Homogeneous catalysis

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Catalytic Epoxidation and 1,2-Dihydroxylation of Olefins with Bispidine–Iron(II)/H_2O_2 Systems**

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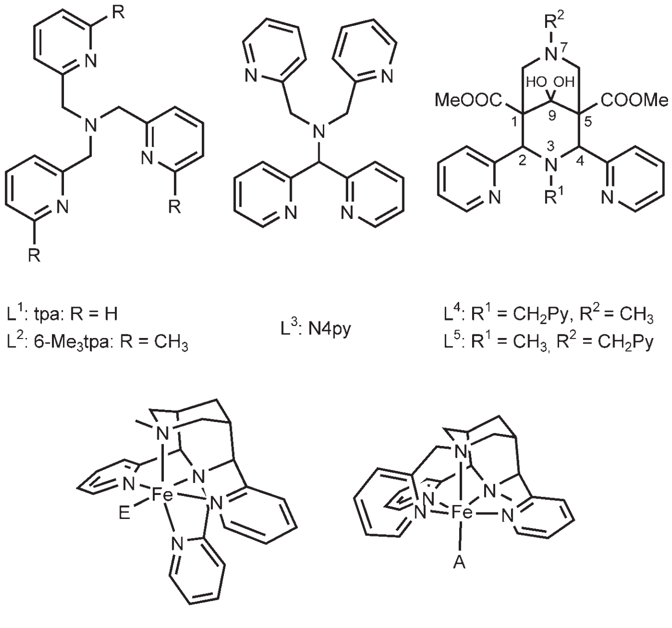
Non-heme iron-catalyzed oxidation of hydrocarbons has attracted considerable attention in the last decade.[1–4] Mononuclear Fe^{III}–peroxide and –hydroperoxide species are believed to be involved in biological oxygen activation in systems such as those which involve the heme iron enzyme cytochrome P450,[5,6] the non-heme iron antitumor drug bleomycin,[7,8] and the non-heme Rieske dioxygenases.[9–11] Hetero- or homolytic O–O bond cleavage of the end-on-bound Fe^{III}–hydroperoxide complexes yield formally the corresponding {Fe^{V}=O} or {Fe^{IV}=O} compounds, respectively, which are assumed to be the catalytically active species. Homolytic cleavage of the O–O bond also yields oxygen-centered radicals, which may give rise to typical radical reactions. For a number of synthetic, low-molecular-weight model systems with tetra- and pentadentate amine/pyridine-containing ligands there is unambiguous spectroscopic and/or structural evidence for end-on {Fe^{III}-OOH}, side-on {Fe^{III}-(O_2)}, and {Fe^{IV}=O} intermediates,[4,12–19] but evidence for {Fe^{V}=O} complexes is more circumstantial.

The various Fe^{III}–peroxide complexes are generally obtained from the Fe^{II} precursors by oxidation with H_2O_2,[12–14] while oxygen transfer from oxo transfer agents such as peracids or iodosylbenzene is used to produce the ferryl products.[15–19] Direct formation of {Fe^{IV}=O} complexes from the Fe^{II} precursor, using H_2O_2, without formation of the usual Fe^{III} intermediates, is another possible pathway.[20,21] On the basis of spectroscopic and theoretical investigations of low-molecular-weight model complexes, as well as studies of the corresponding reactivities, mechanisms were proposed for the iron-catalyzed olefin oxidation, and pathways for pentadentate ligands as well as strong- and weak-field tetradentate ligands were proposed.[3,4] Systems which were studied in detail include tetradentate (L^1, L^2) and pentadentate derivatives (L^3) of tris(2-pyridylmethyl)amine (tpa). These are shown Scheme 1, together with the two isomeric pentadentate bispidine ligands L^4 and L^5 discussed herein.



$[(L^4)FeX]^{n+}$, **1** $[(L^5)FeX]^{n+}$, **2**

Scheme 1. Ligands L^1–L^5 as well as two isomeric Fe^{II} complexes of L^4 and L^5 (substituents on the bispidine backbone are omitted); Py = pyridyl,; X = MeCN, MeOH; A = axial X; E = equatorial X.

