

## Factors Affecting the Catalytic Activity of Aryl Substituted Ironporphyrins

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Neste trabalho, estudamos como o solvente, o modo de agitação, a presença de água e de imidazol afetam a atividade catalítica de Fe(III)porfirinas, em reações de hidroxilação de cicloexano, utilizando-se como doador de oxigênio o iodosobenzeno ( $\Phi\text{IO}$ ). As Fe(III)porfirinas estudadas foram a Fe(TPP)<sup>+</sup> **1** [5,10,15,20 tetra(fenil)porfirina ferro (III)]; Fe(TDCPP)<sup>+</sup> **2** [5,10,15,20 tetra(2,6-dicloro-fenil)porfirina ferro (III)]; Fe(TNPP)<sup>+</sup> **3** [5,10,15,20 tetra(o-nitrofenil)porfirina ferro (III)]; Fe(TFPP)<sup>+</sup> **4** [5,10,15,20 tetra (pentafluorofenil)porfirina ferro (III)] e Fe(MNPP)<sup>+</sup> **5** [5 mono(o-nitrofenil) 10,15,20 tri(fenil) porfirina ferro (III)]. Agitação por ultra-som é mais efetiva na homogeneização e hidroxilação do que agitação magnética para a 2-Cl, 3-Cl, 5-Cl. Para a 1-Cl, ultra-som diminui o rendimento de cicloexanol (C-ol) devido à destruição do anel porfirínico. Presença de água no solvente diminui a atividade catalítica da 2-Cl, 3-Cl e 5-Cl. Para a 2-Cl e 3-Cl, 1,2-dicloroetano (DCE) é melhor solvente que diclorometano (DCM) porque neste caso a espécie intermediária **I** (Fe<sup>IV</sup>(O)P<sup>•+</sup>) é capaz de abstrair o átomo de hidrogênio do DCM, o qual compete com o substrato. Devido à presença dos substituintes pentafluorofenil, a 4-Cl é capaz de utilizar O<sub>2</sub>, além do  $\Phi\text{IO}$ , levando a um mecanismo radicalar de hidroxilação. Fatores que favorecem a formação de radical e dímero  $\mu$ -oxo (ultra-som e presença de água) dão origem a altos rendimentos: 134% e 205%, respectivamente. Adição de imidazol ao sistema favorece complexos 4-Im<sub>2</sub>, os quais impedem a formação do dímero, evitando o mecanismo paralelo de O<sub>2</sub> e diminuindo o rendimento para 100%.

We studied how the solvent, the stirring method and the presence of water and imidazole affect the catalytic activities of ironporphyrins (FeP) for cyclohexane hydroxylation with iodosylbenzene (PhIO) as the oxygen donor. We studied the following FeP: Fe(TPP)<sup>+</sup> **1** [iron (III) 5,10,15,20 tetraphenylporphyrin]; Fe(TDCPP)<sup>+</sup> **2** [iron (III) 5,10,15,20 tetra-2,6-dichloro-phenylporphyrin]; Fe(TNPP)<sup>+</sup> **3** [iron (III) 5,10,15,20 tetra*ortho*nitrophenylporphyrin]; Fe(TFPP)<sup>+</sup> **4** [iron (III) 5,10,15,20 tetrafluorophenylporphyrin] and Fe(MNPP)<sup>+</sup> **5** [iron (III) 5 mono*ortho*nitrophenyl 10,15,20 triphenylporphyrin]. Ultrasound stirring homogenizes the reaction mixture more effectively and provides higher yields than magnetic stirring for 2-Cl, 3-Cl, and 5-Cl. For 1-Cl, ultrasound decreases the cyclohexanol (C-ol) yield due to porphyrin ring destruction. Water in the solvent media decreases the catalytic activity of 2-Cl, 3-Cl, and 5-Cl. For 2-Cl and 3-Cl, 1,2-dichloroethane (DCE) is a better solvent than dichloromethane (DCM) because in this case the intermediate species **I** (Fe<sup>IV</sup>(O)P<sup>•+</sup>) is capable of abstracting hydrogen atoms from DCM, which competes with the substrate. Due to the presence of pentafluorophenyl groups, 4-Cl is capable of utilizing O<sub>2</sub> in addition to PhIO, leading to a radicalar mechanism of hydroxylation. Factors favoring radical formation and  $\mu$ -oxo dimer (ultrasound and presence of water) give high yields: 134% and 205% respectively. The addition of imidazole to the system favors 4-Im<sub>2</sub> complexes which do not enable the formation of the  $\mu$ -oxo dimer, preventing the O<sub>2</sub> parallel mechanism and decreasing the yield to 100%.

