohexanol	18
	cyclohexanone	21
cyclohexanol	cyclohexanone	108
toluene	benzyl alcohol	5
	benzaldehyde	16
benzyl alcohol	benzaldehyde	116
adamantane[b]	1-adamantanol	4
	2-adamantanol	1
	2-adamantanone	1
propane[c]	propionaldehyde	1
	acetone	6
	2-propanol	3
	1-propanol	1
ethane[c]	ethanol	1
	acetaldehyde	2

[a] Gas chromatographic (GC) analyses were performed on a Hewlett-Packard Model 5880A instrument with FI detection and a 30 m × 0.25 mmol DB-17 (J&W Scientific) capillary column, while GC-MS analyses were performed on a HP 5971 MSD instrument (EIMS) that was computer controlled and has a DB-5 capillary column. Typical reaction conditions for the oxidation studies were as follows: $[Fe_2(tmima)_2O(OAc)](ClO_4)_3$ (5.4 mg, 5×10^{-3} mmol), and substrate (4.5 mmol) were dissolved in 5 ml of CH_3CN and stirred vigorously while TBHP (0.75 mmol) was added at room temperature in the presence of oxygen gas. The complete consumption of TBHP, in general, required less than 24 h. To the final solutions were added an internal standard (cyclopentanone) and the products quantified by GC and GC-MS analyses.

[b] When adamantane was the substrate, 10 mg (0.075 mmol) was used.

[c] The propane and ethane reactions were run in a Parr Kinetic apparatus at 90 and 250 psi, respectively.

(table 2). When 900 mM of cyclohexane is used, the ratio of CyOH/CyONE was ~ 0.9 (24 h). Over the course of this reaction (24 h), the ratio of CyOH/CyONE remains ~ 1.0 suggesting that the alcohol and ketone are produced from a common intermediate oxidation product. However, as the concentration of cyclohexane is lowered, for example to 150 mM, the ratio of CyOH/CyONE drops to 0.5 indicating that CyOH is also oxidized further to CyONE in a subsequent oxidation process.

Table 2
Effect of concentration of cyclohexane on the amount of products and the CyOH/CyONE ratio[a]

Cyclohexane (mM)	mmol/mmol Fe CyOH (CyONE)	CyOH/CyONE ratio
150	3.3 (6.6)	0.50
300	6.7(11.3)	0.60
600	14.0(19.7)	0.70
900	22.1(27.5)	0.80
1200	26.1(31.8)	0.82

[a] See table 1 for conditions.

Increased amounts of CyONE were also found when additional equivalents of TBHP were added. For example, if a second 150 mM of TBHP was added after 24 h, then the mmol of products/mmol of **1** increased from 50 to 95; however, the relative amount of CyOH/CyONE changed from 0.8 to 0.4.

In an independent reaction, 900 mmol of CyOH was reacted with complex **1**, under normal conditions, to establish the relative rate and efficiency for alcohol oxidation. We have found that the reaction is initially very fast with 30 mmol of CyONE/mmol of **1** resulting in the first 5 min. The reaction slows down considerably after 24 h giving 100 mmol of CyONE/mmol of **1**. We considered the possibility that the drop in the rate after the first 5 min may be a consequence of competitive inhibition; however, incubation of solutions before additions of TBHP, with CyOH or a mixture of CyOH/CyONE, gave similar results. As well, trace amounts ($<1\%$) of diols (1,2-, 1,3-, and 1,4-cyclohexanediols) were also found as was their corresponding difunctional alcohol–ketone derivatives by GC/MS analysis, while no diones were detected. *It is also important to note that no coupling products, i.e., t-butylperoxycyclohexane or di-t-butyl peroxide, were detected by GC/MS analysis or by* ^{1}*H NMR spectroscopy.*

The alkane functionalization reactions were found to be dependent on complex **1**, TBHP, and oxygen gas concentrations. *When solutions were thoroughly flushed with argon gas throughout the course of the reactions, the functionalization reactions were found to be totally inhibited.* In addition, at 900 mM of cyclohexane, the concentration of oxygen gas was found to have a direct effect on the CyOH/CyONE ratio, with the amount of CyONE staying constant, but the CyOH decreasing with increased oxygen gas concentrations (table 3). For example, at 250 psi of O_2, the relative amount of CyONE was four times that of CyOH. Significantly, under these reaction conditions, the overall mmol of products/mmol of **1** did not increase appreciably, just the CyOH/CyONE ratios changed.

Since the cyclohexane oxidation reaction (900 mM) with TBHP was found to give an approximately constant ratio (~ 1.0) of CyOH/CyONE, we thought that cyclohexyl hydroperoxide (CyOOH) might be an intermediate to both products as previously shown with other transition-metal complex initiated TBHP oxidations

Table 3
Effect of oxygen gas pressure on the amount of product and the CyOH/CyONE ratio[a]

Oxygen (psi)	mmol/mmol Fe CyOH (CyONE)	CyOH/CyONE ratio
0[b]	0 (0)	0
air (~ 3)	22(28)	0.80
50	22(39)	0.56
125	11(26)	0.31
250	8(31)	0.26

[a] See table 1 for reaction conditions.
[b] Continuous argon purge.