A wide variety of bispidine ligands are relatively easy to prepare in respectable yields.[22–25] The two isomeric Fe^{II} complexes of the ligands L^4 and L^5 (**1** and **2**, respectively, Scheme 1) have been structurally, spectroscopically, and electrochemically characterized.[22] In **1** the coligand X is coordinated *trans* to N3 (equatorial, E) through a short and strong Fe^{II}–X bond, while in **2** the X ligand is positioned *trans* to N7 (axial, A) through a long and weak Fe^{II}–X bond.[12,22] The structural difference between the two isomers is manifested in their reactions with H_2O_2 in MeOH at −40 °C, which afford spectroscopically distinct iron(III) complexes.[12] The low-spin end-on hydroperoxo- and high-spin side-on peroxo complexes differ in terms of their thermal stability, with that of L^4 being among the most stable species of this class of compounds.[12] Herein we compare the catalytic capabilities of the two $[(L^n)Fe^{II}(X)]^{2+}$ ($n = 4$ (**1**), 5 (**2**); X = MeCN, MeOH) complexes in the reaction with cyclooctene as the substrate and H_2O_2 as the oxidant.

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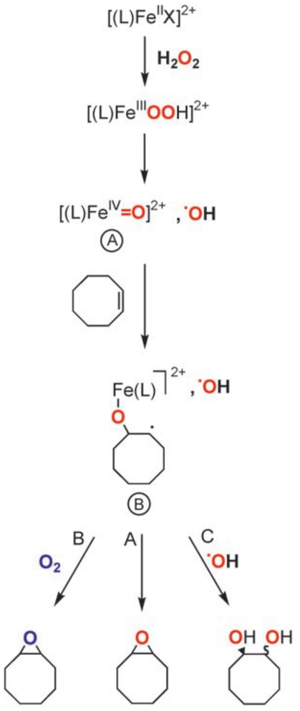
Table 1 lists the product distributions observed in the $[(L^n)Fe^{II}(X)]^{2+}/H_2O_2$/cyclooctene experiments under different reaction conditions. To facilitate comparison with published data[3] the experimental conditions for the oxidation reactions were chosen to resemble those with L^1–L^3 (MeCN, 25.0 °C, catalyst/H_2O_2/substrate = 1:10(100):1000; 30 min reaction time; see *Experimental Section*). Complex **1** yields only about 1 TON (TON = 10 μmol product per μmol {Fe}) of oxidation product in MeCN under aerobic conditions (primarily epoxide; Table 1, entry 4 a), a reactivity similar to that of the iron–L^3 complex (Table 1, entry 3). In contrast, **2** affords 5 TON of epoxide exclusively under aerobic conditions (Table 1, entry 5 a). At first glance, this comparison might suggest that **1** is a rather poor catalyst, but further experiments show that the picture is more complicated. When the reactions are carried out over 6 h, the product yields increase to about 7 TON with **1** (Table 1, entry 4 d) and 8 TON for **2** (Table 1, entry 5 d). Data points obtained at intermediate times indicate that, whereas most of the products are formed in the experiments with **2** within the first half hour, the reactions with **1** take about seven times longer to achieve a comparable product yield (Table 1, entries 4 a–d and 5 a–d). Thus, by this criterion, **1** is almost as effective a catalyst as **2**, but is much slower in activating the H_2O_2 oxidant. When the reactions are carried out for 30 minutes under argon, the product yields decrease by about 20 % and 60 %, respectively (Table 1, entries 4 e and 5 e), thus suggesting a greater susceptibility of **2** than **1** to autoxidation.

Table 1: Product distribution (D = diol, E = epoxide).

Entry	Ligand	Experimental conditions[a]	D + E[d,e]	D/E
1	L^1	[b]	7.4	1.2:1
2	L^2	[b]	5.6	7:1
3	L^3	[b]	0.6	0:1
4a	L^4	air (0.5 h)	1.2	0.1:1
4b	L^4	air (1.5 h)	3.3	0.1:1
4c	L^4	air (3.5 h)	6.0	< 0.1:1
4d	L^4	air (6 h)	6.8	< 0.1:1
4e	L^4	argon (0.5 h)	1.0	0.2:1
4f	L^4	PhIO[c], air	1.1	0:1
4g	L^4	PhIO[c], argon	0.6	0:1
5a	L^5	air (0.5 h)	5	0:1
5b	L^5	air (1.5 h)	6.3	0:1
5c	L^5	air (3.5 h)	7.3	0:1
5d	L^5	air (6 h)	8.1	0:1
5e	L^5	argon (0.5 h)	2.0	1:1
5f	L^5	PhIO[c], air	1	0:1
5g	L^5	PhIO[c], argon	0.4	0:1
5h	L^5	MeOH, air	1.9	0:1
5i	L^5	MeOH, argon	1.7	0:1