**Keywords:** porphyrin, catalysis, meso-aryl substituted ironporphyrin, oxidation

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## Introduction

Aryl substituted ironporphyrins (FeP) have been extensively studied as models of cytochrome P-450 monooxygenase in the last twenty years<sup>1</sup>. In these reactions, iodosylarenes, organic peroxides, oxygen peroxides etc. have been used as oxygen donors in the monooxygenation of hydrocarbons. Iodosylarenes have been selected as the oxygen donor in model systems because they react with FeP, giving rise to the active intermediate species responsible for the activation of inert C-H bonds in alkanes. This species has been established as Compound I of the horseradish peroxidase, characterized as an iron-oxo (IV) porphyrin  $\pi$ -cation radical  $\text{Fe}^{\text{IV}}(\text{O})\text{P}^{\bullet+}\text{I}^2$ .

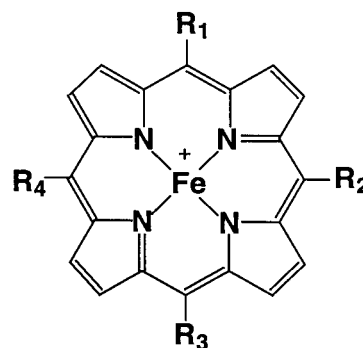
In previous work, we observed that the mono*ortho*nitrophenyl substituted ironporphyrin was efficient as the catalyst in cyclohexane hydroxylation by iodosylbenzene<sup>3</sup>. The active catalytic species in this system was established as the dimeric radical,  $\text{PFe}^{\text{IV}}\text{-O-Fe}^{\text{IV}}(\text{O})\text{P}^{\bullet+}\text{II}^4$ . These results motivated us to extend this study to  $\text{Fe}(\text{TPP})\text{Cl}$  and the active species **II** was also detected<sup>5</sup>. We have used  $\mu$ -oxo dimers such as  $(\text{FeMNPP})_2\text{O}$  and  $(\text{FeTPP})_2\text{O}$  as catalysts with good efficiency, indicating the relevance of dimerization in these processes<sup>6</sup>.

Despite a great deal of work with these biomimetic systems, there are relatively few systematic studies about the factors that affect their catalytic efficiency. A classical study about the hydroxylation of cyclohexane using FeP as catalysts and iodosylbenzene (PhIO) as the oxygen donor was reported by Nappa & Tollman in 1985<sup>7</sup>. Factors such as catalyst and substrate concentration, and the effect of axial ligands and substituents were studied. We have done studies on the optimization of reaction conditions in these kind of systems using *ortho*nitrophenyl and methylpyridil substituted ironporphyrins as catalyst<sup>3,6,8,9</sup>. We observed that the yields of oxidized products were critically dependent on factors such as solvent, stirring method and the presence of water. In this work we investigated how these factors affect the catalytic activities of FeP **1** to **5** (Fig. 1) in the hydroxylation of cyclohexane using PhIO as the oxygen donor. The unusual behavior observed for  $\text{Fe}(\text{TFPP})\text{Cl}$  will be discussed.

## Experimental

### Materials

All the materials were of commercial reagent grade unless otherwise stated. Dichloromethane (DCM) and 1,2-dichloroethane (DCE) were distilled and stored on 4 Å molecular sieves. N,N-dimethylformamide (DMF) was stirred over KOH at room temperature overnight, decanted and then distilled at reduced pressure. Cyclohexane purity was determined by gas chromatographic analysis.



### Ironporphyrin

1 $\text{Fe}(\text{TPP})^+$	$\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 =$	Ph
2 $\text{Fe}(\text{TDCPP})^+$		2,6 diClPh
3 $\text{Fe}(\text{TNPP})^+$		<i>o</i> -NO <sub>2</sub> Ph
4 $\text{Fe}(\text{TFPP})^+$		C <sub>6</sub> F <sub>5</sub>
5 $\text{Fe}(\text{MNPP})^+$	$\text{R}_1 =$ <i>o</i> -NO <sub>2</sub> Ph	$\text{R}_2 = \text{R}_3 = \text{R}_4 =$ Ph

Figure 1. Structure of ironporphyrins.