[10f]. It is interesting to note that in our studies with complex **1** and H_2O_2, CyOOH was found to form from the reaction of oxygen gas with a cyclohexyl radical [1e]. Consistent with this fact is that oxygen gas is known to react with alkyl radicals at a rate near 10^9 [11]. The CyOOH can subsequently undergo the well known transition-metal complex catalyzed decomposition to give a mixture of CyOH and CyONE in the presence of complex **1** [10f]. In fact, an indication that CyOOH was being formed stemmed from the analysis of a 2 h cyclohexane reaction that provided a CyOH/CyONE ratio of 1.2, which was then treated with an isopropyl alcohol solution of NaI to give a CyOH/CyONE ratio of 1.5; NaI predominantly reduces CyOOH to CyOH (CyOH/CyONE = 6) [1e].

To test further whether the cyclohexane reaction was proceeding through a CyOOH intermediate, we reacted CyOOH with **1** in the presence of TBHP. In the absence of TBHP in the CH_3CN solution, CyOOH decomposed very slowly requiring four days to give an alcohol to ketone ratio of 0.63. However, in the presence of TBHP, the reaction was observed to be faster requiring less than 24 h to give a CyOH/CyONE ratio of 0.25! These ratios are lower than the ~ 0.9 ratio we found starting with 900 mM of cyclohexane and reflects the influence of the TBHP and cyclohexane concentrations on the fate of cyclohexyl hydroperoxide and cyclohexanol.

Moreover, the oxidation of CyOH to CyONE with TBHP and 1 was not oxygen gas dependent. If these reaction solutions of CyOH were continually flushed with argon gas, then the normal (~ 108 NOT) mmol of CyONE were still obtained. Since oxygen gas pressures affect the CyOH more than the CyONE concentrations, it appears that the precursor to the alcohol, CyOOH or an alkyperoxy Fe complex, react at higher O_2 pressures to give more CyONE. Additionally, we have determined the primary kinetic isotope effect ($k_H/k_D = C_{12}H_{12}/C_{12}D_{12}$) and have found that the overall ratio was 9.4. However, the k_H/k_D ratio for the CyOH formation was 5, while the k_H/k_D ratio for CyONE formation was 22.5. This result suggests that a significant amount of the CyONE is originating from CyOH, which would necessitate at least two C–H bond breaking processes.

Oxidation reactions with toluene provided 16 mmol of benzaldehyde (PhCHO) and 5 mmol of benzyl alcohol ($PhCH_2OH$)/mmol of complex **1**. These results provide a relative ratio of $PhCH_2OH$/PhCHO of 0.29. Plots of the PhCHO and $PhCH_2OH$ formed over a 10 h period indicate that the concentration of aldehyde is continually increasing, while that of the alcohol plateaus. The smaller $PhCH_2OH$/PhCHO ratio results then because $PhCH_2OH$ is more easily oxidized than toluene. In fact, the direct oxidation of $PhCH_2OH$ is very efficient giving 116 mmol of PhCHO/mmol of **1** after 6 h. Since no *o, m, or p*-cresols were detected, then hydroxyl radical chemistry does not appear to be a factor in these reactions [1e].

Further oxidation studies with adamantane (20 mM) provided 1-adamantanol (4.1), 2-adamantanol (0.5) and 2-adamantanone (0.7 mmol/mmol of **1**). The average mass balance for these reactions was only 85%, suggesting that some secondary oxidation processes do occur. The normalized C_3/C_2 values were found to be 10.5, consistent with a reaction proceeding through free radical intermediates [1e,f].

Several gases, propane and ethane, were also functionalized with **1** and $TBHP/O_2$. Propane provided mostly acetone (a control experiment was run in the absence of propane to show that small amounts of acetone were formed from the decomposition of TBHP in the presence of **1**; this amount was subtracted from the acetone formed) and 2-propanol with smaller amounts of 1-propanol and propionaldehyde, while ethane provided mostly acetaldehyde and some ethanol (table 1).

The functionalization reactions do not appear to proceed via long chain free radical processes, since the free radical traps, 2,4,6-tri-*t*-butylphenol (TBP) and butylated hydroxy toluene (BHT), had no effect on the mmol of product formed. We also note that *no free radical coupling products*, such as *t*-butylperoxycyclohexane or di-*t*-butylperoxide, were detected as was observed by Que et al. using a mononuclear Fe complex with TBHP in CH_3CN under similar reaction conditions; it was also noted in the Que et al. paper that the Fe_2O analogue was catalytically inactive in C–H functionalization reactions [9a].