[a] 1000 equiv cyclooctene, 10 equiv H_2O_2, reaction time 0.5 h under air in MeCN at 298 K unless otherwise noted. [b] Ambient temperature. [c] Oxidant: 1 equiv of $\{Fe^{IV}{=}O\}$; no H_2O_2 used (stoichiometric reaction). [d] TON, 10 = max;[19] the error limit for all data is ca. ± 5 % (relative) for TON. [e] Diol is exclusively *cis* for L^1 and L^2 and a mixture of *cis* and *trans* for L^4 and L^5, when observed.

A mechanism is proposed in Scheme 2 to rationalize the above observations, in which an $\{Fe^{III}\text{-}OOH\}$ intermediate is formed initially and then undergoes O–O bond homolysis to form an $\{Fe^{IV}{=}O\}$ oxidant and $HO^{\bullet}$, as proposed for the FeL^3-catalyzed hydroxylation of alkanes.[26] The difference in catalyst efficiency between **1** and **2** can be associated with their different structural and electronic properties (Scheme 1). The constraints of the bispidine ligand architecture dictate that the HOO ligand in **1** is *trans* to N3 (that is, in a similar configuration as in the complex with L^3),[26] while that in **2** is *trans* to N7. As noted in a number of other metal complexes of the isomeric ligands L^4 and L^5, the two tertiary amine donors differ in their distances to the metal center.[22,24,25] This probably is related to the π-bonding properties of the two equatorially coordinated pyridine groups and gives rise to a stronger Fe–OOH interaction (π-back-bonding) for the $[(L^4)Fe^{III}OOH]$ intermediate.[18]



Scheme 2. Proposed mechanisms for the formation of the epoxide and diol. See text for details.

To ascertain the involvement of ferryl species, the $\{Fe^{IV}{=}O\}$ complexes of the two ligands L^4 and L^5 were synthesized in situ and their reactivities towards cyclooctene were then compared in the absence of other potential oxidizing species. These complexes were independently prepared by following the method for the synthesis of $[(L^3)Fe^{IV}{=}O]^{2+}$,[17] by addition of iodosylbenzene to **1** and **2** in MeCN. Formation of the corresponding ferryl complexes was indicated by the appearance of the expected electronic transition in the NIR region ($\varepsilon^{L^4}_{728nm} = 400\,\text{M}^{-1}\,\text{cm}^{-1}$, $\varepsilon^{L^5}_{728nm} = 380\,\text{M}^{-1}\,\text{cm}^{-1}$, Figure 1), characteristic for this class of complexes.[4] Both $[(L)Fe^{IV}{=}O]^{2+}$ complexes were generated by addition of PhIO in MeCN and react readily with cyclooctene to afford cyclooctene oxide. Under argon $[(L^4)Fe^{IV}{=}O]^{2+}$ forms 0.6 TON, and

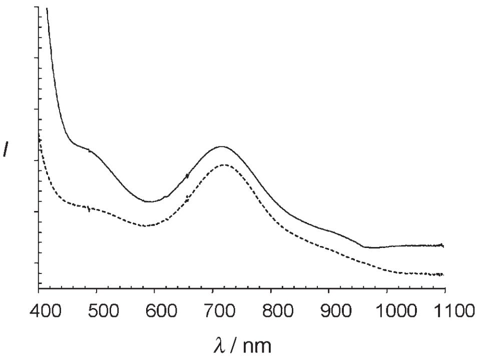


Figure 1. UV/Vis-NIR spectra of the ferryl complexes $[Fe{=}O(L^5)]^{2+}$ (——) and $[Fe{=}O(L^4)]^{2+}$ (-----).

$[(L^5)Fe^{IV}{=}O]^{2+}$ 0.4 TON of epoxide, respectively (Table 1, entries 4g and 5g), thus showing that both ferryl complexes are capable of transferring their oxo atom to cyclooctene, as proposed in Scheme 2. The relative efficiencies of this oxo transfer are mirrored by the yields of the cyclooctene oxidation products obtained with H_2O_2 under argon. In air, the epoxide yields increase by 90% to 1.1 TON with L^4 (Table 1, entry 4f) and 150% to 1.0 TON with L^5 (Table 1, entry 5f), thus emphasizing some difference in the susceptibilities of the two systems to radical autoxidation. Taken together, the data support the proposed formation of a radical intermediate, derived from the reaction of the {Fe=O} unit with cyclooctene (intermediate B in Scheme 2), which can either afford epoxide directly (pathway A) or be intercepted by O_2 to generate more epoxide (pathway B). There is precedent for {M=O} complexes that attack double bonds to yield {M-O-C-C}$^•$ and subsequently form {M···epoxide} complexes.[27]

Table 2: Labeling data.

