

Control of the catalytic oxidations mediated by an oxo-bridged non-heme diiron complex: role of additives and reaction conditions

Stefania Tanase^a, Carole Foltz^a, René de Gelder^b, Ronald Hage^c,
Elisabeth Bouwman^a, Jan Reedijk^{a,*}

^a Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

^b Radboud University Nijmegen, Institute for Molecules and Materials, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

^c Unilever R&D Vlaardingen, Olivier van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands

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Abstract

The catalytic activity of $\{[\text{Fe}(\text{mebpa})\text{Cl}]_2\text{O}\}(\text{ClO}_4)_2$ (**1**) (mebpa = *N*-(2-methoxyethyl)-*N,N*-bis(pyridin-2-yl-methyl)amine) with H_2O_2 for the functionalization of alkanes and alkenes has been investigated. The experimental results show that compound **1** is stable during the catalytic cycle and it is an efficient catalyst for cyclohexane oxidation leading to an alcohol:ketone ratio of 3.5. Compound **1** is also found to be an active and selective catalyst for the epoxidation of alkenes. In all cases, the catalytic efficiency is strongly dependent on the presence of additives and the reaction conditions.

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1. Introduction

Hydrocarbons, especially saturated hydrocarbons, are the main constituents of oil and natural gases, the feedstock for the chemical industry. From an economic point of view, it is obvious that selective transformations of saturated hydrocarbons constitute an extremely important field of the contemporary chemistry, since their oxidation products are versatile intermediates for the further synthesis of a wide variety of chemicals [1,2]. The development of this area stands as an important objective in the synthetic chemistry because the discovery of fundamental new selective routes from hydrocarbons to more valuable products (such as alcohols, ketones, acids and peroxides) are necessary. Furthermore, because of the considerable pressure to replace old technologies with more efficient and sustainable alternatives, H_2O_2 and O_2 are

among the most important oxidants for large-scale industrial applications. As a result, the selective oxidation of hydrocarbons catalyzed by transition-metal complexes has attracted a great deal of interest [3–6].

The μ -oxo dinuclear iron(III) complexes in combination with different additives have emerged to be useful catalysts for alkane hydroxylation by increasing the selectivity and the rate of these transformations [1–5,7,8]. Efficient catalysts for alkane hydroxylation are μ -oxo dinuclear iron(III) complexes with didentate (bipyridine, bpy) [8–10], or tetradentate (tris[(2-pyridylmethyl)amine, tpa; tris(1-methylimidazole-2-yl)methyl]amine, tmima) [5,11–13] pyridine-type ligands and exchangeable μ -acetato or terminal aqua ligands. In these cases, both *tert*-butylhydroperoxide and H_2O_2 have proven to be the most useful oxidants in combination with these catalysts. More recently, a μ -oxo dinuclear iron(III) complex containing a polyimidazole ligand has shown to be a very efficient catalyst for both alkane and alkene oxidation [14]. In addition, the μ -oxo-iron(III) dimer $\{[\text{Fe}(\text{phen})_2(\text{H}_2\text{O})_2\text{O}\}(\text{ClO}_4)_4$

* Corresponding author. Tel.: +31 71 527 4450; fax: +31 71 527 4671.

E-mail address: reedijk@chem.leidenuniv.nl (J. Reedijk).

(phen = 1,10-phenanthroline) is also found an efficient epoxidation catalyst for a wide range of alkenes, using peracetic acid as oxidant [15].

Our current interest in the homogeneous oxidation reactions led us to explore suitable iron compounds as catalysts for the oxidation of the hydrocarbons. It has been reported that the μ -oxo diiron(III) complex $\{[\text{Fe}(\text{mebpa})\text{Cl}]_2\text{O}\}(\text{ClO}_4)_2$ (**1**) (mebpa stands for *N*-(2-methoxyethyl)-*N,N*-bis(pyridin-2-ylmethyl)amine) exhibits high activity for the oxygenation of cyclohexane in the presence of hydrogen peroxide as compared with the tpa (tris(2-pyridylmethyl)amine) analogue [16]. However, the conditions used for this reaction employ dihydrogen peroxide in high concentration; under these conditions dihydrogen peroxide is also catalytically decomposed, and moreover no selectivity in the oxidation products ($A/K = 1$) was observed. The goal of our study was to evaluate the effect of the H_2O_2 concentration and the additives added on the selectivity of oxidation products in the cyclohexane oxidation catalyzed by **1**. We now report that **1** catalyzes efficiently the oxidation of cyclohexane with a alcohol:ketone ratio of 3.5 and the catalytic efficiency is dependent not only on the catalyst and additive, but also on the reaction conditions. Furthermore, compound **1** is also found to be an active catalyst for the oxidation of other substrates, such as alkenes.