Current interest in the functionalization of alkanes to their oxidized products has focused on elucidating the structure of the active metal–oxo complex [8b]. Unfortunately, with complex **1**, it is very difficult to identify the active species using UV–vis spectroscopy, because the spectrum is dominated by the metal–oxo charge transfer bands. Nevertheless, we noticed a slight attenuation of the metal–oxo charge transfer bands during the course of the reaction. The ^1H NMR spectrum of **1** and TBHP shows the formation of *t*-butyl alcohol, while no mononuclear Fe complexes could be detected [8b]. We have also attempted to probe the structure of the intermediate Fe oxidation complex by low temperature EPR. Therefore, 6.8 mM of **1** with 20 mM of TBHP in acetonitrile were mixed in the absence of O_2 and the solution was then cooled rapidly to 77 K and the EPR spectrum recorded. We observe no ESR signal for a high valent iron complex and, in fact, if *t*-$BuO^{\cdot}$ was formed from TBHP we would have also detected it by ESR. Therefore, we conclude that in the reaction of **1** with excess TBHP, the LFeOFeL structure maintains its integrity; a result that is different from the mononuclear Fe complex, $[(L^{\cdot+})Fe{=}O]^{3+}$, thought to be formed from a LFeOFeL complex with H_2O_2 [8b]. It should be noted, however, that significant amounts of O_2 gas were formed during both the ESR and NMR anaerobic experiments in CD_3CN demonstrating the ability of the LFeOFeL complex to decompose TBHP to *t*-butyl alcohol and O_2 gas in the absence of alkane.

The mechanism we propose from our catalysis and spectroscopic results on the hydrocarbon functionalization reactions with complex **1** in the presence of TBHP/O_2, suggests that a putative $Fe^{IV}OFe^{IV}{=}O$ intermediate forms with concomitant formation of *t*-butyl alcohol (eqs. (1) and (2)) and initiates the following sequence of known reactions in the presence of an excess of hydrocarbon (no *t*-butylperoxycylohexane was detected by GC/MS analysis):

$$\mathrm{FeOFe} + t\text{-}\mathrm{BuOOH} \rightarrow \mathrm{FeOFe{-}\overset{H}{O}OBu}\text{-}t\,, \tag{1}$$

$$\mathrm{FeOFe{-}\overset{H}{O}OBu}\text{-}t \rightarrow \mathrm{FeOFe{=}O} + t\text{-}\mathrm{BuOH}\,, \tag{2}$$

$$\mathrm{FeOFe{=}O} + \mathrm{R{-}H} \xrightarrow{\text{initiation}} \mathrm{FeOFe{-}OH} + \mathrm{R}^{\cdot}\,, \tag{3}$$

$$\mathrm{R}^{\cdot} + \mathrm{O_2} \xrightarrow{\mathrm{R{-}H}} \mathrm{ROOH} + \mathrm{R}^{\cdot}\,, \tag{4}$$

$$\mathrm{FeOFe} + \mathrm{ROOH} \rightarrow \mathrm{FeOFe\overset{H}{O}OR}\,, \tag{5}$$

$$\mathrm{FeOFe\overset{H}{O}OR} \rightarrow \mathrm{R{-}OH} + \mathrm{R{=}O} + \mathrm{FeOFe}\,, \tag{6}$$

$$\mathrm{R{-}OH} + \mathrm{FeOFe{=}O} \rightarrow \mathrm{R{=}O} + \mathrm{Fe_2O} + \mathrm{H_2O}\,. \tag{7}$$

The $Fe^{IV}OFe^{IV}{=}O$ complex homolytically reacts with C–H bonds to form a carbon radical (eq. (3)) followed by rapid trapping with O_2 to form the alkyl hydroperoxide (eq. (4)). Complex **1** then catalyzes the decomposition of the alkyl hydroperoxide to alcohol, aldehyde, or ketone (eqs. (5) and (6)). The alcohol formed from the decomposition of the alkylperoxy–Fe complex can then be further oxidized to the ketone, without O_2 involvement (eq. (7)).

Eqs. (1), (2) and (5), (6) have been postulated to occur with other metal complexes [9e,12–14] and the O–O bond cleavage reaction, to form in this case the $Fe^{IV}OFe^{IV}{=}O$ species, has been postulated to occur by a heterolytic mechanism with TBHP [12]. Eq. (3) is well known from transition–metal complex oxidation chemistry [10g]. The critical role of O_2, in the air and from TBHP decomposition, is involved in trapping the carbon radical to form an alkyl hydroperoxide (eq. (4)) that decomposes with complex **1** to provide the alcohol, ketone, or aldehyde (eqs.

(5), (6)) [10e,f]. The further oxidation of alcohols to ketones and aldehydes is well known in both metallo-porphyrin and non-porphyrin mediated oxidation chemistry (eq. (7)) [10g].

Finally, what we wish to emphasize in this communication is that non-porphyrin biomimics of MMO with TBHP/O_2 as oxidants appear to react via mechanisms that are well-known in transition-metal oxidation chemistry, i.e., initiation of carbon free radical formation, trapping of the carbon radical with O_2 to form a alkyl hydroperoxide (autoxidation), alkyl hydroperoxide decomposition to alcohol, ketone, and aldehyde, and further facile oxidation of alcohols to aldehydes and ketones that are independent of the presence of O_2. The intermediate Fe oxidation complex that initiates carbon radical formation and further facile alcohol oxidation is postulated to be a $[Fe^{IV}OFe^{IV}{=}O]$ species. Future studies will focus on the identification of intermediate iron oxidants, mechanistic aspects, and alkane functionalization reactions with silica-supported active site models.

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