Ligand	Experimental conditions[a]	% Epoxide-^{18}O[c]			% 1,2-Diol-^{18}O			
		$H_2{}^{18}O$	$H_2{}^{18}O_2$	$^{18}O_2$	$H_2{}^{18}O$		$H_2{}^{18}O_2$	
					$^{16}O^{16}O$	$^{16}O^{18}O$	$^{16}O^{18}O$	$^{18}O^{18}O$
L^1	H_2O_2, air	9	90	(1)	13[d]	86[d]	97[d]	3[d]
L^2	H_2O_2, air	3	54	(43)	99[d]	1[d]	4[d]	96[d]
L^5	H_2O_2, air	(0)	15	85				
L^5	H_2O_2, argon	18	82	–	70[d] 50[e]	30[d] 50[e]	23[d] 56[e]	77[d] 44[e]
L^5	PhIO[b], air			55[f]				
L^5	PhIO[b], argon	40[g]						

[a] 1000 equiv cyclooctene, 10 equiv H_2O_2, reaction time 0.5 h under air in MeCN, unless otherwise noted. [b] 1 equiv PhIO used as oxidant to form {$Fe^{IV}{=}O$}; no H_2O_2 used. [c] Values in parentheses are calculated by difference. [d] *cis* diol. [e] *trans* diol; *cis*/*trans* = 0.4:0.6. [f] 45% from PhIO. [g] 60% from PhIO.

The oxidation of cyclooctene by **2**/H_2O_2 in MeCN under argon affords 1 TON cyclooctane-1,2-diol (*cis*/*trans* 40:60) in addition to 1 TON epoxide. The diol product was not observed when the reaction was carried out in aerobic MeCN or in MeOH. In the latter solvent, 2 TON of epoxide were obtained, irrespective of whether O_2 was present or not. These results suggest that the precursor to the diol product is also intermediate B (pathway C). The presence of oxygen diverts intermediate B to form more epoxide, while MeOH quenches HO$^•$; hence the diol product is only observed in MeCN under argon.

^{18}O-labeling experiments, focusing on the {FeL^5}-catalyzed reaction (Table 2), support the proposed mechanism (Scheme 2). As expected for pathway A, a large fraction (82%) of the oxygen atom of the epoxide is derived from the $H_2{}^{18}O_2$ oxidant under Ar, with the remainder from $H_2{}^{18}O$, presumably by water exchange with the {Fe=O} unit.[28] On the other hand, the same reaction under aerobic conditions resulted in only 15% of the labeling in the epoxide arising from $H_2{}^{18}O_2$ and the balance derived from $^{18}O_2$, thus supporting the involvement of pathway B. Similar conclusions were reached in labeling experiments using the in situ formed $[(L^5)Fe{=}O]^{2+}$ (Table 2). Pathway B in Scheme 2 consists of the trapping of radical B by O_2 to initiate a radical chain reaction that affords most of the epoxide observed under aerobic conditions. It is well known that the autoxidation of cyclooctene primarily yields epoxide, through the addition of an initially formed alkylperoxy radical to the double bond.[29] However, the autoxidation pathway is apparently quenched in MeOH, as the yield of epoxide is not sensitive to the presence of air.