2. Experimental section

2.1. Materials

All chemicals were of reagent grade, and were used as received. The ligand *N*-(2-methoxyethyl)-*N,N*-bis(pyridin-2-ylmethyl)amine (mebpa) was prepared according to the published procedure [17].

2.2. Synthesis

$\{[\text{Fe}(\text{mebpa})\text{Cl}]_2\text{O}\}(\text{ClO}_4)_2$ (**1**) was obtained as dark orange crystals by slow evaporation of a methanol solution containing 0.1 mmol $\text{Fe}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ and 0.1 mmol mebpa·HCl. The resulting crystals were collected by filtration, washed with diethyl ether and dried in vacuum. Yield: 76%. $\text{C}_{30}\text{H}_{38}\text{Fe}_2\text{N}_6\text{O}_{11}\text{Cl}_4$ (912.17): calcd. C 39.5, H 4.2, N 9.21; found C 39.1, H 4.40, N 9.33. IR (ν/cm^{-1}): 3099w, 2925m, 2823w, 1608s, 1572m, 1478m, 1441s, 1290s, 1160m, 1067s, 1046s, 863m, 834s, 762s, 724m, 650m, 619s, 579w, 480m. UV–vis/NIR, $\lambda_{\text{max}}/\text{nm}$ (ϵ , $\text{mM}^{-1}\text{cm}^{-1}$): 294, 345, 450 and 290 (12.7), 338 (9.2), 458 (1.2) in acetonitrile solution. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 226828. For the earlier structures [16,18] no 3D coordinates are available. The structural parameters of both refinements appear to be the same.

Compound (**2**) was in situ obtained by addition of AgCF_3SO_3 to the acetonitrile solution of **1**, followed by stirring and filtration through Celite to remove the silver salt. UV–vis/NIR, $\lambda_{\text{max}}/\text{nm}$ (ϵ , $\text{mM}^{-1}\text{cm}^{-1}$) in acetonitrile: 290 (12.6), 367 (8.9), 487 (1.1).

$\{[\text{Fe}(\text{mebpa})]_2\text{O}(\text{pca})\}(\text{ClO}_4)_3$ (**3**) was obtained as dark red powder by slow evaporation of a methanol solution containing 0.14 mmol $\text{Fe}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$, 0.14 mmol mebpa·HCl, 0.28 mmol Hpca and 0.42 mmol Bu_4NOH . The resulting compound was collected by filtration, washed with diethyl ether and dried in vacuum. Yield: 45%. $\text{C}_{35}\text{H}_{41}\text{Fe}_2\text{N}_8\text{O}_{17}\text{Cl}_3$ (1063.80): calcd. C 39.52, H 3.88, N 10.53; found C 38.96, H 3.67, N 10.79. IR (ν/cm^{-1}): 2928m, 2820w, 1622s, 1590s, 1539m, 1431m, 1391s, 1165m, 1060m, 864m, 848s, 787m, 735m, 622s, 566w, 483m. UV–vis/NIR ($\lambda_{\text{max}}/\text{nm}$): 265, 378, 524.

2.3. Physical methods

Elemental analyses for C, H, and N were performed on a Perkin-Elmer 2400 Series II analyzer. The infrared spectra ($4000\text{--}300\text{ cm}^{-1}$) were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer equipped with a Golden Gate ATR device, using the reflectance technique. UV–vis spectra were obtained on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO or appropriate solvent used as a reference. A Hewlett Packard 5890 Series II gas chromatograph, equipped with WCOT fused silica column (stationary phase: CP-Was 58 (FFAP) CB) and coupled to a Hewlett Packard 5971 series mass spectrometer with a mass-selective detector or a Varian Star 3400CX gas chromatograph with a J&W Scientific/Fisons DB-1701 (14% cyanopropylphenylmethylpolysiloxane) column were used for analysis of the oxidation experiments.