### Iodosylbenzene (PhIO)

It was obtained through the hydrolysis of iodosylbenzenediacetate<sup>10</sup>. Samples were stored in a freezer and the purity was checked every six months by iodometric assay.

### Porphyrins and Ironporphyrins

$\text{Fe}(\text{TPP})\text{Cl}$  was purchased from Aldrich, and TDCPPH<sub>2</sub>, TNPPH<sub>2</sub> and TFPPH<sub>2</sub> (Fig. 1) were purchased from Midcentury. Iron insertion into the free base porphyrins was done by adapting the method described by Adler *et al.*<sup>11</sup>. DMF was removed in the flash evaporator and the ironporphyrins (FePX) obtained were washed with water, which converted them to  $\text{FePOH}$ , except for **4** which was converted to the  $\mu$ -oxo species. This conversion was confirmed by UV-Vis<sup>12a</sup> and IR<sup>12b</sup> data: 2-OH UV-Vis:  $\lambda_{\text{max}} = 418 \text{ nm}$ ; 580 nm; 3-OH  $\lambda_{\text{max}} = 422$ ; 580 nm; 4- $\mu$ -oxo IR: Fe-O-Fe  $\nu_{\text{stretch}}$  at  $866 \text{ cm}^{-1}$ ; UV-Vis:  $\lambda_{\text{max}} = 326$ ; 400; 560 nm<sup>12b</sup>. The electron-withdrawing substituents favor the formation of these thermodynamically stable hydroxo complexes. We calculated the thermodynamic stability constants ( $\beta_n$ ) for 2-OH and 4-OH:  $\beta_2 = 1.5 \times 10^7 \text{ mol}^{-2} \text{ L}^2$  and  $k_1 = 1.0 \times 10^6 \text{ mol}^{-1} \text{ L}$ , respectively<sup>13</sup>. 2-OH and 4- $\mu$ -oxo were purified by silica column chromatography, using a mixture of 5% methanol in dichloromethane as eluent for 2-OH, and a cyclohexane-dichloromethane 2:3 mixture as eluent for the 4- $\mu$ -oxo form. For 3-OH, a neutral alumina column was used and DCM was utilized to separate the free base porphyrin first, and 3-OH was then eluted with methanol. The dichloromethane solutions of the purified 2-OH,

3-OH and 4- $\mu$ -oxo forms were bubbled with hydrochloric acid gas, converting them to 2-Cl, 3-Cl and 4-Cl, respectively.

The synthesis and purification of Fe(MNPP)Cl has been described previously<sup>4</sup>.

#### Oxidation reactions

The reactions were carried out in a 2 mL vial with an open top screw cap containing a silicone teflon-coated septum. In a standard reaction, the solvent (160  $\mu$ L) and cyclohexane (90  $\mu$ L) were added to the vial containing the FeP (~0.30 mg) and iodosylbenzene (~0.50 mg) under argon atmosphere, and the flask was adapted in a dark chamber. When the mixture was stirred with ultrasound (ultrasound laboratory cleaner Minison-Thornton, 40 W, 50-60 Hz) the temperature was 0 °C, and when magnetic stirring was used the temperature was 25 °C. The reaction mixture was stirred for 1 h, and a saturated sodium bisulfite aqueous solution (20  $\mu$ L) was added to the reaction mixture in order to quench further oxidation.

#### Product analysis

The product was analyzed by gas-chromatography using n-octanol as the internal standard. Yields were based on iodosylbenzene. Gas chromatographic analyses were performed on a CG 37-002 or CG 500 gas chromatograph coupled to a CG 300 integrator. Nitrogen was used as the carrier gas with a hydrogen flame ionization detector. The inox column (length, 1.8 m; internal diameter, 3 mm) was packed with 10% Carbowax 20 M on chromosorb WHP. The products were analyzed by a comparison of their retention times with those of authentic samples. Control of all reactions was carried out under the same experimental conditions, but in the absence of FeP for all runs.

The percentage of FeP recuperation after catalyzed reactions was determined by measuring the absorption intensity of the Soret band on a Hewlett-Packard 8452, Diode Array UV-Vis spectrophotometer.