The labeling experiments also provide insight into the origin of the diol product, which formed (1 TON) only under anaerobic conditions and only in MeCN. The oxygen atoms of the diol mainly originate from $H_2{}^{18}O_2$, but some incorporation from $H_2{}^{18}O$ was also observed. The fact that both *cis* as well as *trans* products were observed indicates that the 1,2-diol must be formed by a pathway different from that proposed for the systems based on L^1 and L^2, which involves a high-valent $[M(L)(O)(OH)]^{n+}$ species that attacks the double bond with high stereoselectivity.[3,4] The fact that no diols are observed in the reaction with directly prepared {$Fe^{IV}{=}O$} suggests that an additional component (H_2O_2 or a H_2O_2-derived species, for example, $^•$OH) is also required for formation of the diol. We thus propose that the diol forms by the reaction of adduct B with HO$^•$ within the solvent cage of the Fe complex (Scheme 2, pathway C). Such caged radical pairs have been proposed before, for example, in Ref. [30]. The involvement of B in a radical reaction (pathway C) is supported by the loss of stereocontrol in diol formation as well as the absence of any diol formation in the presence of O_2, which reacts with B to form more epoxide (Scheme 2, pathway B), and in reactions in MeOH, which traps and quenches O-based radicals such as HO$^•$. The incorporation of oxygen from $H_2{}^{18}O$ into the diol product can be rationalized by solvent exchange of $[(L^5)Fe^{IV}{=}O]^{2+}$, thus supporting the notion that the ferryl species can lead to both epoxide and diol.

Our mechanistic proposal centers around adduct B as a common intermediate for all the observed products. The appearance of products other than epoxide depends on the lifetime of adduct B, which is modulated by the supporting ligand. The adduct lifetime for L^5 must be significantly longer than for L^4 to account for the extensive autoxidation of the epoxide observed, as well as its trapping by HO· or related species to form the diol.

In summary, pentadentate bispidine-based Fe^{II} complexes catalyze the oxidation of cyclooctene with H_2O_2 to afford the expected epoxide product, with the reaction rate dependent on the ligand structure. Unexpectedly, *cis*- and *trans*-1,2-diols are also observed but only under anaerobic conditions in MeCN. The accumulated data support a mechanism which involves formation of a low-spin Fe^{III}–hydroperoxo intermediate that produces $\{Fe^{IV}{=}O\}$. Epoxide is formed both by direct transfer of the ferryl oxygen atom and by a radical-based process with molecular oxygen. Diol formation is proposed to arise from a pathway not previously observed in non-heme iron-based oxidation catalysis.

Experimental Section

Reaction conditions for the cyclooctene oxidation: A 70 mM solution of H_2O_2 in MeCN (or MeOH, 0.3 mL) was delivered by syringe pump over 30 min at 25 °C under argon (or in air) to a vigorously stirred solution of MeCN (or MeOH, 2.7 mL) containing the iron catalyst and the olefin substrate; the resulting concentrations were 0.7 mM iron catalyst, 7.0 mM H_2O_2, and 0.70 M olefin. The solution was stirred for 5 min after the addition of H_2O_2 was complete. 1-Methylimidazole (0.1 mL) and acetic anhydride (1 mL) were added, followed by the addition of ice (these are standard reactions[3] for quenching the reaction and derivatization). After extraction with $CHCl_3$, the organic extract was washed successively with 1 M H_2SO_4 (1.0 mL), saturated $NaHCO_3$, and water. Naphthalene was added to the organic extract as an internal standard for GC analysis.

In experiments with $H_2{}^{18}O$, $H_2{}^{18}O$ (42 mL, 0.70 M) was added to the catalyst solution prior to the injection of H_2O_2 (experiments with the same amount of natural abundance H_2O were also made and shown not to have any influence on the product distribution). In experiments with $H_2{}^{18}O_2$, 70.0 mM $H_2{}^{18}O_2$ (diluted with MeCN or MeOH) was used (2 % $H_2{}^{18}O_2/H_2O$ solution, $H_2{}^{18}O_2/H_2{}^{16}O_2$ 9:1). Experiments with $^{18}O_2$ were performed with $^{18}O_2$-saturated solutions. Fe^{IV} solutions in MeCN were prepared with excess solid PhIO to afford, after filtration of the remaining PhIO, the desired solutions. The concentration of $\{Fe^{IV}{=}O\}$ was determined spectrophotometrically.

For comparison with published data, all yields are reported as TON = 10 µmol product) per µmol {Fe}; for most experiments (10 equivalents of H_2O_2), the maximum TON (without autoxidation) was 10.0. All experiments were run at least in duplicate and subjected to GC analysis (GC/MS for the labeling experiments). The GC was calibrated with the pure epoxide and *cis* diols. No other major products were detected, except for the *trans* diol in one set of experiments (see Table 2), and this had the same mass and fragmentation pattern, but a slightly different retention time. The relatively small yields means the error limit for all data is approximately ± 5 % (absolute) for TON and ± 5 % (relative) for labeling percentages.

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