2.4. Oxidation procedures

- Alkane oxidation.** In a typical run, 50 μmol of H_2O_2 (30%) were added to an acetonitrile solution (5 ml) containing 5 μmol catalyst and 5 mmol alkane (cyclohexane, cyclooctane or adamantane) at room temperature with a final catalyst:substrate: H_2O_2 ratio = 1:1000:10. After 30, 60 and 180 min of reaction at 25 °C, aliquots were taken from the reaction mixtures and analyzed twice by GC–MS: with and without the addition of an excess of triphenylphosphane for the quantitation of the amount of hydroperoxide.
- Alkene epoxidation.** In a typical oxidation experiment, 0.7 mmol of H_2O_2 (30%) were added to an acetonitrile solution (5 ml) containing 5 μmol catalyst and 0.175 mmol alkene (cyclohexene, cyclooctene or styrene) at 0 °C with a final catalyst:substrate: H_2O_2 ratio = 1:35:140. At 180 min reaction times aliquots were taken and analyzed with GC. In both cases, retention times for product peaks were compared with retention times of commercially available products. Chloroben-

zene, decane or 1,2-dibromobenzene were used as internal standards.

3. Results and discussions

3.1. Synthesis

The reaction of mebpa-HCl with $\text{Fe}(\text{ClO}_4)_3$ in methanol afforded the complex **1** in good yield and its crystal structure was redetermined during this study [16,18]. Compound **1** is a dinuclear μ -oxo-bridged diiron(III) complex that contains the ligand mebpa acting as a tetradentate tripodal ligand; the sixth coordination site around the iron(III) center is occupied by a chloride anion (Fig. 1) [16,18]. The electronic spectrum in acetonitrile of **1** shows bands at 337 and 458 nm that can be assigned to the oxo-to-iron LMCT transitions [19]. The less intense band at 458 nm is assigned to the ${}^6\text{A}_1 \rightarrow ({}^4\text{A}_1, {}^4\text{E})$ transition and is the signature of the Fe-(μ -O)-Fe motif, suggesting that the dinuclear structure is maintained in solution [20].

Since it has been reported that the iron(III)–chloride bond is too strong to allow exchange with solvent molecules, or reactants [8], the corresponding in situ prepared CF_3SO_3 complex (**2**) has also been tested for the oxidation of alkanes. The UV–vis spectra of **1** and **2** are almost identical, indicating that the μ -oxo dinuclear unit is also maintained in solution during reaction with $\text{Ag}(\text{CF}_3\text{SO}_3)$. In order to draw conclusions on the mechanism involved in the catalytic oxidations catalyzed by **1** and to ascertain the properties of the oxidant, use of a combination of different substrates has been chosen.

3.2. Alkane oxidation

The catalytic activity of compound **1** was tested during the oxidation of cyclohexane, cyclooctane and adamantane in acetonitrile and acetone under ambient conditions over a 180 min period. The product distributions for cyclohexane and adamantane oxidation are given in Tables 1 and 3.

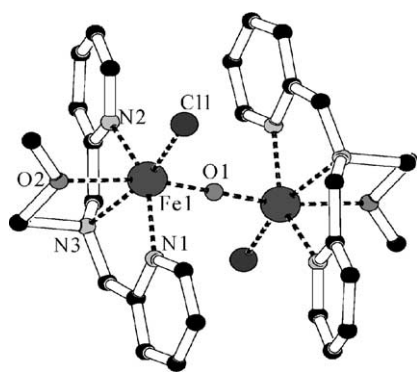


Fig. 1. Crystal structure of $[\text{Fe}(\text{mebpa})\text{Cl}]_2\text{O}^{2+}$ cation of the catalyst **1**, based on the coordinates from our analysis. Distances agree with literature [16,18].