## Results and Discussion

#### Ultrasound effect

The ultrasound aided reactions were carried out at 0 °C in order to have better temperature control since ultrasound promotes high local heating. With magnetic stirring, a higher temperature was used (25 °C) so as to ensure a more effective solubilization of PhIO. We observed a significant increase in the C-ol yield when ultrasound was used as the stirring method, except in the case of (FeTPP)Cl (Table 1). Ultrasound mixes the reactants more effectively, promoting rate enhancement in reactions in which active radical intermediates are chemically produced subsequent to the cavitation<sup>14</sup>. The presence of solid particles of PhIO is responsible for the lack of homogeneity and may act as a cavitation nucleus. This stirring method also favors hydrogen atom abstraction, increasing C-ol yields. For

**Table 1.** Yields of cyclohexanol (%)<sup>a</sup> in the hydroxylation of cyclohexane with PhIO using FeP as catalyst in DCM. Effect of stirring method.

Ironporphyrin	Magnetic		Ultrasound	
	C-ol	C-one	C-ol	C-one
1 Fe(TPP) <sup>+</sup>	40	-	29	-
2 Fe(TDCPP) <sup>+</sup>	42	4	72	3
3 Fe(TNPP) <sup>+</sup>	45	-	63	-
4 Fe(TFPP) <sup>+</sup> <sup>a</sup>	111 <sup>b</sup>	-	134	-
5 Fe(MNPP) <sup>+</sup>	32	-	70	-

Conditions: [FeP] = 2 - 5  $\times 10^{-4}$  mol.L<sup>-1</sup>, PhIO/FeP molar ratio of 8-10:1, magnetic stirring at 25 °C and ultrasound at 0 °C, argon atmosphere.

<sup>a</sup> [FeP] = 2  $\times 10^{-4}$  mol L<sup>-1</sup>, PhIO/FeP molar ratio of 20:1; <sup>b</sup> In oxygen atmosphere the yield was increased to 173%.

\*Based on the starting PhIO.

Fe(TPP)Cl, which has no protection of the electronwithdrawing meso-*ortho*phenyl substituents on the porphyrin ring, the destruction occurs very quickly when ultrasound is used. Fe(TFPP)Cl (4) shows unusual high yields, indicating that there is another parallel oxidation mechanism. Therefore, the results concerning 4 (Tables 1 to 4) will be discussed separately.

#### Water effect

Generally, the C-ol yields decreased when ultrasound and argon saturated with water were used simultaneously (Table 2), except in the case of Fe(TPP)Cl. We have previously observed that water is important in the formation of Fe(MNPP)Cl catalytic species<sup>4</sup>, so that when Fe(MNPP)Cl and PhIO are dry, the efficiency decreases. Therefore, we expected an increase in the C-ol yields for these FeP when water was added to the system. In fact, we observed the opposite, so we concluded that water has a positive effect on FeP activity when it is present in the

**Table 2.** Yields of cyclohexanol (%)<sup>a</sup> in the hydroxylation of cyclohexane with PhIO using FeP as catalyst in DCM. Effect of water when ultrasound stirring is used.

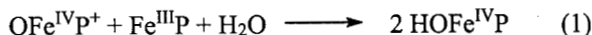
Ironporphyrin	Absence of Water		Presence of Water <sup>a</sup>	
	C-ol	C-one	C-ol	C-one
1 Fe(TPP) <sup>+</sup>	29	-	39	-
2 Fe(TDCPP) <sup>+</sup>	72	3	60	-
3 Fe(TNPP) <sup>+</sup>	63	-	55	-
4 Fe(TFPP) <sup>+</sup> <sup>b</sup>	134	-	205	-
5 Fe(MNPP) <sup>+</sup>	50	-	40	-

Conditions: [FeP] = 3-5  $\times 10^{-4}$  mol L<sup>-1</sup>, PhIO/FeP molar ratio of 8-10:1, ultrasound stirring at 0 °C, argon atmosphere.

<sup>a</sup> Reactions carried out under water saturated argon stream; <sup>b</sup> [FeP] = 2  $\times 10^{-4}$  mol L<sup>-1</sup>, PhIO/FeP molar ratio of 20:1.

\* Based on the starting PhIO.

solvent environment. Lindsay-Smith *et al.*<sup>15</sup> reported the following competitive process in an aqueous system study:



It is probable that this process is responsible for the decrease in the C-ol yields for the more resistant catalysts such as Fe(TDCPP)Cl in the presence of water. The decrease in C-ol yields may also be attributed to the great quantity of OH<sup>•</sup> radicals derived from water when ultrasound stirring is used<sup>14</sup>. In addition, OH<sup>•</sup> participates in the destructive process of the porphyrin ring. This is confirmed by the lower quantity of catalyst recovered after the oxidation reaction under these conditions. For Fe(TNPP)Cl the recovery was 98% for the magnetic method, while it was 50% for the ultrasound stirring method, in the presence of water. On the other hand, with Fe(TPP)Cl an unusual high yield of C-ol was observed in the presence of water. In this case in particular, water may act favorably, involving the dimer active species II<sup>4,5</sup>. In addition, the  $\mu$ -oxo dimer species may be present and it is more resistant to destruction.