Under our standard conditions, 1 mM catalyst **1** was allowed to react with 10 equiv. of H_2O_2 and 1000 equiv. cyclohexane to give 2.8 equiv. cyclohexanol and 0.8 equiv. cyclohexanone in the course of 1 h, with a final conversion of 53% based on H_2O_2 (after 3 h). Similar results are obtained when the catalytic reaction is performed under argon. This reactivity is lower than those observed for $\{[\text{Fe}(\text{bpy})(\text{H}_2\text{O})_2\text{O}]\text{ClO}_4\}_4$ [21] and $\{[\text{Fe}(\text{pb})(\text{H}_2\text{O})_2\text{O}]\text{ClO}_4\}_4$ [22], but comparable to that found for $\{[\text{Fe}(\text{L})(\text{NO}_3)_2\text{O}]\text{ClO}_4\}_2$ [14] ($\text{L} = 2,6$ -bis(*N*-methylbenzimidazol-2-yl)pyridine) (see Table 2). The major product was cyclohexanol, with an alcohol to ketone ratio (A/K) of 3.5, which is significantly higher than reported for radical-chain autooxidation reactions [23]. From the time dependence of the reaction (Table 2) it can be observed that cyclohexanone and cyclohexanol are always formed in constant ratios, showing that the cyclohexanol is not the precursor of cyclohexanone. It should be pointed out that the reactivity of **1** in acetonitrile is comparable with that of $[\text{Fe}(\text{tpa})(\text{ACN})_2]^{2+}$ concerning the oxidant-to-product conversion and the alcohol/ketone ratio [24]. However, in the present case the oxidation rate is four orders of magnitude slower than that obtained with the Fe-tpa system. The fact that the alcohol is the major oxidation product suggests that the action of a metal-based oxidant could be involved in the cyclohexane oxidation [24]. The catalytic activity with Fe(III) ion alone has also been tested in both alkane and alkene oxidation and no catalytic activities were observed under our experimental conditions.

In acetone and in $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ (mixture 90/10, v/v) a lower reactivity was observed as compared to that in acetonitrile, but surprising only minor changes were observed in the A/K ratio. No formation of bicyclohexyl and cyclohexyl chloride was observed. Any free cyclohexyl radical present would undergo dimerisation to give bicyclohexyl, and would also abstract the chloride from CH_2Cl_2 to give cyclohexyl chloride. Since both acetone and CH_2Cl_2 , which are good traps for the HO^\bullet radicals, lead to only partial quenching of cyclohexane oxidation, the possibility is raised that two oxidative species might be involved [25,26]. Furthermore, when 2,6-di-*tert*-butyl-4-methylphenol was added to the ox-

Table 1

Catalytic oxidation of cyclohexane to cyclohexanol (CyOH) and cyclohexanone (CyO) by complexes **1** and **2**^a

Catalyst/additive	Solvent	TON ^a		A/K	Eff. ^b (%)
		CyOH	CyO		
1 /No additive	CH_3CN	4.1	1.2	3.5	53
	Acetone	2.7	0.8	3.3	35
1 /10 Equiv. CH_3COOH	CH_3CN	5.8	3.6	1.6	94
	Acetone	1.4	0.9	1.5	23
2 /No additive	CH_3CN	4.1	1.3	3.2	54
	CH_3CN	2	1.2	1.6	32

^a Results are given as mmol product/mmol of catalyst after 3 h of reaction and are the average of 2 or 3 runs. The experimental errors are in the range ± 0.2 TON.

^b Efficiency based on H_2O_2 .

Table 2

Catalytic oxidation of cyclohexane to cyclohexanol (CyOH) and cyclohexanone (CyO) by (μ -oxo)diiron complexes and H₂O₂^a

Catalyst	Equiv. H ₂ O ₂	Reaction time	CyOH	CyO	A/K	Eff. (%) ^b	Ref.
{[Fe(tpa)(H ₂ O)] ₂ O}(ClO ₄) ₄	150	15 min	1	2	0.5	n.d.	[11]
{[Fe(bpy)(H ₂ O)] ₂ O}(ClO ₄) ₄	580	10 min	18	14	1.3	9	[21]
{[Fe(pb)(H ₂ O)] ₂ O}(ClO ₄) ₄	25	10 min	5	2.5	2	30	[22]
{[Fe(mebpa)Cl] ₂ O}(ClO ₄) ₂ , 1	180	30 min	3.2	3.2	1	n.d.	[16]
			2 h	5	4	1.2	2
{[Fe(mebpa)Cl] ₂ O}(ClO ₄) ₂ , 1	10	30 min	<0.5	<0.5	n.d.	n.d.	This paper
			60 min	2.8	0.8	3.5	36
			3 h	4.1	1.2	3.5	53
2	10	30 min	2.6	0.8	3.2	34	This paper
			60 min	3.5	1.1	3.2	46
			3 h	4.1	1.3	3.2	54
{[Fe(mebpa)Cl] ₂ O}(ClO ₄) ₂	100	3 h	6.4	3.1	2.1	9.5	This paper
{[Fe(L)(NO ₃) ₂ O}(NO ₃) ₂	2500	3 h	28	23	1.2	51	[14]

Abbreviation: tpa = tris[(2-pyridylmethyl)amine], bpy = 2,2'-bipyridine, pb = (-)-4,5 pinene bipyridine, mebpa = *N*-(2-methoxyethyl)-*N,N*-bis(pyridin-2-ylmethyl)amine, L = 2,6-bis(*N*-methylbenzimidazol-2-yl)pyridine.

^a Reactions performed at room temperature and acetonitrile as solvent.

^b Based on H₂O₂

oxidation of cyclohexane prior to H₂O₂ addition, no significant lowering of the yields of the oxidation product was observed.

The oxidation of cyclooctane catalyzed by **1** has proven to be less efficient as compared with cyclohexane oxidation with a final conversion of only 9% based on H₂O₂ (after 3 h of reaction). In this case the ketone was the main product with an A/K of 0.2–0.3 as also observed with {[Fe(bpy)(H₂O)]₂O}(ClO₄)₄ [21]. The behavior of **1**/H₂O₂ towards adamantane oxidation has also been investigated and the formation of both secondary and tertiary products has been observed with a tertiary/secondary ratio (3°/2°) of 6–7.1 (Table 3). For comparison, tertiary/secondary ratios of about 2 have been found for oxidation of alkanes by HO• [5] and values of 3.1–3.3 for [(N4Py)Fe(CH₃CN)](ClO₄)₂ [27]. A tertiary/secondary ratio of 9.5–10 has been observed for oxidations by tBuOOH using the {[Fe(bpy)₂(H₂O)]₂O}(ClO₄)₄ catalyst [9].

Next, the catalytic activity of **1** in the presence of several additives has been evaluated. Addition of 10 equiv. of

acetic acid to **1** results in a slight increase of the oxidation rate in both cyclohexane and adamantane oxidation, but a lower selectivity was observed in the cyclohexane oxidation (A/K = 1.6) (Table 1). In both cases, a higher conversion based on H₂O₂ was reached as compared with the reactivity in the absence of acetic acid, but not in the presence of acetone. Addition of 2 equiv. of 2-pyrazinecarboxylic acid (Hpca) to the catalytic mixture results in the complete inhibition of the oxidation of alkanes. Shul'pin [3] reported that using Hpca as co-catalyst in the alkane functionalizing reactions, the yield of oxygenated products can be improved. However, those conditions are quite different; Shul'pin used an iron compound prepared in situ to which a large excess of Hpca was added, while we can use a simple compound as isolated and which is stable under reaction conditions (*vide infra*). In our case, even high concentrations of Hpca does not lead to improved catalytic efficiency.

Regarding the data shown in Table 2, it can be observed that when chloride is replaced by more exchangeable ligands (such as the solvent molecule in the present case), the complex **2** becomes more reactive in the initial phase in cyclohexane hydroxylation, in the absence of additives. Similar behavior was also observed for the adamantane oxidation. Complex **2** catalyzes the oxidation of cyclohexane to the corresponding alcohol and ketone with 54% conversion based on H₂O₂ and an A/K ratio equal to 3.2 after 3 h of reaction. However, as compared with **1**, a 34% conversion is reached in the first 30 min. Once more, addition of Hpca results in complete inhibition of cyclohexane oxidation.