#### Solvent effect

C-ol yields were better in 1,2-dichloroethane (DCE) when compared with the results attained in dichloromethane (DCM) using tetraaryl FeP containing electron-withdrawing groups such as 2-Cl and 3-Cl (Table 3). In these cases, the more stable and very active intermediate species I abstracts protons from the DCM, which competes with the substrate, producing HCl and CO<sub>2</sub><sup>16</sup>. This fact was previously observed with 5-Cl during the intermediate formation<sup>3b</sup>. Hydrogen abstraction from DCE is more difficult. However, with Fe(TPP)Cl, the active species is not effective to oxidize DCM, so the yield is higher in this solvent in which it is more soluble.

#### Imidazole axial ligand effect

The role of imidazole as the axial ligand is observed in Table 4. For Fe(TPP)Cl, imidazole slightly increases the C-ol yields. According to Gunter and Turner<sup>17</sup>, the nitrogenous axial ligand in Fe(TPP)Im accelerates the rate of oxygen transfer to the substrate. The weakening in the iron-oxo bond through  $\sigma$  charge donation from the trans axial ligand favors this oxygen transfer. However, the presence of imidazole is responsible for a decrease in C-ol yields when 2-Cl and 3-Cl are used (Table 4). It is known that tetraaryl FeP bearing electron-withdrawing groups such as 2-Cl and 3-Cl have a high tendency to hexacoordinate<sup>18</sup>. The electronegative substituents make the iron more electrophilic, increasing its affinity for electron donor nitrogenous bases. The equilibrium constant value for the complexation of Fe(TDCPP) with the ligand (Fe(TDCPP)Im<sub>2</sub>) is  $\beta_2 = 2.5 \times 10^8 \text{ mol}^{-2} \text{ L}^2$ , which is very high if

**Table 3.** Yields of cyclohexanol (%)<sup>\*</sup> in the hydroxylation of cyclohexane with PhIO using FeP as catalyst. Effect of solvent.

Ironporphyrin	DCM		DCE	
	C-ol	C-one	C-ol	C-one
1 Fe(TPP) <sup>+</sup>	40	-	29	-
2 Fe(TDCPP) <sup>+</sup>	42	4	75	5
3 Fe(TNPP) <sup>+</sup>	45	-	51	-
4 Fe(TFPP) <sup>+</sup> <sup>a</sup>	161	-	103	-

Conditions: [FeP] =  $2 - 5 \times 10^{-4} \text{ mol L}^{-1}$ , PhIO/FeP molar ratio of 8 - 10:1, magnetic stirring at 25 °C, argon atmosphere.

<sup>a</sup> [FeP] =  $2 \times 10^{-4} \text{ mol L}^{-1}$ , PhIO/FeP molar ratio of 20:1

\* Based on the starting PhIO.

**Table 4.** Yields of cyclohexanol (%)<sup>\*</sup> in the hydroxylation of cyclohexane with PhIO using FeP as catalyst in DCE. Effect of imidazole as axial ligand.

Ironporphyrin	Imidazole Absence		Imidazole	
	C-ol	C-one	C-ol	C-one
1 Fe(TPP) <sup>+</sup>	22	3	27	3
2 Fe(TDCPP) <sup>+</sup>	75	5	60	-
3 Fe(TNPP) <sup>+</sup>	51	-	40	-
4 Fe(TFPP) <sup>+</sup> <sup>a</sup>	158	-	103	-

Conditions: [FeP] =  $3 - 5 \times 10^{-4} \text{ mol L}^{-1}$ , PhIO/FeP molar ratio of 20:1, Imidazole/FeP molar ratio of 2:1, magnetic stirring at 25 °C, argon atmosphere.

<sup>a</sup> [FeP] =  $2 \times 10^{-4} \text{ mol L}^{-1}$ , PhIO/FeP molar ratio of 50:1

\* Based on the starting PhIO.