Using a high catalyst concentration and a large excess of hydrogen peroxide, catalase activity is observed and lower selectivity is obtained in the cyclohexane oxidation catalyzed by **1**, results which are in agreement with the early work on a similar compound (Table 2) [16]. So, the reaction of 5 mM catalyst **1** with 250 equiv. of H₂O₂ and 1000 equiv. cyclohexane leads to 6.4 equiv. cyclohexanol and 3.1 equiv. cyclohexanone in the course of 3 h with a A/K ratio equal

Table 3

Catalytic oxidation of adamantane to 1-adamantol (1-ol), 2-adamantol (2-ol) and 2-adamantanone (2-one) by complexes **1** and **2**^a

Catalyst/additive	Time (min)	TON ^a			3°/2° ^b	Eff. ^c (%)
		1-ol	2-ol	2-one		
1 /No additive	CH ₃ CN	3.4	0.7	n.d.	n.d.	n.d.
	Acetone	2.5	0.7	0.4	6.8	36
1 /CH ₃ COOH	CH ₃ CN	2.8	0.8	0.4	7.1	46
	Acetone	0.6	n.d.	0.2	n.d.	n.d.
2 /No additive	CH ₃ CN	3.4	1.1	0.5	6.2	51
	CH ₃ COOH	3.4	0.7	0.2	11.7	43

^a Results are given as mmol product/mmol of catalyst after 3 h of reaction and are the average of 2 or 3 runs. The experimental errors are in the range ±0.2 TON.

^b 3°/2° = 1-ol/(2-ol + 2-one) multiplied by three to correct the three-fold higher number of secondary C–H bonds.

^c Efficiency based on H₂O₂.

to 2 (results not shown in the table). In the present case, addition of 2 equiv. of Hpca results in the formation of 4.6 equiv. cyclohexanol and 1.7 equiv. cyclohexanone. All differences emphasize the sensitivity of the catalytic reactions, not only to the catalyst structure, but also to the reaction condition.

3.3. Alkene oxidation

The behavior of **1**/H₂O₂ towards olefins (cyclohexene, cyclooctene and styrene) supports the mechanistic conclusions derived from the alkane oxidation experiments, i.e. the involvement of two types of oxidizing species. In all cases, both epoxidation and allylic oxidation are observed: HO• radicals cannot enforce stereospecific oxidation of olefins to epoxide (performed by metal-based oxidants), but instead abstract allylic hydrogen and initiate radical-chain reactions in the presence of dioxygen, being efficient hydroxylation agents [5]. Besides this, a free radical mechanism initiated by the homolysis of a tentative Fe^{III}-OOH intermediate might also be present [28,29].

In acetonitrile and using cyclohexene as substrate, cyclohexene oxide and cyclohexanone were found as the main products along, with small amounts of cyclohexenol (TON < 1) (Table 4). Since this substrate is very susceptible to allylic oxidation, the effect of acetone as solvent used has been tested. In this solvent, the cyclohexene oxide (12.6 turnovers) is the main product. Cyclooctene as a substrate afforded the epoxide (5.8 turnovers) as main product and many different oxidation products (each accounting for <1 turnover) in acetonitrile, but only the epoxide (4.8 turnovers) in acetone (Table 4). Styrene is converted to styrene oxide (2.5 turnovers) and benzaldehyde (11.2 turnovers) in acetonitrile,

whereas only benzaldehyde has been obtained in acetone (4.8 turnovers).

The observation that allylic products are mainly formed in the oxidation of cyclohexene and styrene, combined with the fact that cyclooctene epoxide formation is also observed in radical based reactions, indicate that the main reaction pathway might involve a radical based oxidant [28]. On the other hand, the **1**/H₂O₂-catalyzed oxidation of cyclohexene and cyclooctene gives mainly epoxide in both acetonitrile and acetone, which indicate that a second reaction pathway involves a metal-based oxidant. This result is in agreement with those for {[Fe(L)(NO₃)₂O]}(NO₃)₂ [14], [Fe(tpa)(ACN)₂](ClO₄)₂ [24] and [Fe(mep)(ACN)₂](ClO₄)₂ [30] (mep = *N,N'*-dimethyl-*bis*(2-pyridylmethyl)-ethane-1,2-diamine), non-heme iron complexes that are able to catalyze the stereospecific oxidation of olefins to epoxide in the presence of H₂O₂ as oxidant.

The effect of several additives has been also evaluated in the oxidation of alkenes by **1**/H₂O₂. The presence of 10 equiv. of acetic acid or 5 equiv. *N*-methylimidazole does not change significantly the products yield. However, the effect of the solvent used is similar to that observed for the catalytic reactions in the absence of additives (Table 4). Both epoxide and allylic oxidation products have been found in acetonitrile, but mainly epoxide in acetone (cyclohexene and cyclooctene oxidation) and benzaldehyde (styrene oxidation). In contrast to White et al. [30] who have reported an efficient epoxidation reaction in acetic acid/acetonitrile conditions, we found no changes in the selectivity for epoxide formation during 180 min. Once again, the addition of 2 equiv. of 2-pyrazinecarboxylic acid (Hpca) to the catalytic mixture results in a dramatically decreased catalytic activity in all alkene oxidation reactions catalyzed by **1**/H₂O₂.