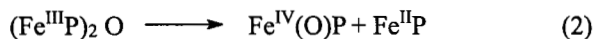
compared to  $\beta_2 = 4.8 \times 10^5 \text{ mol}^{-2} \text{ L}^2$  for Fe(TPP)Im<sub>2</sub>, explaining the C-ol yield decrease for 2-Cl and 3-Cl.

#### Fe(TFPP)Cl 4 unusual behavior

This FeP according presents an irregular catalytic activity in relation to the time passed after iron insertion and whether it has been recently purified or not<sup>19</sup>. Following iron insertion and purification, this FeP was very hygroscopic and the catalytic activity was considered high and normal (C-ol yield of 96%), higher than Chang and Ebina's results<sup>20</sup>. After about eight months, the same FeP batch, which was dry this time, was tested again and the catalytic activity was extremely low (about 36% of C-ol yield). It may be possible that the presence of water in the reaction site is important for the process, as mentioned above. This FeP, which had been kept in DCE solution, was used for this work. This FeP showed unusually high yields (as reported in this work), indicating the participation of another parallel oxidation mechanism. Some of these reactions were repeated with FeP from another source (Midcentury) and these high yields were reproduced. The high selectivity towards cyclohexanol is interesting. Based on these preliminary results we have proposed that, besides

PhIO, O<sub>2</sub> also participates as an oxygen atom source, as the argon bubbling does not assure the total removal of oxygen from the system. This is evidenced by the fact that when the reaction is carried out under O<sub>2</sub> atmosphere the yield increases up to 173%.

Ellis and Lyons<sup>21</sup> proposed for FeTFPP<sup>+</sup> a mechanism dependent on a μ-oxo diiron(III) species which disproportionates into Fe(II) and Fe(IV)oxo according to the following equilibrium:



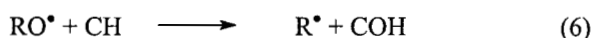
More recently, Gray *et al.*<sup>22</sup> proposed a catalytic cycle for the hydroxylation of alkanes by Fe(TFPPBr<sub>8</sub>) and O<sub>2</sub> similar to the O<sub>2</sub> parallel mechanism proposed in this work (Eqs. 3-6). According to Gray *et al.*'s proposition for the hydroxylation of alkanes, the radicals are generated by oxidation and reduction of alkyl hydroperoxides, with the participation of the monomers Fe<sup>III</sup>(TFPPBr<sub>8</sub>) and Fe<sup>II</sup>(TFPPBr<sub>8</sub>)Cl. Based on the higher selectivity towards the tertiary position (> 99%) Gray *et al.* suggest that the oxidizing species in the O<sub>2</sub> reactions are radicalar, differing from those involved in the PhIO reactions.

According to the catalytic results obtained with FeTFPPCl, the yields attained with ultrasound stirring are much higher than those attained with magnetic stirring (Table 1). When ultrasound stirring and presence of water are used simultaneously, the yield increases even more (from 134% to 205%, Table 2). However, in the presence of imidazole, the yield is around 100%, because this ligand inhibits the dimer formation, preventing the parallel oxygen mechanism. Therefore, we suggest that the mechanism for the participation of O<sub>2</sub> is probably dependent on a μ-oxo diiron(III) species, as proposed by Ellis and Lyon<sup>21</sup>, and the high Fe<sup>III</sup>/Fe<sup>II</sup> reduction potential<sup>22</sup> readily stabilizes the iron(II) species, formed according to Eq. 2, which can participate in a radical-chain mechanism. While ultrasound favors the radical formation through the abstraction of a hydrogen atom from the solvent, resulting in the R<sup>•</sup> species, water can produce the μ-oxo diiron(III) species<sup>3</sup>. There is a particular condition in which the iron(II) species originated from μ-oxo diiron(III) species disproportionation intervenes, giving rise to the high yield (205%).

The side path involving the participation of these iron(II) species and O<sub>2</sub> in the presence of R<sup>•</sup> may be represented by the following equations.



The Fe<sup>II</sup>P intervenes in the reductive cleavage of ROOH<sup>23</sup>.



Mansuy<sup>1b</sup> reported a "dioxygenase-like" mechanism for cyclohexane oxidation, in which, photochemically produced Fe<sup>II</sup>P and •OH form cyclohexylperoxoiron(III) in the presence of O<sub>2</sub>, yielding cyclohexanone. In our study, the absence of cyclohexanone in the product supports the mechanism proposed above (Eqs. 3-6) and gives an indication that the "dioxygenase-like" mechanism does not occur in this case.

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