Table 4
Catalytic oxidation of alkenes by complex **1**^a

Substrate	Additive	Products	TON in ACN	TON in acetone
Cyclohexene	10 Equiv. CH ₃ COOH	Cyclohexenone	18.2	–
		Cyclohexene oxide	11.5	12.6
		Cyclohexene	16	–
	5 Equiv. Nmiz ^b	Cyclohexene oxide	11.4	9.4
		Cyclohexene	19	–
		Cyclohexene oxide	8.8	9.7
Cyclooctene	10 Equiv. CH ₃ COOH	Cyclooctene oxide	5.7	4.8
		Other products	<1	<1
		Cyclooctene oxide	8.3	7.6
	5 Equiv. Nmiz	Other products	<1	<1
		Cyclooctene oxide	9.5	8.4
		Other products	9.5	<1
Styrene	10 Equiv. CH ₃ COOH	Benzaldehyde	11.2	4.8
		Styrene oxide	2.5	<1
		Benzaldehyde	12.1	2.9
	5 Equiv. Nmiz ^b	Styrene oxide	1.6	<1
		Benzaldehyde	8.5	3.2
		Styrene oxide	<1	<1

^a Results are given as mmol product/mmol of catalyst after 3 h of reaction and are the average of 2 runs. The experimental errors are in the range ±0.3 TON.

^b Nmiz = *N*-methylimidazole.

3.4. Catalyst stability

The stability of compound **1** under the conditions of catalysis was investigated using UV–vis spectroscopy. The UV–vis spectrum of the reaction mixture does not change during the catalytic process; it suggests that the catalyst is quite stable under these conditions and its catalytic activity is not affected. However, the addition of a second aliquot of H₂O₂ to the reaction mixture after 3 h results only in a slight increase of the reaction yields. Addition of CH₃COOH or Nmiz to the reaction mixture results only in insignificant spectroscopic changes. However, based on the UV–vis spectra alone, the nature of the active species has been difficult to assess and other spectroscopic studies are required. In the presence of Hpca as additive, the UV–vis spectrum shows the disappearance of the characteristic absorption band for a dinuclear oxo-bridged complex, indicating the decomposition of compound **1**. Attempts to isolate possible active species from the reaction mixture containing **1** in acetic acid medium, resulted in the crystallization of compound **1**. From 1 and 2 equiv. of Hpca in methanol as solvent, a red compound with tentative formula {[Fe(mebpa)₂O(pca)}(ClO₄)₃ (**3**) was obtained. However, because of its poor solubility in most of the solvents, this compound could not be tested in the catalytic oxidations.

4. Conclusions

In this paper we have shown that the iron complex {[Fe(mebpa)Cl]₂O}(ClO₄)₂ efficiently catalyzes both the oxidation of alkanes and alkenes with H₂O₂ as oxidant under mild conditions. In acetonitrile and acetone as solvents, moderately catalytic reactivity was found, but the results are strongly solvent dependent. However, in the oxidation of alkenes good conversion yield was observed as compared to the oxidation of alkanes. The experimental results suggest that two competitive mechanistic pathways might be involved: one leading to oxidation products formed via radicals/H• abstraction mechanisms, and the second one leading to oxygen-transfer processes. The radical-based processes may have been formed via hydroxyl radicals or other secondary radicals such as cyclohexane-alkoxy radicals. Alternatively, these products can also be formed via reactivity of putative Fe^{IV}O species formed during the hemolytic cleavage of the FeOOH bond that are also able of hydrogen abstraction and can hydroxylate further the C–H bond of alkanes [31]. The second oxygen-transfer pathway may involve Fe^VO species generated by the heterolytic cleavage of the O–O bond [28,32]. However, the involvement of this species and the nature of the oxidizing complex need to be elucidated further. In all cases, the observed catalytic activity is highly dependent not only on the catalyst and additive, but also on the used reaction conditions.

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